

# JOURNAL OF THE CHEMICAL SOCIETY.

## ABSTRACTS OF PAPERS

ON  
ORGANIC, PHYSIOLOGICAL, AND  
AGRICULTURAL CHEMISTRY.

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## JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
<i>Amer. Chem. J.</i> . . .	American Chemical Journal.
<i>Amer. J. Pharm.</i> . . .	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i> . . .	American Journal of Physiology.
<i>Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . .	The Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i> . . .	Annals of Botany.
<i>Ann. Chim. anal.</i> . . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim. Applicata.</i> . . .	Annali di Chimica Applicata.
<i>Ann. Chim. Phys.</i> . . .	Annales de Chimie et de Physique.
<i>Ann. Falsif.</i> . . .	Annales des Falsifications.
<i>Ann. Inst. Pasteur</i> . . .	Annales de l'Institut Pasteur.
<i>Ann. Physik</i> . . .	Annalen der Physik.
<i>Ann. sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.
<i>Ann. Soc. Quím. Argentina.</i> . . .	Anales de la Sociedad Química Argentina.
<i>Arch. expt. Path. Pharm.</i> . . .	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Hygiene</i> . . .	Archiv für Hygiene.
<i>Arch. Néerland.</i> . . .	Archives Néerlandaises des sciences exactes et naturelles.
<i>Arch. Pharm.</i> . . .	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i> . . .	Archives des Sciences physiques et naturelles.
<i>Arkiv Kem. Min. Geol.</i> . . .	Arkiv för Kemi, Mineralogi och Geologi.
<i>Atti R. Accad. Sci. Torino.</i> . . .	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i> . . .	Atti della Reale Accademia dei Lincei.
<i>Ber.</i> . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i> . . .	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i> . . .	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i> . . .	Berichte der Deutschen physikalischen Gesellschaft.
* <i>Bied. Zentr.</i> . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Biochem. Bull.</i> . . .	Biochemical Bulletin.
<i>Biochem. J.</i> . . .	The Biochemical Journal.
<i>Biochem. Zeitsch.</i> . . .	Biochemische Zeitschrift.
<i>Boll. chim. farm.</i> . . .	Bollettino chimico farmaceutico.
<i>Bull. Acad. roy. Belg.</i> . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i> . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. Sci., St. Pétersbourg.</i> . . .	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
<i>Bull. Assoc. chim. Sucr. Dist.</i> . . .	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
<i>Bull. Geol. Soc. Amer.</i> . . .	Bulletin of the Geological Society of America.
<i>Bull. Imp. Inst.</i> . . .	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i> . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i> . . .	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. franç. Min.</i> . . .	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. ind. Mulhouse</i> . . .	Bulletin de la Société industrielle de Mulhouse.
<i>Centr. Bakt. Par.</i> . . .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Centr. Min.</i> . . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* <i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.

\* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

# JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
<i>Chem. News</i> . . . . .	Chemical News.
<i>Chem. Rev. Fett-Harz-Ind.</i> . . . . .	Chemische Revue über die Fett- und Harz-Industrie.
<i>Chem. Weekblad</i> . . . . .	Chemisch Weekblad.
<i>Chem. Zeit.</i> . . . . .	Chemiker Zeitung.
<i>Compt. rend.</i> . . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Exper. Stat. Record</i> . . . . .	Experiment Station Record.
<i>Gazzetta</i> . . . . .	Gazzetta chimica italiana.
<i>Geol. Mag.</i> . . . . .	Geological Magazine.
<i>Jahrb. Min.</i> . . . . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie.
<i>Jahrb. Min. Beil.-Bd.</i> . . . . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie. Beilage-Band.
<i>Jahrb. Radioaktiv. Elektronik.</i> . . . . .	Jahrbuch der Radioaktivität und Elektronik.
<i>J. Agric. Sci.</i> . . . . .	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i> . . . . .	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i> . . . . .	Journal of Biological Chemistry, New York
<i>J. Chim. phys.</i> . . . . .	Journal de Chimie physique.
<i>J. Franklin Inst.</i> . . . . .	Journal of the Franklin Institute.
<i>J. Geol.</i> . . . . .	Journal of Geology.
<i>J. Hygiene</i> . . . . .	Journal of Hygiene.
<i>J. Ind. Eng. Chem.</i> . . . . .	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Brewing</i> . . . . .	Journal of the Institute of Brewing.
<i>J. Landw.</i> . . . . .	Journal für Landwirtschaft.
<i>J. Med. Research</i> . . . . .	Journal of Medical Research.
<i>J. Path. Bact.</i> . . . . .	Journal of Pathology and Bacteriology.
<i>J. Pharm. Chim.</i> . . . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . . . .	Journal of Physiology.
<i>J. pr. Chem.</i> . . . . .	Journal für praktische Chemie.
<i>J. Roy. Agric. Soc.</i> . . . . .	Journal of the Royal Agricultural Society.
<i>J. Roy. Soc. New South Wales.</i> . . . . .	Journal of the Royal Society of New South Wales.
<i>J. Russ. Phys. Chem. Soc.</i> . . . . .	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i> . . . . .	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers</i> . . . . .	Journal of the Society of Dyers and Colourists.
<i>J. Washington Acad. Sci.</i> . . . . .	Journal of the Washington Academy of Sciences.
<i>K. Svenska Vet.-Akad. Handl.</i> . . . . .	Kongl. Svenska Vetenskaps-Akademien Handlingar.
<i>Kolloid Zeitsch.</i> . . . . .	Kolloid Zeitschrift.
<i>Koll. Chem. Beihefte</i> . . . . .	Kolloidchemische Beihefte.
<i>Lancet.</i> . . . . .	The Lancet.
<i>Landw. Versuchs-Stat.</i> . . . . .	Die landwirtschaftlichen Versuchs-Stationen.
<i>Le Radium</i> . . . . .	Le Radium.
<i>Mem. Accad. Sci. Torino</i> . . . . .	Memorie della Reale Accademia delle Scienze di Torino.
<i>Mem. Coll. Sci. Eng. Kyōtō.</i> . . . . .	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
<i>Mem. Dept. Agric. India</i> . . . . .	Memoirs of the Department of Agriculture in India.
<i>Mem. Manchester Phil. Soc.</i> . . . . .	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Metallurgie</i> . . . . .	Metallurgie.
<i>Milch. Zentr.</i> . . . . .	Milchwirtschaftliches Zentralblatt.
<i>Min. Mag.</i> . . . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i> . . . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Nuovo Cim.</i> . . . . .	Il Nuovo Cimento.
<i>Pflüger's Archiv</i> . . . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i> . . . . .	Pharmaceutical Journal.
<i>Pharm. Weekblad</i> . . . . .	Pharmaceutisch Weekblad.
<i>Pharm. Zeit.</i> . . . . .	Pharmazeutische Zeitung.

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ABBREVIATED TITLE.	JOURNAL.
<i>Pharm. Zentr.-h.</i> . . .	Pharmazeutische Zentralthalle.
<i>Philippine J. Sci.</i> . . .	Philippine Journal of Science.
<i>Phil. Mag.</i> . . . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i> . . . . .	Philosophical Transactions of the Royal Society of London.
<i>Physikal. Zeitsch.</i> . . .	Physikalische Zeitschrift.
<i>Proc. Amer. Physiol. Soc.</i> .	Proceedings of the American Physiological Society.
<i>Proc. Camb. Phil. Soc.</i> . .	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam.</i> . . . . .	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Phil. Soc. Glasgow</i> .	Proceedings of the Glasgow Philosophical Society.
<i>Proc. Physical Soc. London</i> .	Proceedings of the Physical Society of London.
<i>Proc. Physiol. Soc.</i> . . .	Proceedings of the Physiological Society.
<i>Proc. Roy. Soc.</i> . . . . .	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.
<i>Quart. J. exp. Physiol.</i> . .	Quarterly Journal of experimental Physiology.
<i>Quart. J. Geol. Soc.</i> . . .	Quarterly Journal of the Geological Society.
<i>Rec. trav. chim.</i> . . . . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rend. Accad. Sci. Fis. Mat. Napoli.</i> . . . . .	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
<i>Rev. de Métallurgie</i> . . . .	Revue de Métallurgie.
<i>Sci. Proc. Roy. Dubl. Soc.</i> .	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Trans. Roy. Dubl. Soc.</i> .	Scientific Transactions of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> . . . . .	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. München.</i> . . . . .	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
<i>Trans. Amer. Electrochem. Soc.</i> . . . . .	Transactions of the American Electrochemical Society.
<i>Trans. Faraday Soc.</i> . . . .	Transactions of the Faraday Society.
<i>Trans. Nova Scotia Inst. Sci.</i> . . . . .	Transactions of the Nova Scotia Institute of Science.
<i>Trans. Path. Soc.</i> . . . . .	Transactions of the Pathological Society.
<i>Trans. Roy. Soc. Canada</i> . .	Transactions of the Royal Society of Canada.
<i>Trans. Roy. Soc. Edin.</i> . . .	Transactions of the Royal Society of Edinburgh.
<i>Trans. Roy. Irish Acad.</i> . . .	Transactions of the Royal Irish Academy.
<i>Tsch. Min. Mitt.</i> . . . . .	Tschermak's Mineralogische Mittheilungen.
<i>U. S. A. Dept. Agric. Bull.</i> .	Bulletins of the Department of Agriculture, U. S. A.
<i>U. S. A. Dept. Agric. Rep.</i> . .	Reports of the Department of Agriculture, U. S. A.
<i>Verh. Ges. deut. Naturforsch. Aerzte</i> . . . . .	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
<i>Wiss. Abhandl. Phys.-Tech. Reichsanstalt.</i> . . . . .	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
<i>Zeitsch. anal. Chem.</i> . . . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . . . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Biol.</i> . . . . .	Zeitschrift für Biologie.
<i>Zeitsch. Elektrochem.</i> . . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . . . .	Zeitschrift für Kristallographie und Mineralogie.
<i>Zeitsch. Nahr. Genussm.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. öffentl. Chem.</i> . . . .	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie
<i>Zeitsch. prakt. Geol.</i> . . . .	Zeitschrift für praktische Geologie.
<i>Zeitsch. Ver. deut. Zuckerind.</i> .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeitsch. wiss. Photochem.</i> . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
<i>Zeitsch. Zuckerind. Böhm.</i> . .	Zeitschrift für Zuckerindustrie in Böhmen.

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## PART I.

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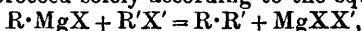
### Organic Chemistry.

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**The Expression "Asymmetric Carbon Atom."** CH. M. VAN DEVENTER (*Chem. Weekblad*, 1913, **10**, 1046—1047).—A criticism of the expression "Asymmetric carbon atom," pointing out the unsatisfactory nature of the term. The author suggests the name "Molecular asymmetry" for the subject; "Asymmetric carbon molecule" for the molecule, and "Characteristic" or "Anisodetic" atom for the carbon atom itself. A. J. W

**Historical Documents Dealing with Stereoisomerism.** E. PATERNÒ (*Gazzetta*, 1913, **43**, ii, 501—503).—Facsimiles are given of three letters addressed to the author respectively by (1) Lieben (1869), concerning the supposed existence of isomeric compounds of the formula  $C_2H_4Cl_2$ ; (2) van't Hoff (1889), dealing with Paternò's paper on the action of phosphorus pentachloride on chloral, and (3) Meyerhoffer (1891), asking for information as to Paternò's publication, prior to that of van't Hoff, of the idea of the stereochemical tetrahedron. T. H. P.

**Action of Alkyl Haloids on Magnesium Alkyl Haloids.** ERNST SPÄTH (*Monatsh.*, 1913, **34**, 1965—2014).—The author has made a systematic examination of the interaction of alkyl haloids with magnesium alkyl and aryl haloids, and finds that, in general, the reaction does not proceed solely according to the equation:



but gives rise to a variety of both saturated and unsaturated hydrocarbons. From the results described below, the conclusion is drawn that the first stage in the reaction consists in the formation of the free

radicles R and R'; thus:  $R \cdot MgX + R'X = R + R' + MgXX'$ , which may then react according to the following schemes: (I)  $R + R' = R \cdot R'$ ; (II)  $R + R = R \cdot R$ ; (III)  $R + R' = R_{-H} + R'_{+H}$ ; (IV)  $R + R = R_{-H} + R_{+H}$ ; (V)  $R_{-H} + R' + R = R'R_{-H}R$ .

When R and R' are both methyl, the reaction proceeds solely according to equation (I) with the formation of ethane. Magnesium ethyl haloids, on the other hand, react with ethyl haloids, yielding ethane and ethylene, and only a small amount of butane. With the higher homologues the yield of hydrocarbon produced by reaction (I) is generally small, olefines and saturated hydrocarbons containing the same number of carbon atoms as the alkyl radicles R and R' forming the main products. Magnesium phenyl haloids react with alkyl haloids, yielding in addition to diphenyl and benzene, the corresponding alkylbenzenes in yields varying from 20—51%; the alkyl chlorides and bromides give much better yields than the iodide.

A similar difference in the behaviour of iodides as compared with the chlorides and bromides has been observed in the behaviour of the benzyl haloids and their derivatives towards magnesium alkyl chlorides, bromides, and iodides.

Thus, benzyl haloids enter into reaction very readily with the magnesium alkyl chlorides and bromides, giving good yields of hydrocarbons according to scheme I, but if the magnesium alkyl iodides are employed, the yield is very poor, or the reaction proceeds in another direction.

*p*-Methoxybenzyl bromide, for example, reacts with magnesium phenyl bromide to form  $\alpha$ -phenyl- $\beta$ -*p*-anisylethane in good yield, whilst with magnesium phenyl iodide it gives rise to  $\alpha$ -phenyl- $\alpha\beta$ -*p*-anisylethane.

The interaction of the magnesium compound and alkyl or aryl haloid was generally carried out as follows; the magnesium compound was prepared in the usual manner in ethereal solution, the ether removed as far as possible, and, after the addition of the alkyl haloid, the mixture was heated generally in the neighbourhood of 100°. In some cases the reaction proceeds so readily that the removal of the ether was unnecessary.

Magnesium methyl iodide and propyl iodide yield propylene, methane, ethane, propane, and butane.

Magnesium ethyl iodide and propyl iodide give rise to ethylene, propylene, ethane, propane, and possibly a little *n*-butane and *n*-pentane; the same mixture is obtained from ethyl iodide and magnesium propyl iodide. The interaction of magnesium methyl iodide and *tert*-butyl bromide yields butylene, methane, ethane, butane,  $\beta\beta$ -dimethylpropane, and  $\beta\beta\gamma\gamma$ -tetramethylbutane.

*iso*-Amyl bromide and its magnesium compound give rise to amylene,  $\beta\eta$ -dimethyloctane,  $\beta$ -methyl- $\Delta^{\beta}$ -butene, and pentane.

$\gamma$ -Bromopentane, b. p. 117—119°/755 mm., reacts with its magnesium compound to form *s*-tetraethylethane [ $\gamma\delta$ -diethylhexane] in an impure condition, b. p. 149—155°.

Magnesium propyl bromide and *tert*-amyl chloride interact vigorously in ethereal solution, yielding, amongst other products, dimethylethylpropylmethane [ $\gamma\gamma$ -dimethyl-*n*-hexane],  $CMe_2EtP_1^a$ , b. p. 105—111°, and

*s*-bisdimethylethylethane [ $\gamma\gamma\delta\delta$ -tetramethylhexane],  $\text{CMe}_2\text{Et}\cdot\text{CMe}_2\text{Et}$ , b. p. 150—156°.

*sec*-Octyl iodide and magnesium methyl iodide give rise to methane, ethane, and  $\beta$ -methyloctane, whilst *sec*-octyl bromide and magnesium ethyl bromide yield ethylene, *n*-octane, octylene,  $\beta$ -ethyloctane, b. p. 150—160°, and  $\eta\theta$ -dimethyltetradecane.

*sec*-Octyl bromide reacts with magnesium propyl bromide to form octane, octylene, and  $\eta\theta$ -dimethyltetradecane; with magnesium *iso*-propyl chloride it yields in addition to the three last-mentioned compounds,  $\beta\gamma$ -dimethylnonane, b. p. 170—180°, and  $\eta$ -isopropylhexadecane, b. p. 175—185°/10 mm.

The interaction of hexadecyl iodide and magnesium methyl iodide gives rise to methane, ethane, hexadecane, hexadecylene, heptadecane, and dotriacontane.

Magnesium phenyl bromide reacts with *isobutyl* bromide, yielding benzene, diphenyl, and *isobutyl*benzene; with *tert*-butyl bromide it forms  $\beta$ -methylpropylene, diphenyl, and *tert*-butylbenzene.

The interaction of magnesium phenyl iodide (or bromide) with  $\gamma$ -bromo- or  $\gamma$ -iodo-pentane yields diphenyl, decane ( $\gamma\delta$ -diethylhexane), and  $\gamma$ -phenylpentane. Bromobenzene reacts only slowly at a high temperature (140—170°) with magnesium phenyl bromide to form diphenyl.

On treatment with magnesium methyl iodide, benzyl chloride gives rise to  $\alpha\beta\gamma$ -triphenylpropane, dibenzyl, and ethylbenzene. With magnesium ethyl bromide it yields *n*-propylbenzene, dibenzyl,  $\alpha\beta$ -diphenylbutane, and  $\alpha\beta\gamma$ -triphenylpropane; the latter products are also formed with magnesium ethyl iodide, but the yield of propylbenzene is much smaller than is the case when the bromide is employed.

*o*-Methoxybenzyl bromide, prepared by passing hydrogen bromide into a benzene solution of *o*-methoxybenzyl alcohol, has b. p. 115°/10 mm., and reacts with magnesium ethyl haloids, yielding *oo'*-dimethoxydibenzyl, *o*-tolyl methyl ether, which forms a *nitro*-derivative, m. p. 65°, and *o*-methoxy-*n*-propylbenzene.

*o*-Methoxydiphenylmethane, prepared from magnesium phenyl bromide and *o*-methoxybenzyl bromide, has b. p. 154—156°/10 mm.

*m*-Methoxybenzyl bromide, prepared in a similar manner to that given above for the *o*-isomeride, forms a pungent smelling liquid, b. p. 123·5°/13 mm., and reacts with magnesium methyl bromide to form ethane, *m*-methoxyethylbenzene, and *mm'*-dimethoxydibenzyl, b. p. 195—200°/10 mm., m. p. 39—40°.

*p*-Methoxybenzyl bromide, obtained from the alcohol and hydrogen bromide in benzene solution, is a colourless liquid, b. p. 126°/12 mm., which loses hydrogen bromide very readily, and becomes green or brown on exposure to air. It reacts with the magnesium compounds of methyl, ethyl, and propyl haloids to form di-*p*-methoxydibenzyl, together with the *p*-methoxy-derivatives of ethyl-, propyl-, and butylbenzenes respectively.

*p*-Methoxyisobutylbenzene, obtained together with *p*-tolyl methyl ether and di-*p*-methoxydibenzyl by the interaction of magnesium *iso*-propyl chloride and *p*-methoxybenzyl bromide in ethereal solution, has b. p. 92—94°/8 mm.



*p*-Methoxyisoamylbenzene, b. p. 126—127°/18 mm., and *p*-methoxy-*tert*-amylbenzene are prepared from magnesium *iso*- and *tert*-butyl bromides in a similar manner.

*p*-Methoxybenzyl bromide reacts with magnesium *iso*amyl bromide, yielding *p*-methoxyisohexylbenzene, b. p. 125—125·5°/9 mm., together with  $\beta\eta$ -dimethyloctane and di-*p*-methoxydibenzyl, whilst with the magnesium compound of  $\gamma$ -bromopentane it gives  $\alpha$ -*p*-anisyl- $\beta$ -ethylbutane,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHEt}_2$ , a liquid, b. p. 124—125°/9 mm. With magnesium phenyl bromide it forms phenyl-*p*-anisylmethane, b. p. 157—158°/8 mm., m. p. 20—21° (compare PATERLO, *Gazzetta*, 1871, i, 589), but with magnesium phenyl iodide it gives rise to  $\alpha$ -phenyl- $\alpha\beta$ -di-*p*-anisylethane,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , which has b. p. 333—340°/10 mm., solidifies to a resinous mass, and is accompanied by a little phenyl-*p*-anisylmethane.

Magnesium benzyl chloride and *p*-methoxybenzyl bromide yield *p*-methoxy- $\alpha\beta$ -diphenylethane.

$\alpha$ -Chloro- and  $\alpha$ -bromo- $\alpha$ -phenylpropane, prepared from the corresponding alcohol and hydrogen haloids, react with magnesium ethyl bromide to form  $\gamma$ -phenylpentane and  $\gamma\delta$ -diphenylhexane.

$\beta$ -Bromo- $\beta$ -phenylbutane is a liquid, which loses hydrogen bromide at the ordinary temperature; with magnesium methyl bromide it forms  $\beta$ -phenyl- $\Delta^\beta$ -butene and  $\beta$ -phenyl- $\beta$ -methylbutane.

Diphenylmethyl bromide reacts with magnesium methyl bromide, yielding ethane, *aa*-diphenylethane, and *s*-tetraphenylethane; the latter compound is also formed, together with *aa*-diphenylpropane by the interaction of magnesium ethyl bromide or iodide with diphenylmethyl bromide.

$\omega$ -Chlorotriphenylmethane and magnesium methyl bromide give rise to *aaa*-triphenylethane in almost theoretical yield.

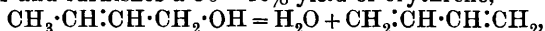
$\alpha$ -*tert*-Butylnaphthalene, prepared from magnesium  $\alpha$ -naphthyl bromide and *tert*-butyl bromide has b. p. 278—287°. F. B.

**Preparation of isoPentene and its Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 263017).—When *n*-pentene obtained from *chloro-n*-pentane (b. p. 36—38°) is passed over aluminium oxide at 450°, it undergoes isomeric change and furnishes  $\beta$ -methyl- $\Delta^\beta$ -butene, which can be purified by conversion into its chloride, etc.

Hexene, prepared from *chloro-n*-hexane, similarly yields a distillate which by treatment with concentrated hydrochloric acid is converted into  $\gamma$ -chloro- $\beta$ -methylpentane (b. p. 110—115°), and when methyl *n*-propyl ketone (86 parts) dissolved in a mixture of 30% sodium hydroxide and ether is slowly treated with sodium, it furnishes the corresponding alcohol, b. p. 115—117°, which when passed over aluminium oxide at 450—475° gives rise to  $\beta$ -methyl- $\Delta^\beta$ -butene.

F. M. G. M.

**Preparation of Erythrene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 263016, 263066, and 264264).—When crotonyl alcohol is heated at 140—160° with toluidine hydrogen sulphate, it loses water and furnishes a 30—40% yield of erythrene,



if oxalic acid is used a 40—50% yield is obtained, and other dehydrating agents, such as phosphoric acid, aluminium oxide or aluminium trichloride, can also be employed.

II. states that when chlorobutylene glycol ether is heated at  $350^{\circ}$ /30—40 mm. with barium chloride it decomposes into erythrene, hydrogen chloride and water:  $C_8H_{17}O_2Cl = 2C_4H_6 + 2H_2O + HCl$ ; the erythrene (in 30% yield) can be isolated as its tetrabromide, m. p.  $116^{\circ}$ ; with aluminium oxide, a temperature of  $450$ — $500^{\circ}$  and a pressure of 50 mm. are employed, and furnishes a 40% yield of erythrene.

III. describes the preparation of erythrene in about 15% yield by heating *n*-butyl alcohol either in the presence or absence of such dehydrating agents as aluminium oxide or kieselguhr, when it decomposes into erythrene, water, and hydrogen. F. M. G. M.

**Preparation of Erythrene and Isoprene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 267040. Compare A., 1912, i, 742).—In the previous patent it was shown that quaternary halogen ammonium bases containing the group  $\cdot NMe_3X$  ( $X$  = halogen) are decomposed by alkalis with the production of erythrene or isoprene. It is now found that this reaction proceeds similarly if the methyl groups attached to the nitrogen atom are partly or wholly replaced by ethyl.

*Diethyl- $\gamma$ -keto- $\beta$ -methylbutylamine*,  $CH_3 \cdot CO \cdot CHMe \cdot CH_2 \cdot NEt_2$ , prepared by the combination of diethylamine and methyl methylethyl ketone, or by the condensation of methyl ethyl ketone with diethylaminomethyl alcohol or tetraethylmethylenediamine, is an oil having a faintly ammoniacal odour, and sparingly soluble in water, b. p.  $77$ — $80^{\circ}$ /16 mm. On reduction it yields *diethyl- $\gamma$ -hydroxy- $\beta$ -methylbutylamine*, an oil with an ammoniacal odour and soluble in water, b. p.  $84^{\circ}$ /13 mm. This base furnishes the quaternary bases used in the above reaction when treated with methyl iodide or ethyl iodide. J. C. C.

**Preparation of Isoprene.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 264007).—When  $\beta\gamma$ -dibromo- $\beta$ -methylbutane is heated at  $130$ — $150^{\circ}$  in the presence of an organic base (for example, quinoline), a good yield of isoprene is obtained. F. M. G. M.

**Preparation of Polymerisation Products from Butadiene and its Homologues.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264925). When butadiene or its homologues are treated with boron haloids at low temperatures, they give rise to the corresponding polymerides; the preparation of the following compounds is described: (1) from isoprene and boron fluoride, a yellowish-brown, transparent substance; (2) from  $\beta\gamma$ -dimethylethylene and boron fluoride, a viscid, opaque liquid which when dissolved in benzene yielded a yellow substance; (3) from isoprene and boron trichloride, a pale yellow substance, and (4) from  $\beta\gamma$ -dimethylethylene and boron trichloride, a dark yellow substance. F. M. G. M.

**Preparation of Diolefines.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 264008).—When the vapours of dihalogenated paraffins or

monohalogenated alkylenes are passed at a high temperature and under a diminished pressure over acid absorbents, such as soda lime, calcium oxide, hydroxide or carbonate, they yield diolefines; thus  $\beta\gamma$ -dibromo- $\beta$ -methyl- $\Delta^{\beta}$ -butylene, when passed over calcium oxide at  $450^{\circ}$  and 30—50 mm., furnishes a satisfactory yield of pure isoprene, and the same is also obtained from  $\beta\delta$ -dibromo- $\beta$ -methylbutane or  $\gamma\delta$ -dibromo- $\beta$ -methylbutane, whilst  $\gamma$ -bromo- $\beta$ -methyl- $\Delta^{\beta}$ -butylene at  $500$ — $600^{\circ}$  and 30 mm. gives rise to  $\gamma$ -methyl- $\Delta^{\alpha\beta}$ -butadiene, m. p.  $39$ — $41^{\circ}$ .

F. M. G. M.

### Mechanism of the Reaction in the Formation of Iodoform.

A. PIERONI and E. TONNIOLI (*Gazzetta*, 1913, 43, ii, 620—625)—As with acetone (A., 1912, i, 526) so also with acetaldehyde, the formation of iodoform by the action of iodine in presence of potassium hydroxide is due to the action of hypiodite, the amount of the latter which reacts determining the yield of iodoform. Application of the formula for reactions of the second order gives constant values for  $K$ , but the divergence of the experimental from the calculated yields is greater than when acetone is used. In the case of alcohol, with which minimal yields of iodoform are obtained, part of the hypiodite probably oxidises alcohol to aldehyde and itself undergoes reduction to potassium iodide.

According to the theory which is generally accepted, the hypiodite decomposes with liberation of two atoms of iodine, the latter acting on the enolic form of acetone, thus:  $\text{CH}_2\text{:CMe}\cdot\text{OH} \rightarrow$

$\text{CH}_2\text{I}\cdot\text{CMeI}\cdot\text{OH} \rightarrow \text{CH}_2\text{I}\cdot\text{COMe} \rightarrow \text{CHI}\cdot\text{CMe}\cdot\text{OH} \rightarrow \text{CHI}_2\cdot\text{CMeI}\cdot\text{OH} \rightarrow \text{CHI}_2\cdot\text{COMe} \rightarrow \text{CI}_2\cdot\text{CMe}\cdot\text{OH} \rightarrow \text{CI}_3\cdot\text{COMe}$ ; then,  $\text{CI}_3\cdot\text{COMe} + \text{KOH} = \text{CHI}_3 + \text{CH}_3\cdot\text{CO}_2\text{K}$ . This theory, however, assumes the loss of 50% of the hypiodite as hydrogen iodide, whereas actual experiment shows that as much as 93.42% of the calculated amount of hypiodite yields iodoform.

From the analogy between hypochlorite and hypiodite, the author supposes that the latter forms an additive compound with the enolic form of acetone and subsequently with its iodo- and di-iodo-derivatives:  $\text{CH}_2\text{:CMe}\cdot\text{OH} \rightarrow \text{CH}_2\text{I}\cdot\text{CMe(OH)}\cdot\text{OK} \rightarrow \text{CH}_2\text{I}\cdot\text{COMe} \rightarrow \text{CHI}\cdot\text{CMe}\cdot\text{OH} \rightarrow \text{CHI}_2\cdot\text{CMe(OH)}\cdot\text{OK} \rightarrow \text{CI}_2\cdot\text{CMe}\cdot\text{OH} \rightarrow \text{CI}_3\cdot\text{CMe(OH)}\cdot\text{OK} \rightarrow \text{CHI}_3 + \text{CH}_3\cdot\text{CO}_2\text{K}$ . A similar series of changes occurs with the enolic modification of acetaldehyde,  $\text{CH}_2\text{:CH}\cdot\text{OH}$ , the lower yield of iodoform being explained by the diminished mobility of the enolic hydrogen atom. That the passage from the ketonic to the enolic form must precede formation of iodoform is supported by the observation that paracetaldehyde, for which no enolic modification exists, does not give iodoform.

T. H. P.

**Electro-syntheses.** S. M. LOSANITSCH (*Chem. Zentr.*, 1913, ii, 754—755; from *Bul. Soc. Științe București*, 1913, 22, 5—10).—Mixtures of ethylene, acetylene, or benzene with hydrogen chloride have been submitted to the influence of the silent electric discharge. It is found that after condensation has taken place, partial substitution of hydrogen occurs, resulting in the formation of complex chloro-derivatives.

Equal volumes of ethylene and the acid gave, in thirty hours, a

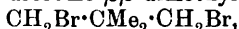
brown liquid from which a mixture of dichloropentanes, b. p.  $80^{\circ}/16$  mm., was obtained. On distilling the brown liquid obtained from a mixture of acetylene and two volumes of hydrogen chloride, a *trichlorobutane*, yellow, pungent smelling oil, b. p.  $90^{\circ}/16$  mm., and Henninger's  $\alpha\beta\gamma\delta$ -tetrachlorobutane were isolated, whilst the residue was separated by alcohol into a brown, amorphous *product*,  $C_{14}H_{14}Cl_4$ , and a yellow oil,  $C_{12}H_{10}Cl_6$ .

The distilled products in the case of benzene were *trichlorocyclohexene*,  $C_6H_7Cl_3$ , a yellow, unpleasant-smelling liquid, b. p.  $180-200^{\circ}/16$  mm., which yielded chlorobenzene after treatment with alcoholic potassium hydroxide, and an isomeric, crystalline derivative, m. p.  $223^{\circ}$ , whilst the residue was separated by alcohol, ether, and benzene into a yellowish-brown, soluble, resinous *substance*,  $C_{15}H_{17}Cl_7$ , a brown *solid*,  $(C_8H_8Cl_3)_n$ , and a black *solid*,  $(C_8H_5Cl)_{10}$ .

Acraldehyde alone evolved carbon monoxide, hydrogen, and hydrocarbons, and formed a liquid which gave a colourless distillate,  $(C_5H_{10}O_2)_2$ , b. p.  $105^{\circ}/16$  mm., and a residue,  $(C_6H_{10}O_2)_4$ , both of which had aldehydic properties, and were probably polymerides.

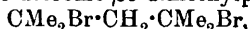
J. C. W.

**Abnormal Behaviour of Certain  $\alpha\gamma$ -Dibromo- and  $\alpha\gamma$ -Dihydroxy-paraffins.** ADOLF FRANKE [and, in part, with NIKOLAUS OBERMAYER, FRANZ STRENG, FRIEDRICH FRANK, and LEOPOLD MAYER] (*Monatsh.*, 1913, **34**, 1893—1913).—In comparison with  $\alpha\gamma$ -tribromopropane,  $\alpha\gamma$ -tribromobutane, and other  $\alpha\gamma$ -dibromo-compounds of the type  $:CBr\cdot CH_2\cdot CBr:$ ,  $\alpha\gamma$ -dibromo- $\beta\beta$ -dimethylpropane,



shows a remarkable stability toward reagents which bring about the replacement of the halogen atoms by other groups. Thus, it does not react with potassium cyanide, is converted by the action of silver acetate into the diacetate (Just, A., 1896, i, 403) only at a high temperature ( $190^{\circ}$ ), and can be boiled for a long time with aqueous sodium carbonate without undergoing appreciable change. A similar stability is shown by  $\beta\beta$ -di-bromomethyl-butane and other compounds of the type (I.),  $CH_2Br\cdot CMeR\cdot CH_2Br$ .

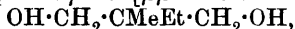
On the other hand,  $\beta\delta$ -dibromo- $\beta\delta$ -dimethylpentane,



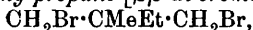
readily reacts with aqueous potassium cyanide and with silver acetate in glacial acetic acid solution, yielding  $\beta\gamma$ -dimethyl  $\Delta^2$ -penten- $\delta$ -ol and its acetyl derivative respectively (compare A., 1907, i, 816). From the formation of these compounds the conclusion is drawn that the action of silver acetate, water, potassium cyanide, and other reagents takes place in two stages, an unsaturated compound being first produced by the removal of a halogen and a hydrogen atom from adjacent carbon atoms, and this is then followed by the addition of acetic acid, water, or hydrogen cyanide, to the double linking. In the case of compounds of the type I, the formation of an unsaturated compound is excluded on account of the presence of a tertiary carbon atom adjacent to that combined with the halogen, and an explanation is thus afforded of the remarkable stability of these compounds. A similar stability is shown by  $\beta\beta$ -dimethylpropan- $\alpha\gamma$ -diol (Franke and

Kohn, A., 1907, i, 171), which does not react with phosphorus trichloride or fuming hydrochloric acid, and is converted into the corresponding dibromo-compound (Gustavson and Popper, A., 1899, i, 263) by the action of phosphorus tribromide only at a high temperature; with fuming hydrobromic acid at 100° it yields  $\gamma$ -bromo- $\beta\beta$ -dimethylpropyl alcohol,  $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , which forms a colourless, viscid oil, b. p. 78°/12 mm., and is reduced by sodium amalgam to *tert.*-butyl carbinol ( $\beta\beta$ -dimethylpropyl alcohol), crystallising in colourless needles, m. p. 53°, b. p. 112°.

$\beta$ -Methyl- $\beta$ -ethylpropane- $\alpha\gamma$ -diol [ $\beta\beta$ -dimethanolbutane],



prepared by condensing methylethylacetaldehyde [ $\beta$ -methylbutaldehyde] with formaldehyde by means of potassium hydroxide, has b. p. 218–220°, m. p. 42°, and yields with phosphorus tribromide,  $\alpha\gamma$ -dibromo- $\beta$ -methyl- $\beta$ -ethylpropane [ $\beta\beta$ -di-bromomethyl-butane],



as a colourless liquid, b. p. 97°/25 mm., 92°/18 mm. It is converted by fuming hydrobromic acid at 100° into  $\beta$ -methyl- $\beta$ -bromomethyl butyl alcohol,  $\text{CH}_2\text{Br}\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{OH}$ , a colourless, viscid liquid, b. p. 98°/17.5 mm.

$\beta\beta$ -Dimethylpentane- $\alpha\beta'$ -diol, [ $\beta\beta$ -dimethanolpentane],



prepared from  $\alpha$ -methylvaleraldehyde, formaldehyde, and potassium hydroxide, has b. p. 121°/10 mm., 230°/753 mm., solidifies to a white, crystalline mass, m. p. 44°, and yields with acetic anhydride and sodium acetate a diacetyl derivative as a colourless, viscid liquid of an agreeable odour, b. p. 115°/10 mm. Its constitution has been established by oxidation with potassium permanganate to methylpropylmalonic acid and conversion of the latter into  $\alpha$ -methylvaleric acid. With phosphorus tribromide it yields  $\alpha$ -bromo- $\beta$ -methyl- $\beta$ -bromomethylpentane, a colourless liquid, b. p. 98–103°/12 mm.

$\beta$ -Phenyl- $\beta$ -methylpropane- $\alpha\gamma$ -diol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{CH}_2\cdot\text{OH}$ , prepared from methylphenylacetaldehyde [ $\alpha$ -phenylpropaldehyde], formaldehyde, and potassium hydroxide, has b. p. 295–296°/753 mm., 165°/12 mm., crystallises from alcohol in rectangular plates, m. p. 75°, and yields with phosphorus tribromide,  $\alpha\gamma$ -dibromo- $\beta$ -phenyl- $\beta$ -methylpropane, b. p. 140°/12 mm.

$\beta\beta$ -Dimethylpentane- $\beta\delta$ -diol (Franke and Kohn, A., 1907, i, 171) forms a diacetate, b. p. 98°/11 mm., m. p. 51°, and reacts with hydrogen bromide in glacial acetic acid solution, yielding  $\beta\delta$ -dibromo- $\beta\delta$ -dimethylpentane, which forms glistening, snow-white crystals. F. B.

**Preparation of Trichloroethylene from *s*-Tetrachloroethane.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 263457).—*s*-Tetrachloroethane is vaporised over the chloride of one of the heavy metals, such as nickel, cobalt, cadmium, iron, lead, calcium, or barium, heated at 300°, when it is decomposed into trichloroethylene and hydrogen chloride. F. M. G. M.

**The Action of Chlorine Peroxide on Ethyl Alcohol.** KSITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem.*, 1913, 84, 113–114).—Potassium chlorate, sulphuric acid, and ethyl alcohol react together

with the production of ethyl acetate, chloroform, chlorohydrin, chloral, and chloroacetic acid. Acetaldehyde is formed only when the oxidation is incomplete.

C. H. D.

**Chemical Action of Light. XXVIII. Autoxidations. VI.** GIACOMO CIAMICIAN and P. SILBER (*Ber.*, 1913, **46**, 3894—3899).—Although not directly autoxidisable, ethyl alcohol, amyl alcohol, mannitol, dextrose, glycerol, and naphthalene are capable of being oxidised in the presence of substances such as *p*-xylene, *m*-xylene, and toluene, which readily undergo autoxidation.

Thus, ethyl alcohol, when exposed to light for three and a-half months in an atmosphere of oxygen and in the presence of water and *p*-xylene, is oxidised to acetic acid, the *p*-xylene being oxidised to *p*-xylylic acid; amyl alcohol under similar conditions yields formic and valeric acids, whilst mannitol gives rise to mannose.

In the presence of *m*-xylene, dextrose is oxidised to glucosone, which was isolated in the form of its phenylosazone; the products from glycerol could not be isolated.

In the presence of toluene, naphthalene is oxidised to phthalic acid.

F. B.

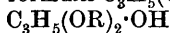
**Physical Relations between Inorganic and Organic Substances, Especially of Water to Alcohols and Acids.** KONRAD KUBIERSCHKY (*Zeitsch. angew. Chem.*, 1913, **26**, 730—731).—The author plots the relation between the boiling points (ordinates) and molecular weights (abscissæ) of water, the primary aliphatic alcohols, and the ethers derived from the alcohols. By joining the point for water with those for each of the alcohols, and the points for the alcohols with those of the ethers derived from them, a kind of lattice-diagram is obtained, which, according to the author, proves that water is the mother substance of the alcohols and the ethers. Similar results are obtained when water, the fatty acids, and the corresponding acid anhydrides are considered.

Instead of using the boiling points as ordinates, the densities or heats of formation from the elements may be used, when similar results are obtained.

The curve showing the relation between the boiling points and the molecular weight of the saturated hydrocarbons,  $C_nH_{2n+2}$ , and including hydrogen ( $n=0$ ), is held to prove that hydrogen is the first member of the series; similarly, the hydrogen haloids are the first members of the various series of alkyl haloids.

T. S. P.

**Preparation of Allyl Derivatives.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 263456).—When mono- or di-glycerides of the general formulæ  $C_3H_5(OH)_2 \cdot OR$  or



(where R is an acidic group) are heated with oxalic or formic acid they give rise to allyl derivatives.

A mixture containing equal quantities of allyl formate, b. p. 80—83°, and of allyl acetate, b. p. 100—103°, is obtained when glycerol mono-acetin (10 parts), anhydrous oxalic acid (10 parts), and ammonium chloride (3 parts) are boiled during four hours and the reaction

products subsequently separated by distillation and afterwards fractionated.

F. M. G. M.

**Catalytic Esterification in Aqueous Solution of Some Primary Alcohols of the Series  $C_nH_{2n+2}O$ .** F. BODROUX (*Compt. rend.*, 1913, 157, 938—940).—The preparation of ethyl acetate in aqueous solution using sulphuric acid as a catalyst (compare this vol., i, 440) can be applied to the esterification of formic, acetic, and propionic acids with the primary alcohols of the series  $C_nH_{2n+2}O$ . The yield is excellent if the resulting esters have boiling points below  $100^\circ$ . If above  $100^\circ$ , the yield is medium, but is increased towards a definite limit by prior heating under reflux. At the laboratory temperature the esterification is very slow, requiring one hundred and fifty days to reach the limit. The process can be greatly accelerated without the use of heat if the water is replaced by a saturated aqueous solution of sodium chloride to which 8% of sulphuric acid is added. In some cases it is better to add to the mixture of alcohol and organic acid its own weight of pure hydrochloric acid. The process can be carried out in a separating funnel, and rendered continuous if the density of the resulting ester is greater than unity as in the case of the chloroacetic esters. The ester is run off from time to time as formed at the bottom, and more of the alcohol-acid mixture added at the top. Attempts to apply this method to the esterification of benzoic, salicylic and cinnamic acids were not successful, but an excellent yield of ethyl phenylacetate was obtained from phenylacetic acid, ethyl alcohol, and hydrochloric acid as catalyst.

W. G.

**The Formation of Per-acids from Organic Acids and Hydrogen Peroxide.** J. D'ANS and W. FREY (*Zeitsch. anorg. Chem.*, 1913, 84, 145—164. Compare A., 1912, i, 601).—Quantitative experiments on the direct formation of per-acids from organic acids and hydrogen peroxide have now been made. The product is diluted with ice-water, and mixed with cold  $N/1$ -sulphuric acid. The hydrogen peroxide is then titrated with permanganate, and after addition of potassium iodide, the iodine liberated by the per-acid is titrated. With rapid working, the errors are very small.

Acetic acid and hydrogen peroxide react with appreciable velocity. The acceleration caused by acids is proportional to the concentration of the added acid. The same equilibrium concentration is reached in the reverse direction by the action of water on peracetic acid. Rise of temperature lessens the formation of per-acid, and the heat of formation of peracetic acid is calculated to be 1.5 Cal. per mol. The velocity constant falls as the reaction proceeds. Acetic, propionic and butyric acids behave very similarly, but the curve for formic acid passes through a maximum, owing to simultaneous decomposition of performic acid into carbon dioxide and water.

C. H. D.

**The Suitability of Bromoacetic Esters for Grignard Syntheses.** A. C. RÖTTINGER and F. WENZEL (*Monatsh.*, 1913, 34, 1867—1891).—Meyer (A., 1906, i, 757) has shown that acyl chlorides react with the magnesium compound of ethyl bromoacetate to form ketonic esters. In attempting to synthesise a ketonic ester by this method, the

authors found that whilst magnesium readily reacts with an ethereal solution of ethyl bromoacetate, it remains practically unattacked by the methyl ester. This difference in behaviour is due to the greater reactivity of the methyl ester towards the initially formed magnesium compound as compared with the ethyl ester, the magnesium compound of methyl bromoacetate at once entering into reaction with the unchanged bromo-ester to form an insoluble magnesium compound metal which coated the magnesium and thus preventing further action.

In view of this greater reactivity of the methyl ester, the synthesis of ketonic esters is best carried out in two stages; the magnesium compound of ethyl bromoacetate is first prepared in ethereal solution in the usual manner, and this is then allowed to react with a methyl ester. Thus, the action of magnesium (1 atom) on ethyl bromoacetate (2 mols.) yields only traces of ethyl  $\gamma$ -bromoacetate, whilst the action of methyl bromoacetate on the magnesium compound of ethyl bromoacetate gives rise to a 20% yield of the bromo-ketonic ester. Ethyl acetoacetate is obtained in 34% yield by the interaction of methyl acetate and the magnesium compound of ethyl bromoacetate.

In place of the ethyl ester of bromoacetic acid, the higher homologues may also be used; the yields, however, are not so good on account of the formation of by-products and the greater instability of the resulting ketonic esters.

*iso*Propyl bromoacetate is a colourless liquid, b. p. 59—61°/10 mm., and forms a magnesium compound, which reacts with methyl bromoacetate to form *isopropyl  $\gamma$ -bromoacetate*, a mobile liquid, b. p. 85—95°/17 mm. with decomposition.

*iso*Butyl bromoacetate is a colourless liquid, b. p. 74·5°/10 mm.; its magnesium compound yields with methyl bromoacetate in ethereal solution, *isobutyl  $\gamma$ -bromoacetate*, which on distillation decomposes into butylene, carbon dioxide, and  $\omega$ -bromoacetone, and, therefore, could not be obtained in a pure condition.

*tert.-Butyl bromoacetate*, obtained (1) by heating *tert.*-butyl alcohol with bromoacetic anhydride, and (2) by the interaction of silver bromoacetate and *tert.*-butyl iodide in ethereal solution, is a colourless liquid, b. p. 59°/12 mm.

*Benzyl bromoacetate*, prepared by esterifying benzyl alcohol with bromoacetic acid by the hydrogen chloride method, has b. p. 144°/10 mm.; the magnesium compound reacts with methyl bromoacetate, yielding *benzyl  $\gamma$ -bromoacetate*, which decomposes on distillation into benzyl bromide and tetrionic acid.

*Benzyl acetoacetate*, obtained from methyl acetate and the magnesium compound of benzyl bromoacetate, has b. p. 97°/12 mm. F. B.

**Soaps.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1913, 27, 300—303. Compare A., 1913, i, 6, 699, 955).—The author has attempted to improve the yield of diethylhexadecylamine by allowing silver oxide to react with the crude product obtained from hexadecyl iodide and triethylamine; the results are only partly satisfactory, since the base is contaminated, probably with hexadecyl alcohol.

The simplest and most general explanation of the detergent action of soap lies in the assumption of multimolecular aggregates in the



latter, which are composed of a hydrocarbon nucleus attached to groups which are hydrolysable and decomposable by water ( $\cdot\text{CO}_2\text{Na}$  group in sodium oleate,  $\cdot\text{SO}_3\text{H}$  group in hexadecylsulphonic acid,  $\cdot\text{NHCl}$  group in diethylhexadecylamine hydrochloride). The grease of the soiled article becomes incorporated with the nucleus, which, to be efficient, must still remain in the form of an emulsion. H. W.

**The Saturated Fatty Acid of Kephalin.** P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1913, 16, 419—422).—Kephalin contains only one saturated fatty acid, namely, stearic acid. W. D. H.

**Isomeric Oleic Acids.** ALFRED ECKERT and OTTOKAR HALLA (*Monatsh.*, 1913, 34, 1815—1824).—An account of the preparation of  $\Delta^\beta$ - and  $\Delta^\gamma$ -oleic acids by the removal of hydrogen iodide from  $\beta$ - and  $\gamma$ -iodostearic acids.

*$\beta$ -Iodostearic acid*, prepared by the addition of concentrated hydriodic acid to a glacial acetic acid solution of  $\Delta^\alpha$ -oleic acid (Ponzio, A., 1904, i, 548), separates in white needles, m. p. 60—61°, and yields a *methyl* ester, crystallising in spherical aggregates of needles, m. p. 46°. When heated with alcoholic potassium hydroxide, it is converted into  $\Delta^\beta$ -oleic acid,  $\text{C}_{14}\text{H}_{29}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which is separated from the accompanying small amounts of  $\Delta^\alpha$ -oleic acid and  $\beta$ -hydroxystearic acid by extraction with light petroleum and crystallisation from glacial acetic acid.  $\Delta^\beta$ -Oleic acid crystallises in pearly, lustrous, white scales, m. p. 56—57°, forms a crystalline *potassium* salt and *methyl* ester (lustrous, silky scales, m. p. 36°), and combines with bromine in light petroleum solution, yielding  *$\beta\gamma$ -dibromostearic acid*, crystallising in white leaflets, m. p. 67°. Its constitution has been established by its oxidation with potassium permanganate in alkaline solution to pentadecic acid, which forms a *methyl* ester, m. p. 10°, and a *lithium* salt, crystallising in slender, white needles.

*$\gamma$ -Iodostearic acid*, prepared by the addition of concentrated hydriodic acid to a glacial acetic acid solution of  $\Delta^\alpha$ -oleic acid, and purified by means of its sparingly soluble *lithium* salt, forms white needles, m. p. 58·5°, and is converted by boiling with alcoholic potassium hydroxide into  $\Delta^\gamma$ -oleic acid,  $\Delta^\beta$ -oleic acid,  $\gamma$ -hydroxystearic acid, and  $\gamma$ -ethoxystearic acids. The oleic acids are removed from the mixture by extraction with light petroleum and then separated by taking advantage of the sparing solubility of the potassium salt of the  $\Delta^\beta$ -acid in alcohol.

$\Delta^\gamma$ -Oleic acid,  $\text{C}_{13}\text{H}_{27}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises in white flakes, m. p. 52—53°, and forms a *dibromide*, m. p. 62°, crystallising in white leaflets, which become yellow on exposure to light.

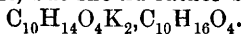
The accompanying  *$\gamma$ -hydroxy-* and  *$\gamma$ -ethoxy-stearic acids* could not be isolated in a pure condition. The iodine value, determined by Hübl's method, of the above-mentioned oleic acids increases as the double linking becomes more remote from the carboxyl group, the  $\Delta^\alpha$ -acid having an iodine value 9·04, the  $\Delta^\beta$ -acid 16·27, and the  $\Delta^\gamma$ -acid 26·96, in comparison with the theoretical value 89·4. F. B.

**Preparation of Esters of Alkyl-lactic Acids.** WALTHER NEUBERGER (D.R.-P. 266120).—Esters of alkyl-lactic acids which are

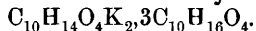
of therapeutic value can be obtained by the action of alkyl haloids, silver oxide, and a dehydrating agent (such as anhydrous copper or sodium sulphates) on esters of lactic acid. Ethyl methyl-lactate is thus prepared from ethyl lactate (59 parts), methyl iodide (74 parts), anhydrous sodium sulphate (20 parts), and silver oxide (60 parts); *menthyl ethyl-lactate* has b. p.  $133^{\circ}/10$  mm., and *menthyl methyl-lactate*, b. p.  $130^{\circ}/10$  mm. F. M. G. M.

**A Jubilee of Acetoacetic Ester.** GEORG COHN (*Chem. Zeit.*, 1913, 37, 1469—1471).—Historical. An account of the discovery fifty years ago of diacetic ester (ethyl acetoacetate) by F. G. Anton Geuther. L. de K.

**The Acid Salts of Dibasic Acids. The Dextro-camphorates.**  
**I. Potassium Camphorates.** É. JUNGFLEISCH and PH. LANDRIEU (*Compt. rend.*, 1913, 157, 826—831).—A study of the conditions governing the formation of normal potassium *d*-camphorate, potassium hydrogen camphorate, and monopotassium di- and tetra-camphorates. A curve is given showing the constitution of the mother liquors, which have furnished these various salts at  $13$ — $15^{\circ}$ . The stability of normal potassium camphorate towards water, as well as the heats of neutralisation of the two acid functions, indicate that *d*-camphoric acid is a strong acid. Potassium hydrogen camphorate by its instability in the presence of water does not behave as an ordinary acid salt of a strong acid, and the authors suggest that its constitution is not that ordinarily attributed to it, but should rather be expressed by



Potassium dicamphorate should be similarly represented by

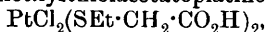


W. G.

**An Occurrence of Tartronic and Mesoxalic Acids.** EDMUND O. VON LIPPMANN (*Ber.*, 1913, 46, 3862—3864).—The author mentions that Mittelstaedt has attempted to decolorise and purify sugar solutions by means of a preparation termed “zinc hydrocarbonate,” but these attempts lead to no results of technical importance. Details are given of the isolation of tartronic and mesoxalic acids from the precipitate formed by treating a dilute alcoholic solution of a somewhat acid syrup, containing invert sugar, with this preparation. F. B.

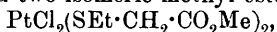
**Configuration of the Two Isomeric Platinous Ethylthiolacetates.** LUDWIG RAMBERG (*Ber.*, 1913, 46, 3886—3894).—The author has shown previously (*A.*, 1910, i, 218) that potassium platinous chloride reacts with potassium ethylthiolacetate, yielding a pale greenish-yellow  $\alpha$ -platinous ethylthiolacetate, which is transformed by exposure to light in aqueous solution into a canary-yellow  $\beta$ -isomeride. The configuration of these two isomerides has now been determined in the following manner.

On treatment with hydrochloric acid the  $\alpha$ -form is converted into two isomeric  $\alpha$ - and  $\beta$ -diethylthiolacetatoplatinous chlorides,

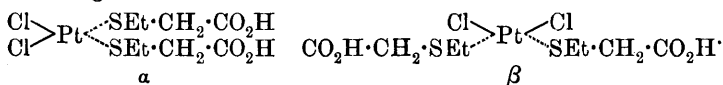


the relative amounts of which vary with the concentration of the

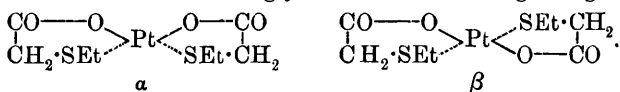
hydrochloric acid employed. Of these two isomerides, the  $\alpha$ -form yields only  $\alpha$ -platinous ethylthiolacetate when shaken with aqueous silver nitrate, whilst the  $\beta$ -isomeride gives rise to a mixture of both  $\alpha$ - and  $\beta$ -platinous ethylthiolacetates. From this the conclusion is drawn that the  $\alpha$ - and  $\beta$ -diethylthiolacetatoplatinous chlorides correspond in configuration to the  $\alpha$ - and  $\beta$ -platinous ethylthiolacetates. On esterification the chlorides yield two isomeric methyl esters,



of which only the one obtained from the  $\alpha$ -compound reacts readily with silver oxalate, yielding the compound  $\text{PtC}_2\text{O}_4(\text{SEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me})_2$ ; the  $\beta$ -ester apparently enters into reaction with silver oxalate only after transformation into the  $\alpha$ -isomeride. The  $\alpha$ -chloro-compound is therefore considered to have the *cis*-configuration and the  $\beta$ -compound the *trans*-configuration :



The original  $\alpha$ - and  $\beta$ -platinous ethylthiolacetates from which these compounds are derived accordingly receive the following configurations :



$\alpha$  (or *cis*)-Diethylthiolacetatoplatinous chloride, prepared by warming  $\alpha$ -platinous ethylthiolacetate with 10–12*N*-hydrochloric acid, crystallises in greenish-yellow prisms, m. p. 146–148°; the methyl ester is obtained by the action of methyl alcohol and sulphuric acid at the ordinary temperature, and crystallises in greenish-yellow plates of rhombic outline, m. p. 131–132°.

$\beta$  (or *trans*)-Diethylthiolacetatoplatinous chloride is best prepared by dissolving  $\alpha$ -platinous ethylthiolacetate in ten times its weight of 4–5*N*-hydrochloric acid and allowing crystallisation to proceed at 25–30°. It forms golden-yellow, prismatic crystals containing 2H<sub>2</sub>O. The anhydrous compound has m. p. about 110°, but owing to transformation into the  $\alpha$ -isomeride, the m. p. varies with the rapidity of the heating. With methyl alcohol and sulphuric acid it yields the  $\beta$ -methyl ester, which, after separation from the accompanying  $\alpha$ -ester, crystallises in orange-yellow prisms, has m. p. 75–76°, and then solidifies owing to transformation into the  $\alpha$ -form.

The oxalate,  $\text{PtC}_2\text{O}_4(\text{SEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me})_2$ , obtained by shaking the  $\alpha$ -ester with silver oxalate and acetone, forms lustrous, colourless crystals, m. p. 156°, and on treatment with hydrochloric acid is converted into the original ester. F. B.

**Sulphur Derivatives of Stearic Acid.** ALFRED ECKERT and OTTOKAR HALLA (*Monatsh.*, 1913, 34, 1811–1813).— $\alpha$ -Thiolstearic acid, C<sub>16</sub>H<sub>33</sub>·CH(SH)·CO<sub>2</sub>H, prepared by heating the potassium salt of  $\alpha$ -bromostearic acid with sodium hydrogen sulphide in alcoholic solution, crystallises in white, pearly, lustrous leaflets, m. p. 74°, yields a potassium salt, crystallising in needles, and is oxidised by

alcoholic iodine to *aa-disulphidodistearic acid*,  $S_2(C_{17}H_{34} \cdot CO_2H)_2$ , which forms white leaflets, m. p.  $70-71^\circ$ , and yields a *potassium* salt, crystallising in microscopic flakes; oxidation with potassium permanganate gives rise to  *$\alpha$ -sulphostearic acid*, which forms a *potassium* salt (microscopic needles), but has not yet been obtained in a pure condition. F. B.

**Action of Calcium on Acetone.** P. N. RAIKOW (*Chem. Zeit.*, 1913, 37, 1455).—When anhydrous acetone is brought into contact with calcium turnings, a slow evolution of hydrogen commences after some time, which ceases after about ten days. The acetone meanwhile has acquired a pale golden-yellow colour, and, when fractionated, yields mainly mesityl oxide,  $COMe \cdot CH : CMe_2$ , b. p.  $125-125.25^\circ/715$  mm. H. W.

**Mechanism of Oxidative Changes.** A. BACH (*Ber.*, 1913, 46, 3864—3868).—The author adversely criticises Wieland's view (*A.*, 1913, i, 1304) that all oxidative processes consist in the addition of water to the oxidisable substance and subsequent dehydrogenation of the hydrate thus formed, and maintains that the oxidation can take place both by the direct addition of molecular oxygen as well as by the decomposition of water into hydroxyl and hydrogen in the manner suggested by Traube. F. B.

**Fucitol.** EMIL VOTOČEK and R. POTMĚŠIL (*Ber.*, 1913, 46, 3653—3655).—Of the pentahydric alcohols corresponding with the methylpentoses, only rhamnitol (Fischer and Piloty, *A.*, 1891, 31) and rhodeitol (Votoček and Bulíř, *A.*, 1905, i, 483) have hitherto been described.

*Fucitol*,  $C_6H_{14}O_5$ , the enantiomorphous isomeride of rhodeitol, has now been prepared by the prolonged reduction of fucose with sodium amalgam in aqueous solution, maintained feebly acid by the addition of sulphuric acid. It crystallises from alcohol in lustrous, silvery leaflets, m. p.  $153-154^\circ$ , has  $[\alpha]_D^{20} 4.7^\circ$  in aqueous solution (containing 0.3991 gram of the alcohol and 1.3 gram borax in 13 c.c.), and combines with rhodeitol in alcoholic solution, yielding racemic fucitol, identical with the racemic rhodeitol described previously (*loc. cit.*).

The preparation of fucose from *Fucus vesiculosus* is also described (compare Widtsoe and Tollens, *A.*, 1900, i, 207). F. B.

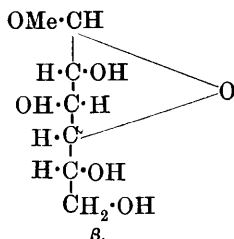
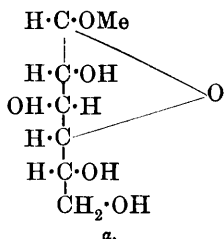
**Influence of Dextrose and Lævulose on Sodium Hyposulphite.** LEOPOLD RADLBERGER and WILHELM SIEGMUND (*Chem. Zentr.*, 1913, ii, 854; from *Österr.-ung. Zeitsch. Zucker Ind. Landw.*, 1913, 42, 526—538).—Attempts to isolate compounds of these aldehydic and ketonic sugars with sodium hyposulphite were without result. Indirect proof of their formation was obtained, however, by the titration method devised by Stewart in the investigation of compounds of ketones with sodium hydrogen sulphite (*T.*, 1905, 87, 185). It seems possible that the compound,  $NaHSO_2 \cdot C_6H_{12}O_6$ , exists in alkaline solution. Such a substance would scarcely exist in acid solutions, and the low titration values obtained under those conditions

indicate that the sugars are reduced to some extent by sodium hyposulphite. J. C. W.

**The Acid Dissociation Constants of Alcohols and Sugars, Especially of the Methylglucosides.** LEONOR MICHAELIS (*Ber.*, 1913, 46, 3683—3693).—The author re-describes the electrometric method of determining the dissociation constants of very weak acids (Michaelis and Rona, A., 1913, ii, 379), and gives the following new data: ethylene glycol,  $5.7 \times 10^{-15}$ ; erythritol,  $1.25 \times 10^{-14}$ ; rhamnose,  $6.2 \times 10^{-13}$ ; sorbose,  $27.8 \times 10^{-13}$ ; xylose,  $7.2 \times 10^{-13}$ ;  $\alpha$ -methylglucoside,  $1.97 \times 10^{-14}$ , and  $\beta$ -methylglucoside,  $2.64 \times 10^{-14}$ .

In the case of alcohols, the dissociation constant increases with the number of hydroxyl groups. Pentose and hexoses have approximately the same strength, but are considerably stronger acids than the corresponding alcohols.

The difference in the strength of  $\alpha$ - and  $\beta$ -methylglucosides is referred by the author to the position of the methyl group, which,



owing to its positive influence, depresses the acid character of the adjacent hydroxyl group, the depression being greater when the two groups are in the *cis*-position.

$\alpha$ -Methylglucoside, being a weaker acid

than the  $\beta$ -compound, must therefore have the methoxy- and adjacent hydroxyl groups in this position, and the above formulæ are accordingly assigned to these compounds. F. B.

**Preparation of Derivatives of the Sugars with Hydroxybenzoic Acids and their Alkylcarbonato-, Acetyl- and Alkyl-derivatives.** KARL JOH. FREUDENBERG (D.R.-P. 264654).—When sugars suspended in an indifferent solvent are treated with the chlorides of monoalkylcarbonato-, acetoxy-, or alkyloxy-benzoic acids in the presence of a tertiary base they furnish compounds which on hydrolysis give rise to the corresponding derivatives of the hydroxybenzoic acids.

*Penta-p-methylcarbonatobenzoyl-glucose* is obtained when dextrose is treated with *p*-methylcarbonatobenzoyl chloride in the presence of quinoline and chloroform, the mixture cooled during one hour, and subsequently left during about forty-six hours at the ordinary temperature; the product is isolated as hard, brittle masses.

*Penta-p-hydroxybenzoyl-glucose* is obtained as a colourless, flocculent mass when the foregoing compound is hydrolysed. It is dextro-rotatory.

*Penta-o-methylcarbonatobenzoyl-glucose* is prepared in a similar manner with carbomethoxysalicyl [*o*-methylcarbonatobenzoyl] chloride; it is a pale yellow, tasteless powder. Acetylsalicyl [*o*-acetoxybenzoyl] chloride and anisoyl chloride give rise respectively to *penta-o-acetoxybenzoyl-glucose* and *penta-anisoylglucose*. F. M. G. M.

**The Hydrolysis of Levulosans and its Application to Plant Analysis.** PH. DE VILMORIN and F. LEVALLOIS (*Bull. Soc. chim.*, 1913, [iv], 13, 1060—1063, 1063—1068. Compare *ibid.*, 1908, [iv], 3, 681).—A theoretical discussion of their results and those of other workers on the hydrolysis of inulin, the authors having repeated their hydrolysis with three samples of inulin obtained from different sources.

The second paper is a comparison of the reducing powers of dextrose, lævulose, and invert sugar under different conditions, and in the case of invert sugar with different inverting agents. W. G.

**Preparation of Methylamine.** J. D. RIEDEL (D.R.-P. 264528 Compare A., 1904, ii, 180).—When an aqueous solution containing 20 grams of ferrocyanic acid is shaken with about 8 litres of hydrogen in the presence of colloidal palladium (0.1 gram) and hydrochloric acid, it gives rise to 11.3 grams of pure methylamine hydrochloride; the ferrocyanic acid can be replaced by potassium cyanide or ferrocyanide, and the palladium by other metals of the platinum group in a colloidal condition. F. M. G. M.

**The Nature of Subsidiary Valencies. VI. The Influence of the Neutral Part on the Stability of the Complex.** FRITZ EPHRAIM and RICHARD LINN (*Ber.*, 1913, 46, 3742—3762).—In order to determine how the dissociation temperature, and consequently the affinity (compare A., 1912, ii, 546; A., 1913, ii, 129, 130), varies when the ammonia in complexes of the type  $M[NH_3]_nX_2$  is replaced by other neutral parts, the compounds formed from methylamine, ethylamine, propylamine, dimethylamine, trimethylamine, and the halogen salts of nickel, cobalt, iron, manganese, copper, cadmium and zinc have been prepared and their dissociation pressures measured at various temperatures. The various compounds were prepared in most cases by leading the vapour of the amine over the anhydrous halogen salt, whereby similar phenomena were observed to those occurring when the corresponding ammonia compounds are prepared.

The chlorides, bromides and iodides of cobalt, nickel and manganese combine with six molecules; copper iodide, bromide and chloride with four molecules; cadmium iodide and bromide with three molecules, and the chlorides, bromides and iodides of zinc and iron with five molecules of methylamine.

Nickel iodide and bromide, and cobalt and manganese iodides form salts with either six or four molecules; nickel, cobalt and manganese chlorides, and cobalt and manganese bromides with four molecules of ethylamine.

Nickel iodide combines with either six or four molecules; nickel bromide with four, and nickel chloride with two molecules of dimethylamine. Cobalt chloride did not enter into combination. Diethylamine would not combine with salts of either nickel, cobalt or manganese.

With propylamine, nickel iodide forms the salt  $NiI_2 \cdot 2NH_2Pr$ , and with trimethylamine the salt  $NiI_2 \cdot 1.5$  or  $2NMe_3$ . It also combines

with three molecules of pyridine and two molecules of quinoline and aniline respectively.

As in the case of the ammonia compounds (*loc. cit.*), the product  $\sqrt[3]{v} \sqrt[3]{T}$ , where  $v$  is the atomic volume of the metal and  $T$  the absolute dissociation temperature, is a constant, at all events for the compounds of nickel, cobalt, iron and manganese. Comparison of various physical constants shows that the critical pressure ( $P$ ) of the liquid bases, or else the expression  $(T + 273)/P$ , best runs parallel with the dissociation temperature of the salts; there is also a certain amount of parallelism between the dissociation temperature of the salts and the molecular volume of the bases.

Calculation of the various moduli, I : Br, Br : Cl, and I : Cl (compare A., 1912, ii, 546) gives similar relations to those found to hold with the ammonia compounds.

The results hitherto obtained with the various complexes show that the relations are exactly reversed when complex anions are considered instead of complex cations.

T. S. P.

**The Asymmetric Cobalt Atom. IX.** A. WERNER (*Ber.*, 1913, 46, 3674—3683).—The author describes a new series of optically active cobalt compounds which contain two asymmetric cobalt atoms in the molecule, that is, which are analogous to the tartaric acids. They consist of tetraethylenediamine- $\mu$ -aminonitrodicobaltic salts,

$\left[ \text{en}_2 \text{Co} \cdot \overset{\cdot}{\text{NH}_2} \cdot \text{Co} \text{en}_2 \right] \text{X}_4$ , which are obtained from the tetraethylene-

diamine- $\mu$ -aminoperoxo-dicobalt salts,  $\left[ \text{en}_2 \text{Co} \cdot \overset{\text{III}}{\text{NH}_2} \cdot \overset{\text{IV}}{\text{O}_2} \cdot \text{Co} \text{en}_2 \right] \text{X}_4$ , by the action of nitrous acid. The nitrate was prepared in this way, and from this the corresponding  $\mu$ -aminonitrobromide by double decomposition with ammonium bromide.

Resolution was effected as follows: Tetraethylenediamine- $\mu$ -aminonitrodicobaltic bromide was treated with silver *d*-bromocamphorsulphonate, and the reaction product subjected to fractional crystallisation, whereby three different *d*-bromocamphorsulphonates were obtained. The most easily soluble (*A*) crystallised with  $8\text{H}_2\text{O}$ , and was inactive; the less soluble compound (*B*) crystallised with  $7\text{H}_2\text{O}$ , and had  $[\alpha] + 72^\circ$  in 0.25% solution; the least soluble compound (*C*) crystallised with  $6\text{H}_2\text{O}$ , and had  $[\alpha] + 160^\circ$  in 0.25% solution. Each of these bromocamphorsulphonates was then treated with concentrated hydrobromic acid and the corresponding bromide obtained. That from (*A*) was laevorotatory, that from (*B*) inactive, and that from (*C*) dextrorotatory, the *l*- and *d*-bromides having equal and opposite rotations,  $[\alpha] \pm 164^\circ$ .

All attempts to resolve the bromocamphorsulphonate of the inactive series into active components were unsuccessful.

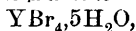
Racemic salts were obtained by mixing the *d*- and *l*- salts, and were quite different from the inactive salts just mentioned (*meso*-salts), both as regards the number of molecules of water of crystallisation and their greater solubility in water (see later).

On long boiling of their aqueous solutions, the active camphorsulphonates change into inactive salts of the *meso*-series.

The constitutional formula which has hitherto been assigned to these compounds is:  $\left[ \text{en}_2 \text{Co} \begin{smallmatrix} \text{NO}_2 \\ \text{NH}_2 \end{smallmatrix} \text{Co en}_2 \right] \text{X}_4$ , that is, the two cobalt atoms, from a valency point of view, are not linked up in absolutely the same way. The optical investigation of the compounds described in this paper does not indicate, however, that there is any difference between the two cobalt atoms, and it therefore follows that there is no essential difference between principal and subsidiary valencies.

*l*-Tetraethylenediamine- $\mu$ -aminonitrodicobaltic d-bromocamphorsulphonate, *l*-Y-d-( $\text{SO}_3 \cdot \text{C}_{10}\text{H}_{14}\text{OBr}$ )<sub>4</sub>·8H<sub>2</sub>O, where  $\text{Y} = \left[ \text{en}_2 \text{Co} \begin{smallmatrix} \cdot \text{NH}_2 \\ \cdot \text{NO}_2 \end{smallmatrix} \text{Co en}_2 \right]$ , crystallises in well-developed, glistening, orange-red crystals. It is optically inactive, but gives rise to salts of the *laevo*-series. The corresponding d-d-salt, d-Y-d-( $\text{SO}_3 \cdot \text{C}_{10}\text{H}_{14}\text{OBr}$ )<sub>4</sub>·6H<sub>2</sub>O, is the least soluble of the bromocamphorsulphonates dealt with, crystallising in rectangular, shimmering leaflets. It has  $[\alpha]^{17} + 160^\circ$  and  $[\text{M}]^{17} + 2828.8^\circ$ , and gives rise to salts of the *dextro*-series.

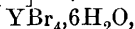
d- and l-Tetraethylenediamine- $\mu$ -aminonitrodicobaltic bromides,



crystallise in lancet-shaped, reddish-orange, efflorescent crystals;  $[\alpha]^{16} + 164^\circ$ ,  $[\text{M}]^{16} + 1361.2^\circ$ ,  $[\alpha]^{17} - 162^\circ$ ,  $[\text{M}]^{17} - 1344.6^\circ$ . The d- and l-iodides,  $\text{YI}_4$ , crystallise in dark red octahedra;  $[\alpha]^{17} + 138^\circ$  and  $-136^\circ$ ,  $[\text{M}]^{17} + 1280.6^\circ$  and  $-1262.1^\circ$ . The d- and l-thiocyanates,  $\text{Y}(\text{SCN})_4 \cdot 3\text{H}_2\text{O}$ , forms monoclinic, reddish-orange, columnar crystals;  $[\alpha]^{18} + 182^\circ$ ,  $[\text{M}]^{18} + 1284.9^\circ$ ,  $[\alpha]^{17} - 184^\circ$ ,  $[\text{M}]^{17} - 1299.0^\circ$ .

The following *racemates* were obtained by mixing equal quantities of the d- and l-isomerides. The *bromide*,  $\text{YBr}_4 \cdot 5\text{H}_2\text{O}$ , forms dark red, cubical crystals; the *iodide*,  $\text{YI}_4$ , crystallises in prisms; the *thiocyanate*,  $\text{Y}(\text{SCN})_4 \cdot 3\text{H}_2\text{O}$ , forms dark red, prismatic crystals.

The following are salts of the *meso*-series. The d-bromocamphorsulphonate, Y-d-( $\text{SO}_3 \cdot \text{C}_{10}\text{H}_{14}\text{OBr}$ )<sub>4</sub>·7H<sub>2</sub>O, crystallises as felted, bright orange needles;  $[\alpha]^{17} + 72^\circ$ ,  $[\text{M}]^{17} + 1285.9^\circ$ . The *bromide*,



forms stout, prismatic, yellowish-red crystals. The *iodide*,  $\text{YI}_4 \cdot \text{H}_2\text{O}$ , separates as a micro-crystalline, orange-coloured precipitate, as also does the *thiocyanate*,  $\text{Y}(\text{SCN})_4 \cdot \text{H}_2\text{O}$ .

The following solubilities were determined, and are expressed as grams of salt in 100 c.c. of water: *meso*-bromide, 1.95 (18°), *r*-bromide, 2.31 (20°), *meso*-iodide, 2.44 (19°), *r*-iodide, 3.75 (19°), *meso*-bromocamphorsulphonate, 0.51–0.52 (17°).

In a succeeding paper it will be shown that the tetraethylenediamine- $\mu$ -aminoperoxo-salts have rotations of opposite sign to those of the corresponding  $\mu$ -aminonitro-salts.

T. S. P.

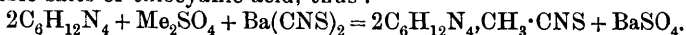
**Preparation of Hexamethylenetriperoxidediamine.** CONWAY (FREIHERR) VON GIRSEWALD (D.R.-P. 263459).—Satisfactory yields of hexamethylenetriperoxidediamine (Legler, A., 1886, 327; Baeyer and Villiger, A., 1900, i, 626) have not been obtained previously, but the following method is found to give a 66% yield and is applicable for its



technical production. Hexamethylenetetramine (28 parts) and citric acid (42 parts) are dissolved in 140 parts of 30% hydrogen peroxide solution; on gently warming, the product separates in small, rhombic crystals.

F. M. G. M.

**Preparation of Hexamethylenetetramine Methyl Thiocyanate.** KARL HEINRICH SCHMITZ (D.R.-P. 266788).—*Hexamethylenetetramine methyl thiocyanate* is prepared by the interaction of hexamethylenetetramine and methyl thiocyanate or by treating the additive compound of the base and the methyl esters of inorganic or organic acids with soluble salts of thiocyanic acid, thus:



The compound crystallises in large, colourless prisms, m. p. 193° (decomp.).

J. C. C.

**Preparation of Dimethylaminomethyl Alcohol.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 266866).—On treatment with water the halogen additive compounds of trimethylamine (for example, trimethylamine dichloride,  $\text{NMe}_3\text{Cl}_2$ ) decompose into dimethylamine hydrohaloid, formaldehyde, and the halogen acid. In the presence of alkalis (such as potassium carbonate), dimethylamine and formaldehyde combine to form dimethylaminomethyl alcohol.

J. C. C.

**Preparation of Amides of Amino-acids and their Derivatives.** CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 264263).—When the additive compounds obtained from hexamethylenetetramine and halogen-substituted acid amides are warmed, or left in contact with alcoholic hydrogen chloride, they give rise to the corresponding amino-amides.

Chloroaceto-*p*-aminophenetidine (213 parts) and hexamethylenetetramine (140 parts) were left together in chloroform solution during several days; after removal of the solvent the residue was heated in alcoholic hydrogen chloride until the separation of ammonium chloride was ended, and the filtrate subsequently evaporated to dryness in a vacuum, whereby the hydrochloride of aminoacetamide is produced.

F. M. G. M.

**Identification of the Amino-acid,  $\text{C}_6\text{H}_{13}\text{O}_2\text{N}$ , from the Protein of Nervous Tissue.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1913, 88, 272—275. Compare A., 1913, i, 450).—The amino-acid,  $\text{C}_6\text{H}_{13}\text{O}_2\text{N}$ , from the spinal marrow has been identified by the analysis, the rotatory power, and the  $\beta$ -naphthalenesulphonyl compound with *d*- $\alpha$ -amino-*n*-hexic acid. Its presence is indicated in other proteins.

An  $\alpha$ -aminobutyric acid of unknown structure has been detected in the products of protein hydrolysis.

E. F. A.

**Preparation of Ferrous Compounds of the Monoamino-series.** F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 266522. Compare this vol., i, 23).—Ferrous salts of amino-acids (for example, histidine and alanine) or of peptones (gliadin) are obtained by boiling the

amino-compound with finely divided iron in a stream of carbon dioxide. J. C. C.

**Preparation of Amino- and Diamino-ketones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 266656. Compare A, 1913, i, 343).—In place of dimethylaminomethyl alcohol or methylenetetramethyldiamine (tetramethyldiaminomethane) as described in the previous patent, their homologues or analogues can be condensed with acetone or its homologues to furnish keto-bases of the general formula  $\text{CH}_3\cdot\text{CO}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NR}_2$ , and keto-diamines of the formula  $\text{CH}_3\cdot\text{CO}\cdot\text{CR}(\text{CH}_2\cdot\text{NR}_2)_2$ , where R denotes hydrogen or alkyl.

The condensation of diethylaminomethyl alcohol and acetone yields *diethyl- $\gamma$ -ketobutylamine*, a colourless oil with an ammoniacal odour and sparingly soluble in water, b. p. 72—76°/16 mm., and  *$\beta$ -acetylpropylenediethyldiamine*, a yellow, viscid oil, b. p. 95—100°/7—8 mm.

Diethylaminomethyl alcohol and methyl ethyl ketone furnish *diethyl- $\gamma$ -keto- $\beta$ -methylbutylamine*, a colourless oil with a faintly ammoniacal odour and sparingly soluble in water, b. p. 77—78°/16 mm., and  *$\beta$ -acetyl- $\beta$ -methylpropylenediethyldiamine*, a yellow, viscid oil, b. p. 105—110°/7 mm.

Methylenephenyldimethyldiamine (m. p. 51°; prepared from formaldehyde, dimethylamine, and aniline) when condensed with acetone gives *dimethyl- $\gamma$ -ketobutylamine*, b. p. 53—57°/18 mm., and  *$\gamma$ -ketobutylaniline*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHPh}$ , b. p. 140—145°/10 mm., which is a yellow oil. J. C. C.

**Preparation of Amino- and Diamino-ketones of the Aliphatic Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 267347. Compare A., 1911, i, 598; 1913, i, 343).—The formation of by-products in the condensation of acetone and its homologues with dialkylaminomethyl alcohol or tetra-alkyldiaminomethane (produced in the one operation by the action of formaldehyde on dialkylamines) is considerably diminished by the addition of an indifferent, non-miscible solvent, such as benzene, and a salt, such as sodium chloride. The products are obtained from the benzene layer already sufficiently dry for fractionation. The relative quantities of the two ketones depends on the amount of acetone used. J. C. W.

**Amides.** ANTOINE P. N. FRANCHIMONT (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 376—379).—It has been previously shown (Moll van Charante, A., 1913, i, 345) that the diamide of sulphisobutyric acid does not react with carbonyl chloride or oxalyl chloride, whereas benzenesulphonamide is converted by the latter reagent into diphenylsulphoxamide (compare Bornwater, A., 1911, i, 617). The author has, therefore, investigated the behaviour of isobutyramide and ethanesulphonamide towards oxalyl chloride, these substances being more closely allied to sulphisobutyrodiamide than is benzenesulphonamide.

*iso*Butyramide readily evolves hydrogen chloride when treated with oxalyl chloride in benzene solution, and yields *isobutyronitrile* and *oxalyl-diisobutyrylamide*,  $\text{C}_2\text{O}_2(\text{NH}\cdot\text{CO}\cdot\text{C}_3\text{H}_7)_2$ , m. p. 160°. A carbonyl derivative was not obtained.

*iso*Butyromethylamide,  $C_8H_7 \cdot CO \cdot NHMe$ , is obtained as a colourless liquid, b. p.  $110^\circ/17$  mm.,  $D_{16}^{20}$  0.9089, m. p. fully  $20^\circ$ , by the action of *isobutyryl* chloride on methylamine in ethereal solution at a low temperature.

Ethanesulphonamide, m. p.  $60^\circ$ , reacts with oxalyl chloride in benzen solution, yielding *oxalyl-di-ethanesulphonamide*,  $C_2O_2(NH \cdot SO_2Et)_2$ , m. p.  $224^\circ$ , which is decomposed on boiling with water.

Ethanesulphonmethylamide (compare Franchimont and Klobbie, A., 1887, 469) may be obtained by the action of an ethereal solution of ethanesulphonyl chloride on an aqueous 33% solution of methylamine. When strongly cooled, it solidifies to a mass which probably melts between  $3^\circ$  and  $7^\circ$ . When boiled with oxalyl chloride in benzene solution, it slowly evolves hydrogen chloride, and gives *oxalyl-diethanesulphondimethylamide*,  $C_2O_2(NMe \cdot SO_2Et)_2$ , m. p.  $144^\circ$ .

*iso*Butyramide and benzenesulphonamide slowly evolve nitrous oxide when treated with absolute nitric acid at the ordinary temperature; under like conditions, ethanesulphonamide gives an almost explosive evolution of the gas. Sulpho*isobutyro*diamide, on the other hand, dissolves slowly in absolute nitric acid without evolution of gas even after two days, and is reprecipitated unchanged by addition of water, particularly on neutralising the acid.

*Ethanesulphon-nitramide*, m. p.  $70^\circ$ , is obtained in poor yield by the action of nitric and sulphuric acids at low temperatures on ethanesulphonamide. H. W.

**Preparation of Derivatives of Glycolylurethane.** ARNOLD VOSWINKEL (D.R.-P. 266121).—In the reaction described in the chief patent (A., 1912, i, 837), bromo- and chloro-acetylurethane can be substituted for bromoacetylcarbamide.

*Methyl chloroacetylcarbamate*, m. p.  $145^\circ$ , is obtained from chloroacetyl chloride and methyl carbamate; the *isobutyl* ester has m. p.  $78^\circ$ . *Methyl bromoacetylcarbamate* has m. p.  $148^\circ$ , and the *isobutyl* ester, m. p.  $87^\circ$ . These esters can also be prepared by the interaction of halogen-substituted fatty esters, and the corresponding sodium urethane.

*Acetoxyacetylurethane*,  $OAc \cdot CH_2 \cdot CO \cdot NH \cdot CO_2Et$ , prepared by boiling a mixture of bromoacetylurethane, sodium acetate, and alcohol, crystallises in colourless needles, m. p.  $98^\circ$ .

*Bromoisovaleroxyacetylurethane* forms needles, m. p.  $103^\circ$ . *Salicyloxyacetylurethane* has m. p.  $146^\circ$ . The condensation of sodium bromoisovalerate and methyl chloroacetylcarbamate yields *methyl bromoisovaleroxyacetylcarbamate*, m. p.  $90^\circ$ , and sodium salicylate and methyl chloroacetylcarbamate furnish *methyl salicylyloxyacetylcarbamate*, m. p.  $150^\circ$ . J. C. C.

**The Sublimation and Decomposition of Acetylcarbamide.** RASIK LAL DATTA and SATYARANJAN DAS GUPTA (*J. Amer. Chem. Soc.*, 1913, 35, 1893—1895).—It is already known that acetylcarbamide when heated decomposes, giving cyanuric acid and acetamide (Zinin, *Annalen*, 1854, 92, 405). The authors find that the decomposition is a quantitative one, but that when the substance is heated in tubes

partially immersed in sulphuric acid at 180—190°, a portion of the substance sublimes unchanged.

D. F. T.

**Preparation of a Ferrous Salt of Glutamic Acid.** F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 264390).—*Ferrous glutamate*,  $[\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2]_2\text{Fe}$ , a colourless or slightly coloured salt, readily soluble in water, and stable in the dry condition, is obtained when an aqueous solution of glutamic acid is boiled with an excess of iron powder in an oxygen-free atmosphere, filtered, and subsequently evaporated to dryness.

F. M. G. M.

**Production of Dialuric Acids and Uramils.** HEINRICH BILTZ and PAUL DAMM (*Ber.*, 1913, 46, 3662—3673).—Uramil and its methyl derivatives are best prepared by heating dialuric acids with ammonium or methylammonium salts in aqueous or acetic acid solution. The preparation of the dialuric acids is most conveniently accomplished by reducing the alloxans with stannous chloride in hot hydrochloric acid solution, or by the reduction of the corresponding alloxantins with sodium amalgam and water.

The dialuric acids are strong monobasic acids, which are quite stable when dry, but in the moist condition are readily oxidised to alloxantins on exposure to air.

Full details of the preparation of the following compounds, most of which have been described previously, are given :

Dialuric acid, stout prisms or narrow, thin leaflets with rounded ends ; it becomes red at 180°, and has m. p. 214—215° (corr.).

1-Methyldialuric acid,  $\text{C}_5\text{H}_6\text{O}_4\text{N}_2$ , prepared by reducing dimethylalloxantin (this vol., i, 167) with sodium amalgam, crystallises in spherical aggregates of slender, lustrous, silky needles or narrow, lancet-shaped leaflets, m. p. 167—168° (corr.), containing  $1\text{H}_2\text{O}$  ; from alcohol it separates in anhydrous, stout, lustrous rhombohedra, m. p. 184—185° (corr.).

1:3-Dimethyldialuric acid, from tetramethylalloxantin and sodium amalgam, crystallises with  $1\text{H}_2\text{O}$  in prisms, which lose their water at 110°, and then have m. p. 218° (corr., decomp.) (compare Techow, A., 1895, i, 83) ; the sodium salt forms long, pointed prisms.

Uramil, from dialuric acid and ammonium chloride, crystallises in slender, jagged leaflets, m. p. 310—320° (corr., decomp.).

1-Methyluramil, hexagonal leaflets, m. p. 272° (corr., decomp.).

7-Methyluramil, from dialuric acid and methylamine in acetic acid solution, acquires a violet colour at 250° and then slowly decomposes.

1:3-Dimethyluramil forms lustrous, silky, felted needles, which become red at 220° and have m. p. about 300° (corr., decomp.) [compare Techow, *loc. cit.*].

1:7-Dimethyluramil crystallises in stout, almost colourless, lustrous rhombohedra, which acquire a deep violet colour at about 225° and have m. p. 276° (corr., decomp.) (compare Fischer and Clemm, A., 1898, i, 178) ; with potassium cyanate in aqueous solution, it yields 1:7-dimethyl- $\psi$ -uric acid,  $\text{C}_7\text{H}_{10}\text{O}_4\text{N}_4$ , crystallising in stout rhombohedra, m. p. 236° (corr., decomp.).

1:3:7-Trimethyluramil is also described.

F. B.

**Preparation of Dialkalicyanamide.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 267595).—When cyanamide or its polymerides, especially dicyanodiamide, is gradually stirred into alkali hydroxides at about 500°, dialkalicyanamides are formed. By adding carbonaceous matter and elevating the temperature, these may be transformed into cyanides.

The main reaction follows the course indicated by the equation:  $4\text{NaOH} + \text{C}_2\text{H}_4\text{N}_4 = 2\text{Na}_2\text{CN}_2 + 4\text{H}_2\text{O}$ . The greater part of the water formed is expelled, but some causes the formation of a carbonate and the evolution of ammonia; thus,  $3\text{H}_2\text{O} + \text{Na}_2\text{CN}_2 = \text{Na}_2\text{CO}_3 + 2\text{NH}_3$ . This may be overcome, to a great extent, by the addition of the oxides, amides, nitrides, carbides, metals, or alloys of the alkalis or alkaline earths.

J. C. W.

**Ethoxymethylenemalononitrile and its Derivatives.** T. PASSALACQUA (*Gazzetta*, 1913, 43, ii, 566—569).—*Ethoxymethylenemalononitrile*,  $\text{OEt}\cdot\text{CH}:\text{C}(\text{CN})_2$ , prepared by the condensation of ethyl orthoformate and malononitrile in presence of acetic anhydride, forms small prisms, m. p. 67°, b. p. 156—157°/15 mm.

*Aminomethylenemalononitrile*,  $\text{NH}_2\cdot\text{CH}:\text{C}(\text{CN})_2$ , obtained by the action of aqueous ammonia on the preceding compound, forms shining, white scales, m. p. 140°.

*Carbamidomethylenemalononitrile*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}:\text{C}(\text{CN})_2$ , prepared from carbamide and ethoxymethylenemalononitrile, forms slender, white needles or a crystalline powder, turning yellow at about 180° and decomposing without melting at about 260°.

*Acetylaminomethylenemalononitrile*,  $\text{NHAc}\cdot\text{CH}:\text{C}(\text{CN})_2$ , similarly prepared, forms white needles, m. p. 134°, unstable towards light.

*Phenylhydrazinomethylenemalononitrile*,  $\text{NH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}:\text{C}(\text{CN})_2$ , similarly prepared, forms shining, orange scales, m. p. 136°.

*p-Toluidinomethylenemalononitrile*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CH}:\text{C}(\text{CN})_2$ , forms slender needles decomposing at 260°.

T. H. P.

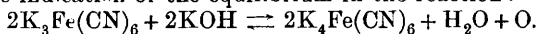
**Ferrocyanides and Mercuric Cyanide.** D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1913, 84, 208—216).—An additive compound of potassium ferrocyanide with mercuric cyanide is known (Kane, *J. pr. Chem.*, 1840, 19, 405). Several such compounds have now been prepared, most of which contain 3 mols. of ferrocyanide to one of mercuric cyanide. This type is the most stable, suggesting the presence of a complex anion,  $\text{Fe}[\text{Hg}(\text{CN})_3]_6$ . The compounds obtained, which vary considerably in solubility and stability, are:

$\text{Rb}_4\text{Fe}(\text{CN})_6\cdot 3\text{Hg}(\text{CN})_2\cdot 4\text{H}_2\text{O}$ ;  
 $(\text{NH}_4)_4\text{Fe}(\text{CN})_6\cdot 3\text{Hg}(\text{CN})_2\cdot 2\text{H}_2\text{O}$ ;  $(\text{NMe}_4)_4\text{Fe}(\text{CN})_6\cdot 3\text{Hg}(\text{CN})_2$ ;  
 $(\text{SMe}_3)_4\text{Fe}(\text{CN})_6\cdot 3\text{Hg}(\text{CN})_2$ ;  
 $(\text{NH}_2\text{Me}_2)_4\text{Fe}(\text{CN})_6\cdot 3\text{Hg}(\text{CN})_2$ ;  $(\text{NH}_2\text{Et}_2)_4\text{Fe}(\text{CN})_6\cdot 2\text{Hg}(\text{CN})_2\cdot 2\text{H}_2\text{O}$ ;  
 $(\text{NH}_3\text{Me})_4\text{Fe}(\text{CN})_6\cdot 2\text{Hg}(\text{CN})_2\cdot 4\text{H}_2\text{O}$ ;  $(\text{NH}_3\text{Et})_4\text{Fe}(\text{CN})_6\cdot 3\text{Hg}(\text{CN})_2$ .

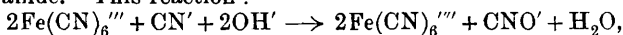
Triethylammonium ferrocyanide forms two compounds of nearly equal solubility, and a second compound has also been observed in the case of tetramethylammonium ferrocyanide. Potassium ferricyanide does not yield a similar compound.

C. H. D.

**The Behaviour of Alkaline Potassium Ferricyanide Solutions.** G. GRUBE (*Zeitsch. anorg. Chem.*, 1913, **84**, 190—207).—The potential experiments of Fredenhagen (A., 1902, ii, 238) have given some indication of the equilibrium in the reaction:



In order to study the reaction under the conditions of technical practice, the present experiments have been carried out at 90°. The velocity of change of ferri- into ferro-cyanide at first diminishes slightly, then increases rapidly to a maximum at forty-eight hours, and then again falls rapidly. The process is one of autocatalysis, the agent being ferrocyanide. The addition of ferrocyanide to a ferricyanide solution is thus found to accelerate the reaction very considerably. The cause is the greater secondary dissociation of the ferrocyanide ion as compared with the ferricyanide, causing an increase in the concentration of the cyanide ions, which are then oxidised to cyanate by the ferricyanide. This reaction:



proceeds very rapidly. The cyanate is then converted at 90° into carbon dioxide and ammonia or into carbamide. Towards the end of the reaction an addition of ammonia accelerates the conversion. Hydrolysis of hydrocyanic acid to formic acid, followed by oxidation of the latter, is also possible, and yields the same end-products, but the lower velocity of the hydrolysis as compared with the direct oxidation indicates the latter as the actual cause of the autocatalysis.

C. H. D.

**Ferro- and Ferri-cyanides of Betaines.** GEORG ROEDER (*Ber.*, 1913, **46**, 3724—3727).—In addition to the well-known use of ferrocyanic acid for the separation of mixtures of aromatic bases, especially of the easily soluble quaternary ammonium hydroxides and also pyridine, it is found that it can be applied with success to the separation of betaines; both ferro- and ferri-cyanic acids form sparingly soluble salts with substances of this class.

*Betaine ferrocyanide*,  $(C_5H_{11}O_2N)_4 \cdot H_4Fe(CN)_6 \cdot 2H_2O$ , forms an almost colourless powder or cubic crystals from water.

*Betaine ferricyanide*,  $(C_5H_{11}O_2N)_4 \cdot H_3Fe(CN)_6 \cdot 2H_2O$ , yellow leaflets or rhombohedra from water.

*Pyridinebetaine ferrocyanide* and *ferricyanide* were obtained as yellow precipitates and separate from water in needles and prisms respectively.

*Trigonelline ferrocyanide* and *ferricyanide* crystallise in red and yellow prisms respectively.

The above salts were prepared by mixing concentrated solutions of the hydrochloride of the base and of potassium ferro- or ferri-cyanide.

The formation of such sparingly soluble salts lends itself well to the extraction of betaine from molasses, and details are given as to the best procedure for precipitation as ferrocyanide from methyl-alcoholic solution and as ferro- or ferri-cyanide from aqueous solution.

D. F. T.

**The Decomposition of Nitroprussides by Reagents.** KSHITIBHUSAN BHADURI (*Zeitsch. anorg. Chem.*, 1913, **84**, 95—96).—Sodium amalgam reduces nitroprussides to ferrocyanides and ammonia:  $12\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5 + 8\text{Na}_2 + 54\text{H} = 10\text{Na}_4\text{Fe}(\text{CN})_6 + 12\text{NH}_3 + \text{Fe}_2\text{O}_3 + 9\text{H}_2\text{O}$ , but in neutral solution, with a copper-zinc couple, nitrogen is formed:  $4\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5 + 10\text{H} = 2\text{Na}_4\text{Fe}(\text{CN})_6 + 8\text{HCN} + 2\text{N}_2 + \text{H}_2\text{O} + \text{Fe}_2\text{O}_3$ . With sodium amalgam and sulphuric acid, a part of the cyanogen is obtained as Prussian-blue and a part as hydrogen cyanide:  $4\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5 + 19\text{H}_2\text{SO}_4 + 14\text{Na}_2 = 2\text{FeNaFe}(\text{CN})_6 + 2(\text{NH}_4)_2\text{SO}_4 + 4\text{H}_2\text{O} + 17\text{Na}_2\text{SO}_4 + 8\text{HCN}$ . Hydrochloric acid decomposes nitroprussides:  $\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5 + 7\text{HCl} = 2\text{NaCl} + 5\text{HCN} + \text{FeCl}_3 + \text{H}_2\text{O} + \text{Cl}_2$ , and the ferric chloride then reacts with excess of the salt to form ferric nitroprusside. All the products have been shown to occur.

Concentrated sulphuric acid forms nitrous fumes, hydrogen cyanide, carbon monoxide, and sulphur dioxide. Neutral potassium permanganate is without action.

C. H. D.

**Hydroxamic Acid Ester and Halogen Imino-ethers of the Aliphatic Series.** J. HOUBEN and ERICH SCHMIDT (*Ber.*, 1913, **46**, 3616—3627).—*Ethyl acethydroximate*,  $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OEt}$ , is obtained on shaking an ethereal solution of the imino-ether with aqueous hydroxylamine hydrochloride. In this way the excess of hydrochloride is prevented from passing into solution with the reaction product. The ester forms a colourless oil of strong and agreeable odour, b. p. 59—60°/13 mm., and crystallising in needles, m. p. 25—26°. It gives a red coloration with ferric chloride which is less pronounced than that given by the hydroxamic acid. Chlorine in carbon tetrachloride gives an intense blue coloration with the ester, probably due to the formation of  $\alpha$ -chloro- $\alpha$ -nitrosoethyl ether,  $\text{CH}_3\cdot\text{CCl}(\text{NO})\cdot\text{OEt}$ .

Ethyl cyaniminocarbonate,  $\text{HN}\cdot\text{C}(\text{CN})\cdot\text{OEt}$ , and phenylcarbimide react to form a *compound*,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ , of unknown constitution, m. p. 184°. Hot concentrated hydrochloric acid converts it into a *compound*, m. p. 210°, which contains the same proportion of nitrogen.

Ethyl cyaniminocarbonate in ether reacts with hydroxylamine hydrochloride to form oxalenediamidoxime, m. p. 202°.

Ethyl di-imino-oxalate,  $\text{HN}\cdot\text{C}(\text{OEt})\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , reacts normally with phenylcarbimide, forming *bisphenylcarbimideoxalyl diethyl ether*,  $\text{C}_2[(\text{OEt})\cdot\text{N}\cdot\text{CO}\cdot\text{NHPh}]_2$ , which begins to decompose at 238°, m. p. 245—246°.

*Ethyl oxaminehydroximate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OEt}$ , prepared from ethyl di-imino-oxalate and hydroxylamine hydrochloride, crystallises in bunches of needles, m. p. 99°. Heating with hydrogen chloride converts it into hydroxyoxamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ .

*Chlorylacetiminoethyl ether*,  $\text{CH}_3\cdot\text{C}(\text{NCl})\cdot\text{OEt}$ , prepared by the action of sodium hydroxide and sodium hypochlorite on the hydrochloride of acetiminoethyl ether, is an oil, b. p. 27°/12 mm., 48°/36 mm., or 127—128°/760 mm. The corresponding *bromo-compound* has b. p. 39—40°/13 mm., 45°/17 mm. The *iodo-compound* was obtained only as a heavy, yellow, impure oil.

E. F. A.

**Preparation of Arrhenal [Disodium Methylarsinate].** G. FAVREL (*Chem. Zentr.*, 1913, ii, 576; from *Bull. Sci. Pharmacol.*, 1913, 20, 337—338).—A cold solution of 99 grams of arsenious oxide and a little more than 60 grams of sodium hydroxide in 250 c.c. of water is shaken during twenty-four hours with 50 c.c. of methyl alcohol and 145 grams of methyl iodide. The product is dissolved in just sufficient boiling water, reprecipitated by alcohol, and redissolved in a little cold water. Impurities are then precipitated by baryta water, and, after removing the excess of reagent by means of carbon dioxide, the filtrate is concentrated and brought to crystallisation by the addition of much alcohol. The yield is at least 95%. Arrhenal crystallises with  $6\text{H}_2\text{O}$ .

J. C. W.

**The Methylation of Metals by the Action of Aluminium Carbide on their Dissolved Salts.** SIEGFRIED HILPERT and MARTIN DITMAR (*Ber.*, 1913, 46, 3738—3741).—An investigation of the behaviour of metallic carbides towards dissolved metallic salts has led with aluminium carbide to a new method for the synthesis of methyl derivatives of the metals.

When a solution of 25 grams of mercuric chloride in 130 grams of 10% hydrochloric acid is treated gradually with 15 grams of aluminium carbide, the temperature being about  $90^\circ$  and the mixture shaken, mercury methyl chloride, m. p.  $170^\circ$ , is produced to the extent of 30% of the chloride taken, and can be separated in a pure condition by distillation with steam. The aqueous solution of mercury methyl chloride on treatment with potassium iodide gives a precipitate of mercury methyl iodide, m. p.  $143^\circ$ , whilst when treated with hydrogen sulphide it gives a white precipitate of *mercury methyl sulphide*; this substance, which has a frightful odour, decomposes into mercuric sulphide and mercury diethyl on warming.

In neutral or feebly acid solution, the interaction of equal weights of mercuric chloride and aluminium carbide give rise to mercury dimethyl.

[With G. GRÜTTNER.]—The action of 60 grams of aluminium carbide added in portions of 5 grams during three hours to a solution of 50 grams of crystalline bismuth chloride in 150 grams of 20% hydrochloric acid in an atmosphere of carbon dioxide, produces bismuth trimethyl, which can be extracted with ether. All operations with the product (20 grams, b. p.  $110^\circ$ ) must be effected in an atmosphere of carbon dioxide or hydrogen.

The isolation of tin methyl chloride is rendered difficult by the concurrent formation of the dimethyl derivative below, but its formation is easily demonstrable on account of its characteristic odour, and provides a delicate test for tin in stannous or stannic chloride, detecting even 0.1 mg. in 2 c.c. The method of the test is to add a little aluminium carbide to the acid solution and heat, when the characteristic odour is perceived. If more carbide is applied, tin dimethyl dichloride, m. p.  $90^\circ$ , is formed, and can be extracted by ether.

By this new process it seems to be possible to produce methyl derivatives, not only of arsenic and antimony, but also of such metals as copper.



The reaction appears to be non-ionic, as mercuric chloride can be replaced by mercuric cyanide. Of the alternative views that the process consists in the simultaneous attack of the carbide by mercuric chloride and water (or acid), or in a primary double decomposition between aluminium carbide and mercuric chloride with formation of a mercuric carbide,  $\text{CHg}_2$ , which subsequently decomposes, the former seems more probable, but the latter agrees with the failure to methylate such organic compounds as chloroacetic acid by means of aluminium carbide and with the interaction which the authors have found to occur between carbide of manganese or iron and copper or mercuric salts with production of substances resembling the original carbides in behaviour, and differing widely from the known "acetylene carbides."

D. F. T.

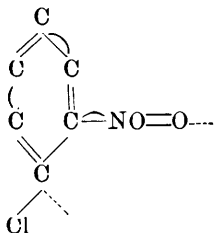
**Constitution of Benzene. The Stereochemistry of Aromatic Compounds.** J. LINDNER (*Chem. Zentr.*, 1913, ii, 854—855; Pamphlet, 24 pp., 1913).—Since unsaturated compounds have larger molecular volumes than saturated compounds with the same number of atoms, it must be assumed that the carbon atoms are farther apart when united by two or three bonds than when by a single linking. The author holds that this proposition is fulfilled when it is further assumed that the carbon valencies are directed towards the centres of the tetrahedron faces rather than towards the corners. Pursuing these ideas, he lays down the following fundamental principle: carbon atoms strive to arrange themselves in space so that the hypothetical tetrahedra described about the atomic centres meet face to face in the case of single bonds, edge to edge for double linkings, and apex to apex for triple bonds, the line joining the atomic centres passing through the middle points of the faces or of the edges, or through the corners, respectively.

The hypothetical tetrahedra are not necessarily present, but an examination of ring compounds, with the aid of models, shows that the ring systems in which this "tetrahedral" arrangement is most possible, are the most stable. Benzene would have three ordinary double bonds and the  $\beta\beta'$ -carbon atoms in naphthalene would have to be doubly linked. In the original paper, explanations are offered of the well-known anomalies associated with the benzene ring. J. C. W.

**Additive Reactions.** H. J. PRINS (*Chem. Weekblad*, 1913, 10, 1001—1003).—A theoretical paper, in which the author cites a number of additive reactions of aromatic hydrocarbons and of compounds of the general formula  $\text{R—OH}$  induced by catalysis. A. J. W.

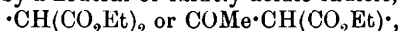
**Difference in the Reactivity of the Chlorine Atoms in 4:6-Dichloro-1:3-dinitrobenzene and its Significance. Experimental Proof of Kekulé's Benzene Formula.** W. BORSCHÉ and H. BAHR (*Annalen*, 1913, 402, 81—109).—According to any benzene formula (for example, the centric) which represents as the same the

linking of any pair of contiguous nuclear carbon atoms, the two chlorine atoms in 4:6-dichloro-1:3-dinitrobenzene should be equally reactive. Experiment shows that they are not. In Kekulé's formula, and also in the extension of it which fulfils the requirements of the oscillation theory, the two chlorine atoms are differently bound; always, only one of the two chlorine atoms is attached to a carbon atom which is linked singly to the neighbouring carbon atom united to

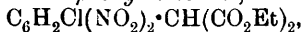


the nitro-group. It is this chlorine atom which is labile, according to Borsche's explanation, indicated by the annexed diagram, of the activation of such halogen atoms (A., 1912, i, 180). Nietzki and others have shown that in the reaction between 4:6-dichloro-1:3-dinitrobenzene and ammonia or primary amines only one chlorine atom is readily replaced by the amino-group, the substitution of the other chlorine atom requiring considerably more

energetic experimental conditions. This example, however, does not serve to prove the authors' contention that the second chlorine atom is bound differently from the one which has been eliminated. It is quite conceivable that the two chlorine atoms originally are similarly bound, and similarly activated by the nitro-groups; however, directly one has been replaced by the amino-group, the latter, in consequence of its basic character, so influences the nitro-groups as to diminish their activating power on the remaining chlorine atom, which, therefore, becomes non-labile or far less labile. However, if the one chlorine atom is replaced by a neutral or faintly acidic radicle, such as

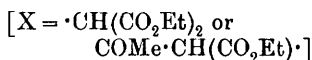
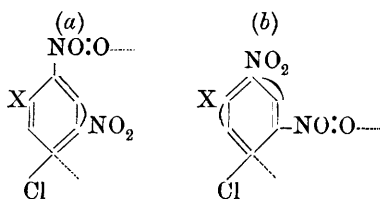


the latter cannot exert any influence on the nitro-groups, which therefore should still activate the second chlorine atom. This is found not to be the case; only one chlorine atom is eliminated from 4:6-dichloro-1:3-dinitrobenzene when it reacts with ethyl sodiomalonate or sodioacetoacetate under conditions in which the halogen is smoothly eliminated from 4-chloro-1:3-dinitrobenzene. Therefore, the second chlorine atom in 4:6-dichloro-1:3-dinitrobenzene is stable *ab initio* and does not acquire its stability after the first chlorine atom has been replaced by a basic, neutral, or faintly acid radicle. 4:6-Dichloro-1:3-dinitrobenzene (1 mol.) and ethylsodiummalonate (2 mols.) react in boiling ether to form after four hours the dark red sodium derivative of *ethyl 5-chloro-2:4-dinitrophenylmalonate*,



colourless needles, m. p. 59—60°, or leaflets, m. p. 63—64°. A similar reaction with ethyl sodioacetoacetate results in the formation of *ethyl 5-chloro-2:4-dinitrophenylacetoacetate*,  $\text{COMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2$ , m. p. 115—116°, stout, yellow crystals.

The chlorine in the preceding two compounds reacts with amines almost as readily as does the halogen in 4-chloro-1:3-dinitrobenzene; also under suitable conditions it can be replaced by a second  $\cdot\text{CH}(\text{CO}_2\text{Et})_2$  or  $\text{COMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot$  group. The authors explain these results by assuming that the two substances change from a



form (a) containing feebly reactive chlorine to a form (b) containing powerfully reactive chlorine. Thus in boiling alcohol containing sodium acetate, ethyl 5-chloro-2:4-dinitrophenylmalonate reacts with aniline to form *ethyl 2:4-dinitro-5-anilinophenylmalonate*,

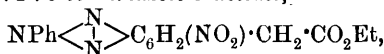
$\text{NHPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , m. p.  $118^\circ$ , yellow leaflets, and with *p*-anisidine to form *ethyl*

*2:4-dinitro-5-p-anisidinophenylmalonate*, m. p.  $132^\circ$ , orange-red needles, whilst ethyl 5-chloro-2:4-dinitrophenylacetoacetate (or ethyl 5-chloro-2:4-dinitrophenylacetate) and aniline yield *ethyl 2:4-dinitro-5-anilino-phenylacetate*,  $\text{NHPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , m. p.  $75-76^\circ$ , yellow leaflets. Ethyl 5-chloro-2:4-dinitrophenylacetoacetate and ethereal ammonia yield *ethyl 5-chloro-2:4-dinitrophenylacetate*, m. p.  $81^\circ$ , yellow needles; the corresponding acid,  $\text{C}_8\text{H}_5\text{O}_6\text{N}_2\text{Cl}$ , obtained by the hydrolysis of ethyl 5-chloro-2:4-dinitrophenylmalonate by warm, slightly diluted sulphuric acid, has m. p.  $161-162^\circ$ , and forms a *methyl ester*, m. p.  $66^\circ$ .

Piperidine reacts with ethyl 5-chloro-2:4-dinitrophenylacetoacetate or 5-chloro-2:4-dinitrophenylacetate in boiling alcohol to form *ethyl 2:4-dinitro-5-piperidinophenylacetate*,  $\text{C}_5\text{NH}_{10}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , m. p.  $100-101^\circ$ , yellow needles.

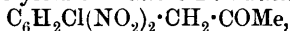
*5-Chloro-2:4-dinitrophenylpiperidine*,  $\text{C}_5\text{NH}_{10}\cdot\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2$ , m. p.  $117-118^\circ$ , orange-red prisms, prepared from 4:6-dichloro-1:3-dinitrobenzene, piperidine hydrochloride, and sodium acetate in boiling alcohol does not react with ethyl sodiomalonate or sodioacetoacetate.

Ethyl 5-chloro-2:4-dinitrophenylacetoacetate and phenylhydrazine react in boiling alcohol containing sodium acetate to form *ethyl 6-nitro-2-phenyl-2:1:3-benzotriazole-5-acetate*,

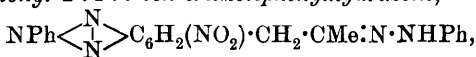


m. p.  $119^\circ$ , brown needles.

By the addition of water, without cooling, to a suspension of ethyl 5-chloro-2:4-dinitrophenylacetoacetate in concentrated sulphuric acid, an almost quantitative yield of *5-chloro-2:4-dinitrophenylacetone*,



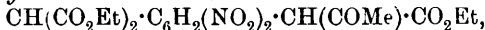
m. p.  $97-98^\circ$ , is obtained. The ketone reacts with phenylhydrazine in lukewarm alcohol to form the *phenylhydrazone*,  $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}_4\text{Cl}$ , m. p.  $148-149^\circ$ , red needles, and in boiling alcohol to form *6-nitro-2-phenyl-5-acetonyl-2:1:3-benzotriazolephenylhydrazone*,



m. p.  $184-185^\circ$  (decomp.), yellow needles.

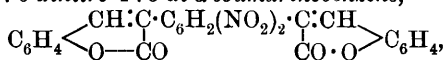
The replacement of both halogen atoms in 4:6-dichloro-1:3-dinitrobenzene by the groups  $\cdot\text{CH}(\text{CO}_2\text{Et})_2$  or  $\text{COMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot$  is effected under the following conditions. The dichlorodinitrobenzene

(1 mol.) and ethyl sodiomalonate (4 mols.), after reacting in boiling ether for 100 hours, yield about 80% of the theoretical amount of *ethyl 4:6-dinitrobenzene-1:3-dimalonate*,  $C_6H_2(NO_2)_2[CH(CO_2Et)_2]_2$ , m. p. 57—58°, colourless needles. 4:6-Dichloro-1:3-dinitrobenzene and ethyl sodioacetate (4 mols.) react in boiling ether to form after 240 hours a 35% yield of *ethyl 4:6-dinitrobenzene-1:3-diacetoacetate*,  $C_6H_2(NO_2)_2[CH(COMe) \cdot CO_2Et]_2$ , m. p. 106—107°, pale yellow crystals. *Ethyl 4:6-dinitrobenzene-3-acetoacetate-1-malonate*,

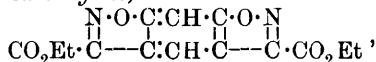


m. p. 76°, pale yellow prisms, is obtained in about 75% yield by boiling ethyl 5-chloro-2:4-dinitrophenylmalonate and ethyl sodioacetate or ethyl 5-chloro-2:4-dinitrophenylacetoacetate and ethyl sodiomalonate in ether for seventy-two hours.

By hydrolysis with boiling acetic and sulphuric acids, ethyl 4:6-dinitrobenzene-1:3-dimalonate is converted into 4:6-dinitrobenzene-1:3-diacetic acid,  $C_6H_2(NO_2)_2(CH_2 \cdot CO_2H)_2$ , m. p. 185—186° (decomp.), brownish-yellow needles. The acid forms a *methyl ester*,  $C_{12}H_{12}O_8N_2$ , m. p. 95—96°, and *ethyl ester*, m. p. 82—83°. The latter reacts with salicylaldehyde and a few drops of piperidine on the water-bath to form 4:6-dinitro-1:3-di- $\alpha$ -coumarinobenzene,



m. p. 267°, yellow needles, with *isoamyl nitrite* and alcoholic sodium ethoxide at the ordinary temperature to form *ethyl benz-1:6,3:4-di-isooxazole-3':3''-dicarboxylate*,



m. p. 151°, colourless leaflets (the corresponding *methyl ester*,  $C_{12}H_{12}O_8N_2$ , has m. p. 229—230°), and in alcoholic solution at 0° with a concentrated aqueous solution of benzenediazonium chloride and sodium acetate to form *ethyl 4:6-dinitrobenzene-1:3-diglyoxylatediphenylhydrazone*,  $C_6H_2(NO_2)_2[C(CO_2Et) \cdot N \cdot NHPh]_2$ , m. p. 201°, orange leaflets. Ethyl 4:6-dinitrobenzene-1:3-diacetoacetate is converted into ethyl 4:6-dinitrobenzene-1:3-diacetate by cold ethereal ammonia, and yields 4:6-dinitro-1:3-diacetylbenzene,  $C_{12}H_{12}O_6N_2$ , m. p. 122—123°, yellowish-white needles (*diphenylhydrazone*, m. p. 174—175° [decomp.], brownish-red needles), by treatment with sulphuric acid.

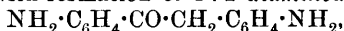
Ethyl 4:6-dinitrobenzene-3-acetoacetate-1-malonate is converted by slightly diluted sulphuric acid on the water-bath into 4:6-dinitro-3-acetylphenylacetic acid,  $COMe \cdot CH_2 \cdot C_6H_2(NO_2)_2 \cdot CH_2 \cdot CO_2H$ , m. p. 174—175° [decomp.], colourless leaflets, the *ethyl ester*, m. p. 109—110°, of which forms a *phenylhydrazone*,  $C_{19}H_{20}O_6N_4$ , m. p. 141—142°, red needles.

C. S.

**Dinitrotolane and Some Tolane Derivatives.** H. REINHARDT (*Ber.*, 1913, 46, 3598—3601).—4:4'-Dinitrotolane, m. p. 207°, is obtainable in 90—95% yield by the action of alcoholic potassium hydroxide on dinitrostilbene dibromide in suspension in boiling alcohol; the product is purified by recrystallisation from acetic acid. It combines

with bromine vapour, giving the  $\alpha$ -dibromide, pale yellow leaflets and tablets, m. p. 235—236°; the  $\beta$ -dibromide, yellow needles (or prisms with  $\text{C}_7\text{H}_8$  from toluene solution), m. p. 181—182°, is formed in the action of alcoholic potassium hydroxide on *p*-nitrobenzylidene bromide.

The reduction of dinitrotolane and the dibromides is best effected in alcoholic suspension by zinc and hydrochloric acid in the cold. The 4 : 4'-diaminotolane, which is accompanied by diaminostilbene, forms straw-yellow needles or prisms, m. p. 236°, which are sparingly soluble in water; the sulphate is also sparingly soluble. When warmed with dilute acids, for example, hydrochloric acid, diaminotolane assumes the elements of water with formation of 4 : 4'-diaminodeoxybenzoin,



pale yellow needles, m. p. 145°; the *sulphate* is sparingly soluble in water. Unlike diaminotolane, which reacts with two molecules of nitrous acid, the diaminodeoxybenzoin on diazotisation first forms a tetrazo-compound, and then passes further into the *oximino*-compound,  $\text{N}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{:NOH}) \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$ . D. F. T.

**Nitrotolanes.** P. PFEIFFER and E. KRAMER (*Ber.*, 1913, 46, 3655—3662. Compare preceding abstract).—In a previous paper (A., 1912, i, 618) it has been shown that the dichlorides of stilbene and 2 : 4-dinitrostilbene differ from the corresponding dibromides in their behaviour towards pyridine, the dichlorides losing hydrogen chloride in the normal manner, whilst the dibromides lose bromine with the formation of the original stilbenes. A similar difference is exhibited by the dichloride and dibromide of 4 : 4'-dinitrostilbene, the former giving rise to  $\alpha$ -chloro-4 : 4'-dinitrostilbene, whilst the latter is converted into 4 : 4'-dinitrostilbene.

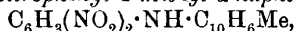
4 : 4'-Dinitrostilbene dichloride,  $\text{C}_2\text{H}_2\text{Cl}_2(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , prepared by saturating a suspension of 4 : 4'-dinitrostilbene in chloroform with chlorine and exposing the mixture to sunlight for five days, crystallises in small, compact, light yellow, transparent crystals, m. p. 302°. On treatment with pyridine at 100° it yields  $\alpha$ -chloro-4 : 4'-dinitrostilbene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CCl} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , which forms lustrous, golden-yellow leaflets, m. p. 144°, and is converted by soda-lime at 170—180° into 4 : 4'-dinitrotolane,  $\text{C}_2(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ . This crystallises in lustrous, flat, light yellow needles, m. p. 211°, combines with bromine in ethereal solution to form a *dibromide* (small, lustrous, yellow, prismatic crystals, m. p. 244°), and has also been prepared by heating 4 : 4'-dinitrostilbene dichloride with alcoholic potassium hydroxide.

The substance obtained by Elbs and Bauer (A., 1887, 151) and Ruggli (this vol., i, 1106) by heating 4 : 4'-dinitrostilbene dibromide with soda-lime and pyridine respectively, and considered by them to be 4 : 4'-dinitrotolane, is shown by the authors to consist of 4 : 4'-dinitrostilbene.

2 : 4-Dinitrotolane,  $\text{CPh} \cdot \text{C} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ , prepared by heating  $\alpha$ -bromo-2 : 4-dinitrostilbene with aqueous alcoholic sodium carbonate, crystallises from glacial acetic acid in yellow, prismatic needles, m. p. 112—112.5°. It slowly acquires an orange to red colour on exposure to light, forms a *dibromide*, crystallising in almost colourless, transparent, prismatic

needles, m. p. 141—142°, and develops a deep bluish-violet coloration with strong sulphuric acid. When exposed to light in pyridine solution, it is converted into 6-nitro-2-phenylisatogen (A., 1912, i, 618). F. B.

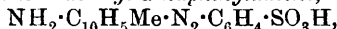
**Methylnaphthalenes.** RUDOLF LESSER (*Annalen*, 1913, 402, 1—51).—[With ALADÁR GLASER.]—Contrary to the statement of Scherler (A., 1892, 493), 1-methylnaphthalene in glacial acetic acid yields by treatment at -5° with 99·8% nitric acid, 4-nitro-1-methylnaphthalene, m. p. 71—72°, b. p. 176°/12 mm., pale yellow needles, and a mixture of liquid products which cannot be satisfactorily separated. 4-Nitro-1-methylnaphthalene, the constitution of which is determined by the formation of 4-nitro- $\alpha$ -naphthoic acid by oxidation with 8% nitric acid at 135—140°, is converted by further nitration into a trinitro-1-methylnaphthalene,  $C_{11}H_7O_6N_3$ , m. p. 180—181°, straw-yellow needles. By reduction with stannous chloride and hydrochloric acid, 4-nitro-1-methylnaphthalene yields 4-methyl- $\alpha$ -naphthylamine, m. p. 51—52°, colourless needles (*hydrochloride*, m. p. 233—234°; *sulphate*, colourless leaflets; *acetyl* derivative, m. p. 166—167°; *benzoyl* derivative, m. p. 238—239°). The base condenses normally with 1-chloro-2:4-dinitrobenzene and with picryl chloride in alcohol in the presence of sodium acetate to form *op-dinitrophenyl-4-methyl- $\alpha$ -naphthylamine*,



m. p. 176—177°, yellow needles, and 2:4:6-trinitrophenyl-4-methyl- $\alpha$ -naphthylamine, m. p. 237—238°, scarlet-red prisms, respectively; it also condenses with phthalic anhydride at about 150° to form *phthal-4-methyl- $\alpha$ -naphthylimide*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot C_{10}H_6Me$ , m. p. 233—234°, flattened, colourless needles.

By diazotisation and the usual treatment, 4-methyl- $\alpha$ -naphthylamine gives about 20% yield of 4-methyl- $\alpha$ -naphthol, m. p. 84—85°, colourless needles (*benzoyl* derivative, m. p. 81—82°, large prisms), which forms a red dye by coupling with alkaline diazobenzenesulphonate.

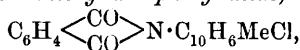
2-p-Sulphobenzeneazo-4-methyl- $\alpha$ -naphthylamine,



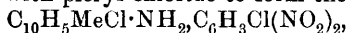
dark violet, metallic leaflets (*sodium* salt,  $C_{17}H_{14}O_3N_3SNa$ , needles), prepared by the addition of sodium diazobenzenesulphonate to a cold solution of 4-methyl- $\alpha$ -naphthylamine in dilute sulphuric acid, yields by reduction with stannous chloride and hydrochloric acid, 4-methyl-1:2-naphthylenediamine, m. p. 91—92°, colourless needles (*diacetyl* derivative, m. p. 291°, colourless prisms), a by-product, or under some conditions the main product, being a sparingly soluble substance,  $C_{22}H_{16}N_2$ , m. p. 305—306°, golden-yellow needles, which is probably

the dimethyldinaphthazine,  $C_{10}H_5Me \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} C_{10}H_5Me$ . The methyl-naphthylenediamine condenses with phenanthraquinone in glacial acetic acid to form the *azine*,  $C_{10}H_5Me \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} C_{14}H_8$ , m. p. 341—342°, yellow needles, which sublimes at about 330° and develops a blue coloration with concentrated sulphuric acid; the diamine does not produce a coloration with this reagent.

[With GÉZA ACZÉL.]—By treatment in cold glacial acetic acid with 99.8% nitric acid, 2-methylnaphthalene (*picramide*, m. p. 145°, yellow needles) yields, after being finally heated at 80°, Schulze's 1-nitro-2-methylnaphthalene, m. p. 81°, b. p. 185—186°/18 mm. (A., 1884, 1183). The constitution of the substance has been proved indirectly, not by oxidation. It reacts directly with bromine to form *bromo-1-nitro-2-methylnaphthalene*,  $C_{11}H_8O_2NBr$ , m. p. 94°, and is reduced by stannous chloride and hydrochloric acid to 4-chloro-2-methyl- $\alpha$ -naphthylamine,  $C_{11}H_{10}NCl$ , m. p. 65°, colourless needles (*hydrochloride* and *sulphate*, both colourless needles; *acetyl* derivative, m. p. 206°; *benzoyl* derivative, m. p. 236—237°), the introduction of the chlorine being evidence, according to Pinnow (A., 1901, i, 485), that the amine contains an alkyl group in the ortho-position to the amino-group. The chlorinated base condenses with phthalic anhydride at about 200° to form *phthal-4-chloro-2-methyl- $\alpha$ -naphthylimide*,



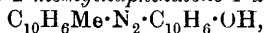
m. p. 171°, colourless needles, but reacts additively with 1-chloro-2:4-dinitrobenzene and with picryl chloride to form the *substances*,



m. p. 78°, red needles, and  $C_{10}H_5MeCl \cdot NH_2, C_6H_2(NO_2)_3Cl$ , m. p. 119°, brownish-red needles, respectively.

By reduction with iron and 50% acetic acid, 1-nitro-2-methylnaphthalene yields 2-methyl- $\alpha$ -naphthylamine, m. p. 32°, colourless needles (*hydrochloride*, decomp. 230°, *sulphate*, colourless needles, *acetyl* derivative, m. p. 188°, *benzoyl* derivative, m. p. 180°), which condenses with phthalic anhydride to form *phthal-2-methyl- $\alpha$ -naphthylimide*,  $C_6H_4 \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} N \cdot C_{10}H_7Me$ , m. p. 233—234°, colourless needles,

and reacts additively with 1-chloro-2:4-dinitrobenzene and picryl chloride to form the *substances*,  $C_{10}H_6Me \cdot NH_2, C_6H_3Cl(NO_2)_2$ , m. p. 93—94°, red needles, and  $C_{10}H_6Me \cdot NH_2, C_6H_2Cl(NO_2)_3$ , m. p. 129—130°, brownish-red needles respectively. The chlorinated base does not react with diazobenzenesulphonic acid, whilst 2-methyl- $\alpha$ -naphthylamine yields 4-p-sulphobenzeneazo-2-methyl- $\alpha$ -naphthylamine,  $SO_3H \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5Me \cdot NH_2$ , green, crystalline mass with a red streak, various metallic salts of which are mentioned. By diazotisation and treatment with cold alkaline  $\beta$ -naphthol, 2-methyl- $\alpha$ -naphthylamine is converted into 2-methylnaphthalene-1-azo- $\beta$ -naphthol,



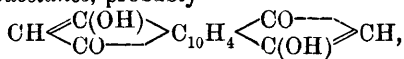
m. p. 162—163°, brownish-red crystals with greenish-gold reflex.

By the decomposition of its diazotised solution in an atmosphere of carbon dioxide, 2-methyl- $\alpha$ -naphthylamine is converted into 2-methyl- $\alpha$ -naphthol, m. p. 61°, colourless needles, which rapidly reddens in air, and in neutral solution reacts with diazotised *p*-nitroaniline to form 4-p-nitrobenzeneazo-2-methyl- $\alpha$ -naphthol, m. p. 267—268°, microscopic, brick-red needles. 4:4'-Dihydroxy-3:3'-dimethyl-1:1'-dinaphthyl,  $OH \cdot C_{10}H_5Me \cdot C_{10}H_5Me \cdot OH$ , m. p. 235° (decomp.), obtained as a by-product in the preparation of 2-methyl- $\alpha$ -naphthol, forms a *diacetyl* derivative,  $C_{26}H_{22}O_4$ , m. p. 235—236°, colourless plates, and readily oxidises, as also does 2-methyl- $\alpha$ -naphthol, to 2:2'-dimethyl-1:1'-di-

naphthone,  $\text{O}:\text{C}_{10}\text{H}_5\text{Me}:\text{C}_{10}\text{H}_5\text{Me}:\text{O}$ , decomp. about  $250^\circ$ , metallic needles with green reflex and carmine-red streak.

Since 2-methyl- $\alpha$ -naphthylamine and 4-chloro-2-methyl- $\alpha$ -naphthylamine react abnormally with 1-chloro-2:4-dinitrobenzene and picryl chloride in forming additive compounds, the behaviour of the xylidines with each of these reagents has been examined. *o*-3-Xylidine forms additive compounds,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ , m. p.  $25^\circ$ , orange-red needles, and  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_3$ , m. p.  $68^\circ$ , red needles (the latter is extremely unstable and readily changes to the yellow substitution compound, m. p.  $212^\circ$ ); the other xylidines react normally and yield 2:4-dinitro-3':4'-dimethyldiphenylamine, m. p.  $141^\circ$ , orange-yellow needles; 2:4-dinitro-2':4'-dimethyldiphenylamine, m. p.  $156^\circ$ , yellow needles, and 2:4-dinitro-2':5'-dimethyldiphenylamine, m. p.  $150^\circ$ , orange-red needles. C. S.

**Synthetic Formation of Pyrene.** MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, 402, 77—81).—The di-anhydride of naphthalene-1:4:5:8-tetracarboxylic acid, which is obtained with comparative ease from diethyl-3:4-acenaphthindandione (this vol., i, 49), reacts with ethyl malonate and zinc chloride at  $170^\circ$  to form a blackish-brown substance, probably



which yields pyrene (m. p.  $134^\circ$ ; picrate, m. p.  $217\text{--}218^\circ$ ; m. p. of mixed picrates,  $217\text{--}218^\circ$ ) by distillation with zinc dust. C. S.

**Preparation of Aromatic Amines from the Corresponding Nitro-compounds.** BADISCHE ANILIN- & SODA-FABRIK (D R.-P. 263396).—Aniline or other aromatic amines can be readily prepared by passing the vapour of the corresponding nitro-compound, mixed with excess of hydrogen, over pumice heated at  $230\text{--}250^\circ$  which has been previously impregnated with either finely divided silver, or gold, a mixture of silver and gold, silver and copper, or silver and nickel; the pumice can also be replaced by asbestos or glass. F. M. G. M.

**Nitration of *p*-Iodoacetanilide.** P. BRENANS (*Compt. rend.*, 1913, 157, 1155—1158).—Michael and Norton (compare A., 1878, 406) succeeded in nitrating and saponifying in one operation *p*-iodoacetanilide, obtaining an iodonitroaniline, m. p.  $122^\circ$ , the constitution of which the author cleared up by preparing it from *o*-nitroaniline by the action of iodine chloride (compare A., 1902, i, 673). The author has tried to repeat Michael and Norton's work, but has not been successful.

Nitric acid (D 1.42), acting on *p*-iodoacetanilide in acetic acid solution at  $80^\circ$  for two hours, then cooling, and pouring the mixture on to ice, yields, on suitable purification, a compound, m. p.  $63^\circ$ , which is shown to be *p*-iodoaniline. Using nitric acid (D 1.50) at  $50^\circ$  for two hours, and after twenty-four hours, further heating at  $60\text{--}70^\circ$  for four hours, the author has obtained four compounds, separable by their ease of precipitation with ice and varying solubility in organic solvents.



A compound, m. p. 214°, which by saponification is shown to be *p*-nitroacetanilide. A compound, m. p. 171°, which is 2:4-di-iodoacetanilide, since on saponification it yields 2:4-di-iodoaniline (compare A., 1904, i, 661). A compound, m. p. 112°, which is 4-iodo-2-nitroacetanilide, and on saponification yields Michael and Norton's iodonitroaniline. A compound, m. p. 167°, the yield of which was too small to allow of orientation. W. G.

**2:3:4:6-Tetranitrophenyl-methylnitroamine and -ethyl-nitramene.** P. VAN ROMBURGH and J. H. SCHEPERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 369—376). An improved method of preparing 2:3:4:6-tetranitrophenylmethylnitroamine (compare van Romburgh, A., 1889, 972—1154) is described and many of its derivatives have been investigated.

A mixture of sulphuric acid and nitric acid (D 1·51) is added drop by drop to a solution of dimethylaniline in concentrated sulphuric acid cooled at -2°. After remaining for half an hour in a mixture of ice and salt, a further quantity of nitric acid (D 1·51) is added; the mixture is then cooled for a day and subsequently allowed to remain during some days at the ordinary temperature. In these circumstances, 2:3:4:6-tetranitrophenylmethylnitroamine separates, whilst 2:4:6-trinitrophenylmethylnitroamine remains in the mother liquor. The former, after purification by solution in a warm mixture of nitric and sulphuric acids and precipitation by addition of excess of the latter, has m. p. 146—147°, whilst the latter melts at 127°.

Cold methyl alcohol decomposes 2:3:4:6-tetranitrophenylmethylnitroamine with formation of the previously-described trinitromethylnitroaminophenylmethyl ether (*loc. cit.*) and methyl nitrite. Nitromethane does not appear to be formed. Ethyl alcohol reacts analogously, giving the ethyl ether and ethyl nitrite, but not nitroethane.

Dry propyl alcohol yields the *propyl* ether, m. p. 118°, and propyl nitrite, b. p. 57.

*iso*Butyl alcohol, when heated with the nitroamine, gives the *isobutyl ether*, m. p. 95°, and *isobutyl* nitrite, b. p. 65°.

*iso*Amyl alcohol forms *iso*amyl nitrite and the *amyl ether*, m. p. 83°. In this case, larger quantities of trinitromethylnitroaminophenol appear to be formed than with the other alcohols, where it always occurs in small quantities.

Allyl alcohol gives allyl nitrite, but no weighable quantity of *ether*. Only free phenol is formed. Benzyl alcohol reacts violently, yielding products containing benzaldehyde and the phenol. The latter is also obtained when *isopropyl* alcohol or *sec*-butyl alcohol is employed together with the nitrites of these alcohols. With *tert*-amyl alcohol, the main product is the phenol. In addition to some nitrite, amylene is also produced. In all the above reactions, the ·NO<sub>2</sub> group of the nitroamine is replaced in the position 3, either by the group ·OAlk or by the group ·OH.

The action of ammonia and amines on 2:3:4:6-tetranitrophenylmethylnitroamine has also been investigated.

Gaseous ammonia produces incandescence; aqueous ammonia (D 0.890—0.903), when acting for a short time at a slightly elevated temperature, gives 2:4:6-trinitro-3-aminophenylmethylnitroamine, m. p. 181.5°; prolonged action of nearly saturated aqueous ammonia leads to the formation of 2:4:6-trinitro-*m*-phenylenediamine.

Ethylamine behaves similarly to methylamine (*loc. cit.*). The 16% solution gives, after half-an-hour, a good yield of 2:4:6-trinitro-3-ethylaminophenylmethylnitroamine, m. p. 131.5°, whilst more prolonged action of a 33% solution gives 2:4:6-trinitrophenylenediethyldiamine (compare Blanksma, A., 1903, i, 158). In a similar manner, 2:4:6-trinitro-3-dimethylaminophenylmethylnitroamine, m. p. 177°, and 2:4:6-trinitro-*m*-phenylenetetramethyldiamine, m. p. 141°, are obtained with dimethylamine. The mobile nitro-group does not appear to be replaced by diisopropylamine, the product of the reaction being the diisopropyl salt of 2:4:6-trinitromethylnitroaminophenol, m. p. 147.5°.

Aniline yields a dark red substance, m. p. 114°, which proves to be a compound of aniline with the yellow 2:4:6-trinitro-3-anilinophenylmethylnitroamine, m. p. 183°. *p*-Toluidine causes the formation of an analogous red toluidino-compound, m. p. 141°.

The behaviour of piperidine is analogous with that of diisopropylamine, the pyridine salt of the phenol, m. p. 172°, being formed. An evolution of gas could not be observed, but an odour resembling that of nitrosopiperidine was noticed.

Pyridine appears to yield the pyridine salt of 2:4:6-trinitromethylnitroaminophenol, m. p. 145°. In this case a mixture of nitrogen and nitric oxide is evolved. The course of reaction has not yet been elucidated. The reaction of quinoline is similar, but the corresponding salt of the phenol does not show a sharp m. p. (173—190°).

2:4:6-Trinitromethylnitroaminophenol is shown to be a powerful acid by measurement of the velocity with which it causes the decomposition of ethyl diazoacetate. Salts of it, with ammonia (m. p. 108°), with ethylamine (m. p. 179°), and dimethylamine (m. p. 183°), have been prepared.

The method described above could not be applied to the preparation of 2:3:4:6-tetranitrophenylethylnitroamine, since, in this case, the separation by means of sulphuric acid was a failure. It could, however, be obtained by dissolving 3:4-dinitrodiethylaniline in nitric acid (D 1.49), adding sulphuric acid (D 1.84), heating for a moment to 70°, cooling rapidly, adding more sulphuric acid, and pouring the mixture into ice-water. The yield is not very favourable. Better results are obtained by treating 3:4-dinitrodiethylaniline with nitric acid (D 1.33) and sodium nitrite, and dissolving the product formed in nitric acid (D 1.49) with addition of sulphuric acid.

2:3:4:6-Tetranitrophenylethylnitroamine, almost colourless crystals, m. p. 96°, evolves ethylamine when heated with bases. Alcohols readily react with it, particularly on heating, with formation of nitrous esters. When heated at 50—60° with ethylamine, it yields 2:4:6-trinitro-*m*-phenylenediethyldiamine, m. p. 142°. Boiling water transforms it into 2:4:6-trinitroethylnitroaminophenol, m. p. 105° (compare Blanksma, *Rec. trav. chim.*, 1902, 21, 260). The replacement of the

alkyl nitroamino-group of this and of the corresponding methyl compound by the ethylamino-group has not been effected. H. W.

**Preparation of Condensation Products from Phenolsulphonic Acids.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 266124. Compare A., 1913, i, 1059).—The compounds described in the chief patent (*loc. cit.*) can be obtained by condensing phenolsulphonic acids under the ordinary pressure in the presence of condensing agents, and choosing the quantity of the latter, conditions of temperature, and time so that no solid products are produced. The substances obtained are syrupy, and possess tanning properties. J. C. C.

**Separation of *m*- and *p*-Cresol.** HENRI TERRISSE and EDOUARD DESSOULAVY (D.R.-P. 267210).—The process depends on the fact that only calcium *m*-cresoxide is decomposed by steam at 105–110°. The technical mixture of *m*- and *p*-cresols is dissolved in sodium hydroxide, then precipitated with calcium chloride, and finally superheated steam is admitted, when *m*-cresol distils over. J. C. W.

**Catalytic Reactions at High Temperatures and Pressures. Hydrogenisation of Phenols with Unsaturated Side-chains. XXVI.** VL. IPATIEV (*Ber.*, 1913, 46, 3589–3593; *J. Russ. Phys. Chem. Soc.*, 1913, 45, 1829–1834).—The author has already shown (A., 1911, i, 137) that with copper oxide as catalyst, hydrogenisation of an ethylenic linking is possible, but that at a temperature of 270–300° the benzene nucleus remains unaffected. By applying reduced nickel as catalyst and using the author's stirring apparatus, it is possible to reduce a side-chain and the benzene nucleus successively at approximately 95° and 190° under a pressure up to 50 atmospheres. At the temperature and pressure required it is found that methoxy- or hydroxy-groups present tend to become removed.

Anethole,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , when mixed with one-tenth its weight of reduced nickel in an atmosphere of hydrogen at 50 atmospheres and 95° with constant stirring, is completely reduced in four hours to dihydroanethole (*p*-anisylpropane), b. p. 212–214°/766 mm.  $D^{20}_D$  0.9462, which by further hydrogenisation under similar conditions' but at 200° for twenty hours, can be converted into cyclohexylpropane' b. p. 160°/760 mm.,  $D^{20}_D$  0.8082.

Eugenol (also isoeugenol) in a similar manner at 92° in two to three hours can be transformed into dihydroeugenol, b. p. 246°/762.3 mm.,  $D^{20}_D$  0.9209, which is further reducible at 195° in seven hours to a mixture of 3-methoxy-4-hydroxycyclohexylpropane and 3-methoxycyclohexylpropane. Reduction of the methyl ether of eugenol (3:4-dimethoxy-1-allylbenzene) produced the corresponding 3:4-dimethoxyphenylpropane, b. p. 244–245°/763 mm.,  $D^{20}_D$  1.0105, which can be further reduced giving only methoxycyclohexylpropane, b. p. 200–210°/759 mm.,  $D^{20}_D$  0.9027.

Proceeding in a similar manner, it is possible to reduce safrole and isosafrole to dihydrosafrole (3:4-methylenedioxyphenylpropane), b. p. 228–230°/747 mm.,  $D^{20}_D$  1.0694, which can be further reduced, giving 4(or 3-)methoxycyclohexylpropane, b. p. 208–209°/746.7 mm.,  $D^{20}_D$  0.9096. D. F. T.

**Preparation of 4-Nitrocatechol.** J. D. RIEDEL (D.R.-P. 264012).—4-Nitrocatechol carbonate, yellowish-brown rods, m. p.  $104^{\circ}$ , is obtained in 90% yield when catechol carbonate (7 parts) is slowly stirred into 32 parts of fuming nitric acid; when heated with water, it furnishes a quantitative yield of 4-nitrocatechol; other acyl derivatives of catechol can be employed in this reaction.

F. M. G. M.

**Dithiocatechol [o-Dithiolbenzene].** J. POLLAK (*Monatsh.*, 1913, 34, 1673—1683. Compare A., 1910, i, 734).—o-Dithiolbenzene, prepared by reducing benzene-o-disulphonic acid with tin and hydrochloric acid, has b. p.  $119-120^{\circ}/17$  mm., and solidifies to a white, crystalline mass, m. p. about  $28^{\circ}$ , having an intensely disagreeable odour. It is accompanied by a red tin compound, the constitution of which has not yet been determined. The dimethyl ether, diacetyl derivative, m. p.  $86.5-88.5^{\circ}$ , and condensation product with chloroacetic acid,  $C_6H_4(S \cdot CH_2 \cdot CO_2H)_2$ , m. p.  $209-211^{\circ}$ , are described; the di-2:4:6-trinitrophenyl ether,  $C_6H_4[S \cdot C_6H_2(NO_2)_3]_2$ , prepared from the dithiol compound and 2:4:6-trinitrochlorobenzene in alcoholic solution, forms yellow crystals, m. p.  $267.5-269^{\circ}$ .

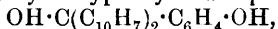
On exposure to air in ammoniacal solution, or when oxidised by hydrogen peroxide in aqueous alcoholic solution, o-dithiolbenzene is converted into an amorphous substance,  $(C_6H_4S_2)_2$ , which begins to melt at about  $104^{\circ}$ , but is not completely fused at  $140^{\circ}$ . The condensation product of m-dithiolbenzene with chloroacetic acid has m. p.  $129-131^{\circ}$ .

F. B.

**Triphenylcarbinols.** IV. HUGO KAUFFMANN and MAX EGNER (*Ber.*, 1913, 46, 3779—3788. Compare Kauffmann and Pannwitz, A., 1912, i, 351).—The ortho-position of the hydroxyl in o-hydroxytriphenylcarbinols, although necessary for the formation of a xanthen, is not the only essential. Diphenyl 1-hydroxy- $\beta$ -naphthylcarbinol,  $OH \cdot CPh_2 \cdot C_{10}H_6 \cdot OH$ , for instance, loses water when heated, giving a substance with the empirical formula of a xanthen, but which is intensely red in colour. It is therefore regarded as a quinone, namely,

o-naphthafuchson,  $CPh_2 \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CO} \cdot C_6H_4 \end{smallmatrix}$ . This dissolves in concentrated sulphuric acid with the same green halochromism as the carbinol, and it is reconverted into the carbinol by boiling with 90% alcohol or by adding sodium hydroxide to the alcoholic solution and decomposing the sodium salt with acetic acid.

On the other hand, o-hydroxyphenyldi- $\alpha$ -naphthylcarbinol,



is very readily converted into the xanthen, even during recrystallisation. Similarly, although at a somewhat higher temperature, diphenyl-3-hydroxy- $\beta$ -naphthylcarbinol,  $OH \cdot CPh_2 \cdot C_{10}H_6 \cdot OH$ , forms a xanthen without difficulty. The presence of the hydroxyl in the naphthelene nucleus is thus not the cause of the non-formation of xanthen.

Similarly, 3:5-dibromo-2-hydroxytriphenylcarbinol, in which both the ortho-positions to the hydroxyl are occupied, forms a xanthen, thus eliminating the possibility of steric hindrance being the cause of the

non-formation of xanthen in the case of the diphenyl hydroxynaphthylcarbinol. It is considered that the first phase in the formation of the xanthen is the formation of a quinone, and that the occurrence of the second phase depends on the stability of this quinone.

*Diphenyl 1-hydroxy- $\beta$ -naphthylcarbinol* forms colourless crystals, m. p. 117°, and colours concentrated sulphuric acid green. *Diphenyl-1-methoxy- $\beta$ -naphthylcarbinol*, prepared from it by means of methyl sulphate, is colourless, m. p. 127°.

*$\beta$ -Naphthafuchson*, prepared by heating the carbinol at 150°, forms orange-red crystals, m. p. 139°. If the carbinol is heated only to 120°, a phosphorus-red compound, m. p. 143°, is obtained, which represents a molecular compound of the quinone and carbinol.

*o-Hydroxyphenyl-di- $\alpha$ -naphthylcarbinol* is colourless, m. p. 140—141° (decomp.), and shows a dark blue halochromism with concentrated sulphuric acid. On crystallisation the m. p. rises, whilst on heating slightly,  *$\alpha$ -naphthyl-naphthaxanthen*, m. p. 171°, is obtained; it gives on coloration with sulphuric acid.

*o-Anisyl-di- $\alpha$ -naphthylcarbinol* has m. p. 233°, and gives a deep blue solution in concentrated sulphuric acid.

*Diphenyl-3-hydroxy- $\beta$ -naphthylcarbinol* is colourless, m. p. 181°, and gives a reddish-brown coloration with sulphuric acid.

*Phenyl- $\beta$ -naphthaxanthen*, obtained on heating it at 165°, forms colourless crystals, m. p. 171°. It slowly dissolves in concentrated sulphuric acid, giving a greenish-yellow coloration.

*3:5-Dibromo-2-hydroxytriphenylcarbinol* is colourless, m. p. 144°. The corresponding *2:4-dibromo-9-phenylxanthen*, obtained by heating it at 190—200°, forms colourless crystals, m. p. 105—107°, which do not dissolve in concentrated sulphuric acid.

*3:5-Dibromo-2-methoxytriphenylcarbinol* has m. p. 115°.

*Benzeneazo-o-hydroxytriphenylcarbinol* separates in pale brown crystals, m. p. 149°, and gives an orange-red coloration with concentrated sulphuric acid. The corresponding *methoxy-derivative* forms orange-red crystals, m. p. 193°.

*Benzeneazophenylxanthen* forms pale brown crystals, m. p. 171°.

E. F. A.

**The Law of the Decentralisation of Chemical Functions.**  
HUGO KAUFFMANN (*Ber.*, 1913, 46, 3801—3808).—It is characteristic for the coloured salts of triphenylcarbinol derivatives containing an auxochrome that the acid residue (acid-ion) even when univalent is attached both to the central carbon atom and to the auxochrome, so as to equalise the valency. Accordingly, chemical functions, such as basic properties, are not located at a particular position of the molecule, where they will be influenced by substitution at this position. The basic function is distributed over the whole molecule, and the decentralisation may increase it or make it apparent where it had been masked previously.

The acid hydrogen goes to the position where the valency attraction for it is greatest. In stable salts the acid hydrogen is firmly fixed; that is, the valencies which link it to the molecule are as little decentralised as is possible.

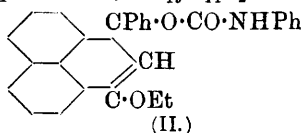
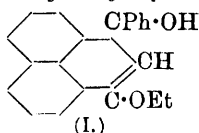
Acid radicles act on the nitrogen to which they are attached in the first place, not so as to make it less basic, but rather to diminish or to take away from it the property of combining with acid hydrogen.

E. F. A.

**Derivatives of Hydroxyketoperinaphthindene.** E. CALDERARO (*Gazzetta*, 1913, 43, ii, 632—636).—In order to demonstrate the presence of a ketonic group in hydroxyperinaphthindone (compare Errera, A., 1911, i, 465), which does not react normally with the ordinary reagents for the ketonic group, the author has subjected it to the action of magnesium phenyl bromide in presence of a crystal of iodine.

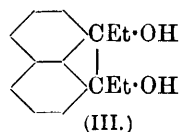
1-Hydroxy-3-ethoxy-1-phenylperinaphthindene (I.), thus obtained, forms a yellowish-brown, crystalline crust, m. p. 156—157°.

1:3-Dihydroxy-1-phenylperinaphthindene,  $C_{19}H_{14}O_2$ , obtained by



hydrolysing the above ethyl ether, forms yellowish-brown crystals, m. p. 253—254°.

With phenylcarbimide the ethyl ether yields the compound (II.), which forms silky, yellow needles, m. p. 183—184°.



The corresponding compound,  $C_{28}H_{23}O_2NS$ , formed by phenylthiocarbimide, forms yellowish-brown, tabular crystals, m. p. 128—129°.

7:8-Dihydroxy-7:8-diethyldihydroacenaphthene (III.), prepared by the action of magnesium ethyl bromide on acenaphthenequinone, crystallises in colourless needles, m. p. 197—198°.

T. H. P.

**The Isomeric *m*-Bromonitrocinnamic Acids.** SIEGMUND REICH and SIEGMUND KOEHLER (*Ber.*, 1913, 46, 3727—3738).—Besides negative substituents and steric hindrance there appear to be other causes which affect the reactivity of an unsaturated linking, but which are little understood. This is an account of a preliminary investigation of the behaviour of *m*-nitrophenylcinnamic acid and *m*-nitrophenylpropionic acid from the point of view of these additional influences. It is found that *m*-nitrocinnamic acid unites with bromine easily, and so falls between the ortho-isomeride, which unites with bromine with great difficulty, and the para-isomeride, which brominates exceedingly readily. *m*-Nitrophenylpropionic acid resembles its ortho- and para-isomerides in combining with only two atoms of bromine (compare Heller and Tischner, A., 1910, i, 37).

*m*-Nitrophenylcinnamic acid, when treated in suspension in acetic acid with bromine, gave  $\alpha\beta$ -dibromo-*m*-nitrophenylpropionic acid, needles, m. p. 172°; methyl ester, needles grouped in rosettes, m. p. 88—89°. When heated with aqueous sodium carbonate solution for two hours at 105°, the acid undergoes partial conversion into  $\omega$ -bromo-

*m*-nitrostyrene, needles, m. p. 59°, the main product being the *α*-bromo-*m*-nitrocinnamic acid, m. p. 116° (see below).

Treatment with a bimolecular proportion of potassium hydroxide in hot alcoholic solution for three hours eliminated the elements of hydrogen bromide from *αβ*-dibromo-*m*-nitrocinnamic acid with formation of a mixture of *α*-bromo-*m*-nitroalloeicinnamic acid, needles with 1H<sub>2</sub>O, m. p. 82–83°, anhydrous, m. p. 116°, with *α*-bromo-*m*-nitrocinnamic acid, needles, m. p. 217°. The latter acid, which was present in small proportion, could be separated by its sparing solubility in benzene; it is very resistant to bromine and gives a pleasant smelling methyl ester, needles, m. p. 104°, which on subjection to the action of bromine vapour for four days, not only united with two atoms of bromine, but received a third as a substituent in the molecule.

*α*-Bromo-*m*-nitroalloeicinnamic acid is attacked only by highly concentrated alcoholic solutions of potassium hydroxide, and then the change is complex, pale yellow needles of a substance, m. p. 208°, being obtained. The *allo*-acid undergoes transformation into its less fusible and less soluble isomeride when exposed in benzene solution to sunlight, or immediately on the addition of bromine to its chloroform solution. When exposed in the solid state to bromine vapour for four days, addition of two bromine atoms occurs. Its methyl ester, needles, m. p. 70°, is without odour.

Treatment of *m*-nitrophenylpropionic acid in glacial acetic acid with concentrated hydrobromic acid gave rise to an isomeride of the two preceding acids, and the product is therefore in all probability *β*-bromo-*m*-nitrocinnamic acid, needles, m. p. 177–179°; its configuration is probably analogous to that of the acid, m. p. 217°, which it resembles in easily losing hydrogen bromide under the influence of 10% alcoholic potassium hydroxide with formation of *m*-nitrophenylpropionic acid, stellar groups of needles, m. p. 143°, which is soluble in hot water, the solution on cooling yielding a jelly of the undecomposed acid. Exposed as a solid to bromine vapour for three days, the acid assumes a diatomic proportion of bromine. Like phenylpropionic acid, and unlike its ortho- and para-isomerides, the acid melts without decomposition, and can also be boiled with water without loss of carbon dioxide. If heated with water for five hours at 150° in a sealed tube, however, it becomes converted into *m*-nitrophenylacetylene, a yellow, aromatic substance, m. p. 26°, b. p. 120°/11 mm., which explodes if heated under ordinary pressure; silver derivative, greenish-yellow; cuprous derivative, a reddish-brown, gelatinous precipitate. When cautiously mixed with sulphuric acid of 80% concentration and subsequently warmed, *m*-nitrophenylacetylene is hydrated to *m*-nitroacetophenone, m. p. 81°.

The action of bromine on *m*-nitrophenylpropionic acid in chloroform solution in the dark produces an additive compound, which from its method of formation is probably *cis-αβ*-dibromo-*m*-nitrocinnamic acid, granular crystals, m. p. 135–136°. If light is not excluded and the mixture is also warmed, the product is a mixture of the previous acid with *trans-αβ*-dibromo-*m*-nitrocinnamic acid, needles, m. p. 162°.

[S. REICH.]—It is suggested that the mechanism of the rearrangement of geometrical isomerides under the influence of chemical

reagents involves the primary formation of additive compounds with the reagent. Thus in the action of bromine on  $\alpha$ -bromo-*m*-nitrocinnamic acid in solution, the bromine molecule attaches itself by means of residual affinity at one of the unsaturated atoms; this causes an opening of the double bond, which allows free rotation of the molecule into the most favourable configuration; but this change effects a greater saturation between the ethylenic carbon atoms, and there is no longer sufficient residual valency to hold the bromine molecule which becomes free.

D. F. T.

**Synthesis of Aromatic Amino-acids.** J. HOUBEN and R. FREUND [and, in part, ERICH KELLNER] (*Ber.*, 1913, **46**, 3833—3839).—As previously shown (1904, i, 1014; 1909, i, 921; 1910, i, 34, 110) it is possible to apply the Kolbe synthesis of hydroxybenzoic acids from phenoxides and carbon dioxide to magnesium haloid compounds of arylamines. When heavier radicles than methyl or ethyl are attached to the nitrogen of the arylamine, the smoothness of the reaction is greatly diminished. Thus from *iso*amylaniline only small quantities of *p*-*iso*amylaminobenzoic acid,  $C_5H_{11} \cdot NH \cdot C_6H_4 \cdot CO_2H$ , were obtained, crystallising in colourless needles, m. p. 124—125°. The acid was prepared in larger quantities by the action of *iso*amyl bromide on *p*-aminobenzoic acid. It forms remarkable spongy salts with alkalis.

*p*-Acetyl*iso*amylaminobenzoic acid has m. p. 176—177°.

The arylamine synthesis only succeeds with the magnesium iodide compounds. In the case of magnesium ethylaniline bromide alone has a small quantity of the carboxylated derivative, *N*-ethylanthranilic acid, been obtained.

*N*-Carbomethoxy-*N*-ethylanthranilic acid,  $CO_2Me \cdot NEt \cdot C_6H_4 \cdot CO_2H$ , prepared from ethyl anthranilic acid and methyl chlorocarbonate. It forms short, colourless crystals, m. p. 137°, and is converted on heating into *N*-ethylsatoic anhydride,  $C_6H_4 \cdot \begin{matrix} NEt \cdot CO \\ \diagup \quad \diagdown \\ CO-O \end{matrix}$ . This crystallises in slightly yellow plates, m. p. 123—124°, and sublimes in almost colourless, radiating crystals.

*N*-Carbomethoxy-*N*-ethylanthranilic acid has m. p. 66—67°.

When the synthesis is applied to derivatives of *o*-amino-acids, only small quantities are obtained. Thus from *N*-methyl-*o*-toluidine-magnesium iodide and carbon dioxide under 28 atmospheres pressure at 200°, *p*-methylamino-*m*-toluic acid is obtained, m. p. 199° (compare Houben and Schottmüller, A., 1909, i, 921). 4-Carbomethoxy-methylamino-*m*-toluic acid,  $CO_2H \cdot C_6H_3Me \cdot NMe \cdot CO_2Et$ , forms colourless platelets, m. p. 143—144°.

In a second experiment, 2-methylamino-*m*-toluic acid (?), m. p. 149°, was obtained; it is characterised by an intense cornflower-blue fluorescence in alcoholic solution. The corresponding 2-ethylamino-*m*-toluic acid has m. p. 137°, and sublimes in needles.

6-Methylamino-*m*-toluic acid has m. p. 128°, sublimes in slender needles, and exhibits the characteristic blue fluorescence. E. F. A.

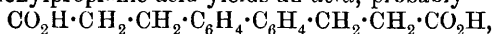
**Some Derivatives of *o*-Chlorobenzaldehyde and Melilotic Acid.** GRETE LASCH (*Monatsh.*, 1913, **34** 1653—1664).—*o*-Chloro-



cinnamic acid, prepared by heating *o*-chlorobenzaldehyde with acetic anhydride and potassium acetate, crystallises in lustrous needles, m. p.  $211^{\circ}$  (compare Gabriel and Herzberg, A., 1883, 1123; Stoermer, A., 1911, i, 297), and forms a *sodium* salt, *potassium* salt, and *methyl* ester, which has b. p.  $278-279^{\circ}$ , and crystallises in large, radiating plates, m. p.  $10.5^{\circ}$ ; the *amide*, obtained from the methyl ester or *chloride* by the action of ammonia, crystallises in long, lustrous needles, m. p.  $168^{\circ}$ , and is converted by heating with thionyl chloride into *o*-chloro-cinnamonitrile, needles, m. p.  $40^{\circ}$ .

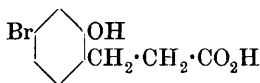
*o*-Chloro- $\beta$ -phenylpropionic acid, prepared by reducing the preceding acid with sodium amalgam, forms long, lustrous needles, m. p.  $97^{\circ}$  (compare Gabriel and Herzberg, *loc. cit.*), yields a methyl ester, b. p.  $255^{\circ}$ , and an *amide*, which crystallises in long needles, m. p.  $119^{\circ}$ , and is transformed by heating with thionyl chloride into *o*-chloro- $\beta$ -phenylpropionitrile. This has b. p.  $267-268^{\circ}$ , and is reduced by sodium and alcohol to  $\beta$ -phenylpropylamine, the *hydrochloride* of which has m. p.  $216^{\circ}$ .

When heated with barium hydroxide and a little water at  $200-220^{\circ}$ , *o*-chloro- $\beta$ -phenylpropionic acid yields an *acid*, probably



crystallising in lustrous needles, m. p.  $180-181^{\circ}$ .

On treatment with thionyl chloride it forms melilotic anhydride (*o*-hydroxy- $\beta$ -phenylpropiolactone), b. p.  $272^{\circ}$ , m. p.  $25^{\circ}$ , which is converted by the action of bromine vapour at  $170-200^{\circ}$  and subsequent distillation into 7-bromocoumarin and bromomelilotic acid (compare Hochstetter, A., 1885, 390). The latter compound is also obtained by reducing 7-bromocoumarin with sodium amalgam in aqueous alcoholic solution, and therefore must have the annexed constitution.



The action of bromine vapour on bromomelilotic anhydride at  $170-200^{\circ}$  gives rise to 7-bromocoumarin, the dibromo-compound,  $\text{CHBr} \begin{array}{c} \text{C}_6\text{H}_3\text{Br}\cdot\text{O} \\ \text{CH}_2\text{---CO} \end{array}$ , being probably formed as an intermediate product.

F. B.

**New Synthesis of Coumarin.** HANS MEYER, ROBERT BEER, and GRETE LASCH (*Monatsh.*, 1913, 34, 1665—1672. Compare preceding abstract).—When bromine vapour is passed over melilotic anhydride (*o*-hydroxy- $\beta$ -phenylpropiolactone),  $\text{O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{CH}_2 \end{array} \text{CH}_2$ , heated at  $270-300^{\circ}$ , two atoms of hydrogen are removed as hydrogen bromide, with the formation of coumarin; the removal of the hydrogen can also be effected by the action of chlorine, oxygen, or sulphur on the fused anhydride. Traces of coumarin are also produced by heating *o*-chlorocinnamic acid with aqueous barium hydroxide. *o*-Chlorocinnamic acid is best prepared by heating a mixture of *o*-chlorobenzylidene dichloride, acetic acid, and potassium acetate at  $210-220^{\circ}$ ; the electrolytic reduction to *o*-chloro- $\beta$ -phenylpropionic acid is described. When heated with sodium hydroxide and water at  $245-250^{\circ}$ , the last-named acid is converted into melilotic acid, which on distillation

yields the anhydride, together with a small amount of *o*-ethylphenol; the latter is removed by digesting the product with cold light petroleum.

The replacement of the halogen in *o*-chloro-, *o*-bromo-, and *o*-iodobenzoic acid by hydroxyl, by heating with aqueous barium hydroxide, has also been investigated. At 170° the iodo-acid is completely converted in eight hours into salicylic acid, whilst the chloro-acid remains unchanged; in the case of the bromo-acid only partial conversion takes place under these conditions.

F. B.

**Preparation of Derivatives of Salicylic Acid.** RICHARD WOLFFENSTEIN (D.R.-P. 267381).— $\beta\beta\beta$ -*Trichloro-tert.-butyl salicylate*, prepared by the interaction of acetonechloroform [ $\beta\beta\beta$ -trichloro-*tert.-butyl alcohol*] and salicyl chloride, has m. p. 81—82°; b. p. 170°.

*Tribromo-tert.-butyl salicylate* has m. p. 90—91°. *Trichloroisopropyl salicylate* is an oily liquid.

These compounds have analgesic properties, and can also be used internally.

J. C. C.

**Preparation of Sulphonyl Chlorides of Phenol-*o*-carboxylic Acids and their Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264786).—When aromatic *o*-hydroxycarboxylic acids (or their esters) are treated with a large excess of chlorosulphonic acid below 100°, the chlorosulphonyl group enters the para-position to the hydroxy-radicle; the following compounds are described.

The *chloride of 5 sulphosalicylic acid* (annexed formula), colourless needles, m. p. 171—172°; the *methyl ester* has m. p. 82—83°; the *chloride of 2-hydroxy-5-sulpho-3-toluic acid* has m. p. 179—180°; the *chloride of 3-hydroxy-6-sulpho-4-toluic acid* forms prisms, m. p. 172—173°, whilst the *chloride of 4-hydroxy-5-sulpho-3-toluic acid* has m. p. 189—190°. The *chloride of 4-hydroxy-5-sulphoisophthalic acid* has m. p. 251°; the *chloride of 3-chloro-5-sulphosalicylic acid* has m. p. 163—164°; the *chloride of 5-chloro-3-sulphosalicylic acid* has m. p. 206—207°; the *chloride of 4-sulpho-1-naphthol-2-carboxylic acid* forms colourless crystals, m. p. 200°, and that of *1-sulpho-2-naphthol-3-carboxylic acid* consists of yellow needles, m. p. 219°.

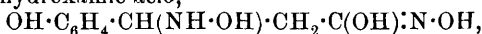
F. M. G. M.

**Preparation of Hexamethylenetetramine Sulphosalicylate.** J. D. RIEDEL (D.R.-P. 266122, 266123. Compare A., 1912, i, 356).—The compound,  $2C_6H_{12}N_4C_7H_6O_6S$ , is prepared by either treating an aqueous or alcoholic solution of the salt,  $C_6H_{12}N_4C_7H_6O_6S$ , with a further quantity of hexamethylenetetramine or by mixing 2 mols. of hexamethylenetetramine with 1 mol. of sulphosalicylic acid in absence of water; the product has m. p. 180°.

F. M. G. M.

**Unsaturated Compounds. X. Action of Free Hydroxylamine on Coumarin.** THEODOR POSNER and RUDOLF HESS (*Ber.*, 1913, 46, 3816—3833).—The products of the action of hydroxylamine on coumarin have been the subject of controversy between Posner (A., 1909, i, 583) and Francesconi and Cusmano (A., 1910, i, 38). It

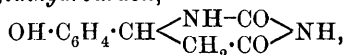
is now shown that the presence or absence of traces of an excess of sodium hydroxide materially affects the course of the reaction. The primary product is  $\beta$ -hydroxylaminohydro-*o*-coumaric acid hydroxamhydrate,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{C}(\text{NH}\cdot\text{OH})_2\cdot\text{OH}$ , which in presence of alkali passes over into  $\beta$ -hydroxylamino-hydrocoumarhydroxamic acid,



and this in turn is converted into  $\beta$ -aminohydro-*o*-coumaric acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

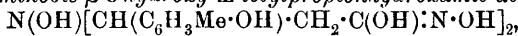
The 8-, 7-, and 6-methylcoumarins react less readily with hydroxylamine than does coumarin. In the cold, 7-methylcoumarin acted least readily, but on boiling it acted the most readily of the three.

4-*o*-Hydroxyphenyldihydrouracil,



obtained from  $\beta$ -aminohydrocoumaric acid on warming with potassium cyanate, is a colourless powder, decomp.  $239\text{--}241^\circ$ .

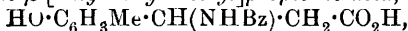
8-Methylcoumarin reacts with hydroxylamine in the cold, forming  $\beta$ -hydroxylaminobis- $\beta$ -*o*-hydroxy-*m*-tolylpropionhydroxamic acid,



which could not be obtained pure; it had decomp.  $90\text{--}95^\circ$ .

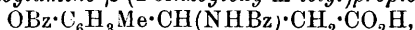
On boiling with hydroxylamine,  $\beta$ -amino- $\beta$ -2-hydroxy-*m*-tolylpropionic acid,  $\text{HO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is obtained. It forms a colourless powder, m. p.  $184\text{--}185^\circ$  (decomp.). The hydrochloride is crystalline, decomp.  $130\text{--}135^\circ$ . On heating with excess of acetic anhydride, anhydro- $\beta$ -acetyl-amino- $\beta$ -2-hydroxy-*m*-tolylpropionic acid is formed. It is a colourless powder, decomp.  $135\text{--}137^\circ$ .

$\beta$  Benzoylamino- $\beta$ -[2-hydroxy-*m*-tolyl]propionic acid,



obtained by the action of benzoyl chloride on the amino-acid in presence of excess of sodium hydroxide and without cooling, is a colourless, crystalline powder, decomp.  $166\text{--}169^\circ$ .

When excess of sodium hydroxide is avoided and the mixture is cooled,  $\beta$  benzoylamino  $\beta$ -(2-benzoyloxy-*m*-tolyl)propionic acid,



is formed; it sinters at  $71\text{--}76^\circ$ , decomp.  $100^\circ$ .

$\beta$ -Carbamido- $\beta$ -(2-hydroxy-*m*-tolyl)propionic acid, obtained by the interaction of the amino-acid with potassium cyanate, forms colourless crystals, m. p.  $210\text{--}217^\circ$ .

Ethyl  $\beta$ -amino- $\beta$ -2-hydroxy-*m*-tolylpropionate hydrochloride is obtained in colourless crystals, decomp.  $99\text{--}104^\circ$ .

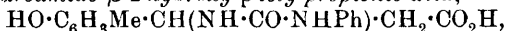
7-Methylcoumarin gives rise to  $\beta$ -amino- $\beta$ -2-hydroxy-*p*-tolylpropionic acid, m. p.  $215\text{--}216^\circ$  (decomp.). The hydrochloride, decomp.  $180\text{--}186^\circ$ , is described. At the same time, 5-methylbenzisoxazole-2-acetic acid,  $\text{C}_6\text{H}_3\text{Me}\begin{matrix} \text{C}(\text{CH}_2\cdot\text{CO}_2\text{H}) \\ \text{O} \end{matrix}\text{N}$ , is formed, separating in colourless crystals, m. p.  $167\text{--}171^\circ$  (decomp.).

The  $\beta$ -benzoylamino-derivative of the amino-acid has m. p.  $186\text{--}187^\circ$  (decomp.), whereas the dibenzoyl compound has m. p.  $145\text{--}148^\circ$  (decomp.).

Ethyl  $\beta$ -benzoylamino- $\beta$ -2-hydroxy-*p*-tolylpropionate, obtained on heat-

ing either benzoyl compound with ethyl alcohol and sulphuric acid, softens at  $150^{\circ}$ , m. p.  $155-159^{\circ}$  (decomp.).

*$\beta$ -Phenylcarbamido- $\beta$ -2-hydroxy-p-tolylpropionic acid,*



forms colourless crystals, m. p.  $169-171^{\circ}$  (decomp.).

6-Methylcoumarin gives rise in a similar manner to  *$\beta$ -amino- $\beta$ -6-hydroxy-m-tolylpropionic acid*, which separates as colourless needles, m. p.  $198-202^{\circ}$  (decomp.). The *hydrochloride* forms yellow needles, decomp.  $157^{\circ}$ .

A by-product which darkens at  $149^{\circ}$ , m. p.  $155^{\circ}$  (decomp.), is either 4-methylbenzisooxazole-2-acetic acid or 6-hydroxy-3-methylcinnam-hydroxamic acid.

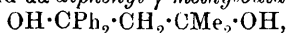
*Anhydro- $\beta$ -diacetyl-amino  $\beta$ -6-hydroxy-m-tolylpropionic acid* forms colourless crystals, m. p.  $150-152^{\circ}$ . The *benzoylamino*-derivative has decomp.  $170-175^{\circ}$ ; the *dibenzoyl* derivative has m. p.  $105-109^{\circ}$  (decomp.), whilst the *ethyl* ester of the benzoylamino-compound, which separates in colourless crystals, has m. p.  $120-121^{\circ}$ .

*$\beta$ -Carbamido- $\beta$ -6-hydroxy-m-tolylpropionic acid* forms crystals, m. p.  $149^{\circ}$  (decomp.).

4-[6-Hydroxy-m-tolyl]dihydrouacil, obtained by heating the foregoing, has m. p.  $245^{\circ}$  (decomp.).

*Ethyl  $\beta$ -amino- $\beta$ -6-hydroxy-m-tolylpropionate* separates as stunted, colourless crystals, m. p.  $149-150^{\circ}$ . E. F. A.

**Action of Organomagnesium Compounds on  $\beta$ -Substituted  $\beta$ -Hydroxyhydrocinnamic Esters.** MIRCEA I. BERBERIANU (*Chem. Zentr.*, 1913, ii, 766-767; from *Bul. Soc. Stiintz Bucuresti*, 1913, 22, 11-25).—Methyl  $\beta$ -hydroxy- $\beta\beta$ -diphenylpropionate and magnesium methyl iodide yield *aa-diphenyl- $\gamma$ -methylbutane- $\alpha\gamma$ -diol*,



in colourless prisms from alcohol or long needles from ether, m. p.  $114^{\circ}$ , and as a by-product, *aa-diphenyl- $\gamma$ -methyl- $\Delta^{a\beta}$ -butadiene*,  $\text{CPh}_2\cdot\text{C}::\text{CMe}_2$ . The latter is also obtained by heating the glycol with fuming hydrochloric acid or formic acid, and is a faintly yellow, mobile, aromatic liquid, b. p.  $140-150^{\circ}/18$  mm., which is stable towards 70% sulphuric acid, yields benzophenone and acetone with chromic acid, and forms a *tetrabromide*,  $\text{C}_{17}\text{H}_{16}\text{Br}_4$ , in colourless leaflets, m. p.  $40^{\circ}$ . The same ester yields with magnesium ethyl iodide, *aa-diphenyl- $\gamma$ -ethylpentane- $\alpha\gamma$ -diol*,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{CET}_2\cdot\text{OH}$ , in colourless prisms, m. p.  $50^{\circ}$ , and with magnesium phenyl bromide, *tetraphenylpropane- $\alpha\gamma$ -diol*.

Methyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\beta$ -anisylpropionate gives with magnesium methyl iodide,  *$\alpha$ -phenyl- $\alpha$ -anisyl- $\gamma$ -methylbutane- $\alpha\gamma$ -diol*,  $\text{C}_{18}\text{H}_{22}\text{O}_3$ , white needles, m. p.  $95-96^{\circ}$ , and with magnesium phenyl bromide,  *$\alpha\gamma$ -triphenyl- $\alpha$ -anisylpropane- $\alpha\gamma$ -diol*,  $\text{C}_{28}\text{H}_{26}\text{O}_3$ , leaflets, m. p.  $152^{\circ}$ . Methyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\beta$ -p-tolylpropionate and magnesium methyl iodide yield  *$\alpha$ -phenyl- $\alpha$ -p-tolyl- $\gamma$ -methylbutane- $\alpha\gamma$ -diol*,  $\text{C}_{18}\text{H}_{22}\text{O}_2$ , in prisms, m. p.  $63^{\circ}$ . J. C. W.

**Preparation of Nitroarylamides of 2-Naphthol-3-carboxylic Acid.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 264527).—When a mixture of 2-naphthol-3-carboxylic acid (188 parts) and

*m*-nitroaniline (135 parts) in toluene (1200 parts) is treated at 60—70° with phosphorus trichloride (60 parts) and subsequently boiled, it gives rise to a 92% yield of the 3-nitroanilide of 2-naphthol-3-carboxylic acid, yellow leaflets, m. p. 246—247°.

The tinctorial properties of the 2-nitroanilide, m. p. 192—193°; 4-nitroanilide, m. p. 258—259°; 4-chloro-2-nitroanilide, m. p. 221—222°; 2:4-dinitroanilide, m. p. 256—257°, and 5-nitro-2-toluidide, m. p. 233—234°, of the acid are also described. F. M. G. M.

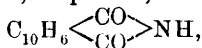
**Synthesis of Higher Indandiones. III.** MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, 402, 51—76).—It has been shown (A., 1910, i, 490) that the condensation of naphthalene and diethylmalonyl chloride (the best yield is obtained when the finely powdered aluminium chloride is added slowly to the solution of the two substances in carbon disulphide) yields three diethylnaphthindandiones: (I) an oil; (II and III), m. p. 79—81° and 120.5—122° respectively. The constitutions of these three substances, previously deduced indirectly, have now been definitely established by the degradation of the three substances to naphthalenedicarboxylic acids.

[With MARTHA COHN.]—By boiling with aqueous potassium hydroxide (1:1), the oil (I) yields, after acidification, 1- $\alpha$ -ethylbutyryl-naphthalene-8-carboxylic acid,  $\text{CHEt}_2 \cdot \text{CO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO}_2\text{H}$ , m. p. 152° (decomp.), colourless needles, which forms a methyl ester, m. p. 87—88°, does not react with phenylhydrazine, and is oxidised to naphthalic anhydride by acetic acid and nitric acid, D 1.4; the last reaction proves that the oil (I) and its hydrolytic fission product are 1:8-disubstituted naphthalene derivatives.

The hydrolytic fission product of III, m. p. 128—130°, yields naphthalene-2:3-dicarboxylic acid by oxidation, and is, therefore, 2- $\alpha$ -ethylbutyrylnaphthalene-3-carboxylic acid, not  $\beta$ -naphthoyl- $\alpha$ -ethylbutyric acid as stated previously (*loc. cit.*); the formation of benzene-1:2:4-tricarboxylic acid, not benzene-1:2:4:5-tetracarboxylic acid, by its energetic oxidation must be due to the loss of one molecule of carbon dioxide. Similarly, the hydrolytic fission product, m. p. 165—166, of II. must be 1(or 2)- $\alpha$ -ethylbutyrylnaphthalene-2(or 1)-carboxylic acid, not  $\alpha$ -naphthoyl- $\alpha$ -ethylbutyric acid (*loc. cit.*), since it yields Cleve's naphthalene-1:2-dicarboxylic anhydride by oxidation.

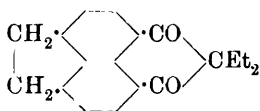
A further proof of the constitutions of the hydrolytic fission products of I, II, and III is obtained by heating the  $\alpha$ -ethylbutyrylnaphthalenecarboxylic acids above their m. p.'s, whereby they are converted into lactones, m. p. 84°, 128°, and 129° respectively, isomeric with I, II, and III (compare A., 1913, i, 1073). 2- $\alpha$ -Ethylbutyrylnaphthalene-3-carboxylic acid reacts with gently boiling phenylhydrazine to form a diazine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}:\text{C}:\text{CO} \\ \text{CH}:\text{C}:\text{C}(\text{CHEt}_2):\text{N} \end{smallmatrix} \begin{smallmatrix} \text{---} \text{NPh} \\ \text{---} \end{smallmatrix}$ , m. p. 175°, colourless needles; diethyl-2:3-naphthindandione, however, does not react with phenylhydrazine.

Naphthalene-2:3-dicarboxylic acid, which can also be obtained by the oxidation of the lactone, m. p. 129°, forms an imide,



m. p. 275°, and *phenylimide*,  $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} NPh$ , m. p. 277—278°; its chloride could not be prepared.

An improved method is described for the preparation of  $\alpha$ - and  $\beta$ -diethylacenaphthindandiones (*loc. cit.*); a third, very small product, m. p. 229—231°, of the reaction has been isolated, which is probably diacenaphthoyl-diethylmethane,  $CEt_2(CO \cdot C_{12}H_9)_2$ .



$\alpha$ -Diethylacenaphthindandione, m. p. 153—155°, which forms a *nitro*-compound,  $C_{19}H_{17}O_4N$ , m. p. 137·5—138·5°, brown needles, is now shown to be the peri-derivative (annexed formula) in the following manner. Its hydrolytic fission product is oxidised to naphthalene-1 : 4 : 5 : 8-tetracarboxylic acid by hot alkaline potassium permanganate, and yields, by heating above its m. p., a *lactone*, m. p. 108—109° (annexed formula), which is oxidised to acenaphthalic acid by glacial acetic and nitric (D 1·4) acids; the fission product of  $\alpha$ -diethylacenaphthindandione, therefore, must be 3- $\alpha$ -ethylbutyrylacenaphthene-4-carboxylic acid.

$\beta$ -Diethylacenaphthindandione, which probably has the  $CEt_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$  group attached in the 1 : 2-position, forms a crystalline hydrolytic fission product,  $C_{19}H_{20}O_3$ , m. p. 168—170° (decomp.), which reacts with phenylhydrazine (product, m. p. 205—207°, not examined owing to lack of material), and is converted above its m. p. into a *lactone*,  $C_{19}H_{18}O_2$ , m. p. about 100° (impure). C. S.

**Dihydroxyphenylalanine, a New Amino-acid from *Vicia faba*.** M. GUGGENHEIM (*Zeitsch. physiol. Chem.*, 1913, 88, 276—284).—Following Torquati's observation (A., 1913, i, 1429) that the green seed pods and seedlings of *Vicia faba* contain a nitrogenous substance which gives the catechol reaction, this substance has been identified as  $\alpha$ -amino- $\beta$ -3 : 4-dihydroxyphenylpropionic acid (*dihydroxyphenylalanine*),  $C_6H_3(OH)_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ . This crystallises in well-formed, stunted prisms or slender needles, m. p. 280° (decomp.),  $[\alpha]_D^{20} - 14 \cdot 28^\circ$ . The *hydrochloride* forms transparent, compact prisms.

2 : 5 : 6-Tribromo-3 : 4-dihydroxyphenylalanine, formed on bromination, separates as a mass of flocculent needles, m. p. about 200° (decomp.). It gives a deep blue coloration with ferric chloride.

*Tribenzoyldihydroxyphenylalanine* forms slender, colourless needles, m. p. 170°.

The inactive form of the new acid has been synthesised by Funk (T., 1911, 99, 554); it has m. p. 263—270°.

The acid is incompletely oxidised in the organism, and has no pharmacological action. E. F. A.

[Resorcinolbenzein and Fluorescein.] HANS VON LIEBIG (*Ber.*, 1913, 46, 3593—3598).—A detailed reply to Kehrman's criticism (A., 1913, i, 1352) of the author's experimental results (A., 1913, i, 865). D. F. T.

**Existence of Humic Acids. Explanation of their Actions.** PAUL EHRENBERG and FRITZ BAHR (*J. Landw.*, 1913, 61, 427—485).—The results of experiments on the evolution of ammonia from ammonium humate when heated indicated that the ammonia is not merely held by the surface of the humus, and further experiments on the adsorption of ammonia and sulphur dioxide respectively showed that the former is taken up in far greater quantity than the latter, being mainly chemically combined.

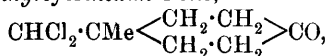
A comparison with guaiaconic acid showed further that humic acid is a true acid and not a phenolic compound.

Humic acid neutralises sodium hydroxide, and the point of neutralisation is sharply indicated by conductivity measurements. The sodium salt of humic acid behaves when diluted as a salt of a tribasic or tetrabasic acid.

When crude ammonium humate is filtered through collodion a colloidal substance remains. Humic acid prepared from the ammonium salt obtained in this manner can be dried and heated to above 100° without becoming insoluble in alkali. N. H. J. M.

**Hydroaromatic Compounds. Hydroaromatic Alcohols and Ketones Containing a *gem*-Dimethyl Group.** K. VON AUWERS and E. LANGE (*Annalen*, 1913, 401, 303—326).—Simple hydroaromatic compounds containing a *gem*-dimethyl group have been prepared and have been compared with corresponding substances which do not contain such a group, in order to ascertain the influence of this group particularly on the physical properties.

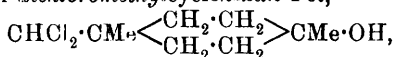
By reduction in aqueous alcohol by the Paal-Skita process, 1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one and 1-methyl-1-dichloromethyl- $\Delta^{3:5}$ -cyclohexadien-2-one are reduced almost quantitatively to 1-methyl-1-dichloromethylcyclohexan-4-one,



m. p. 47—48°, b. p. 142°/15 mm.,  $D_4^{52.8}$  1.2214,  $n_D$  1.49459,  $n_D$  1.49775,  $n_B$  1.50402, and  $n_\gamma$  1.50996 at 52.8°, large rhombohedra, and 1-methyl-1-dichloromethylcyclohexan-2-one,  $\text{C}_8\text{H}_{12}\text{OCl}_2$ , m. p. 33°, b. p. 123°/13 mm.,  $D_4^{26.45}$  1.2282,  $n_D$  1.49434,  $n_D$  1.49691,  $n_B$  1.50372, and  $n_\gamma$  1.50924 at 26.45°, respectively. The two cyclohexanones retain their halogen very tenaciously against the attack of many reducing agents except sodium and moist ether. Thus 1-methyl-1-dichloromethylcyclohexan-4-one (semicarbazone, m. p. 199—200° or 202—203° according to the rate of heating; oxime, stout plates) is converted into 1:1-dimethylcyclohexan-4-ol,  $\text{C}_8\text{H}_{16}\text{O}$ , b. p. 186° or 97.5—98.1°/27 mm.,  $D_4^{24.7}$  0.9220,  $n_D$  1.45896,  $n_D$  1.46128,  $n_B$  1.46716, and  $n_\gamma$  1.47214 at 24.7°, in about 50% yield, and 1-methyl-1-dichloromethylcyclohexan-2-one (semicarbazone, m. p. 195°) into 1:1-dimethylcyclohexan-2-ol, b. p. 77—78°/14 mm.,  $D_4^{24.1}$  0.9256,  $n_D$  1.46276,  $n_D$  1.46521,  $n_B$  1.47093, and  $n_\gamma$  1.47569 at 24.1° (the substance is probably not quite pure) in 45—50% yield (compare Meerwein and Unkel, A., 1910, i, 856). By oxidation with potassium dichromate and moderately concentrated sulphuric acid, the twodimethylcyclohexanols yield the corresponding ketones, 1:1-dimethylcyclohexan-4-one,  $\text{C}_8\text{H}_{14}\text{O}$ , m. p. 38—40°, b. p. 72.4—73.4°/14 mm.,  $D_4^{24.2}$

0.9282,  $n_a$  1.45126,  $n_D$  1.45374,  $n_B$  1.45972, and  $n_\gamma$  1.46478 at 24° (*semicarbazone*, m. p. 202°), and 1:1-dimethylcyclohexan-2-one, b. p. 172—172.5°/757 mm. (Meerwein and Unkel, 170.2—170.4°, *loc. cit.*),  $D_4^{19.9}$  0.9146,  $n_a$  1.44624,  $n_D$  1.44863,  $n_B$  1.45443, and  $n_\gamma$  1.45940 at 19.9°.

1:4-Dimethyl-1-dichloromethylcyclohexan-4-ol,



m. p. 86°, b. p. 142.5—143.5°/16 mm., colourless needles, obtained in almost quantitative yield from 1-methyl-1-dichloromethylcyclohexan-4-one and magnesium methyl iodide in the usual manner, forms an *acetate*,  $\text{C}_{11}\text{H}_{18}(\text{O}_2\text{C})_2$ , m. p. 92—93°, b. p. 162°/23 mm., and gives by reduction with sodium and moist ether about 80% yield of 1:1:4-trimethylcyclohexan-4-ol, m. p. 58°, b. p. 75°/11 mm.

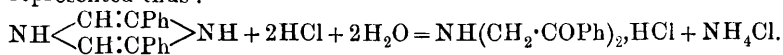
1:1:2-Trimethylcyclohexan-2-ol, b. p. 75.8°/16 mm. (the hydrated form,  $\text{C}_9\text{H}_{18}\text{O}, \frac{1}{2}\text{H}_2\text{O}$ , has m. p. 41° [decomp.]),  $D_4^{19.9}$  0.9258,  $n_a$  1.46542,  $n_D$  1.46788,  $n_B$  1.47367, and  $n_\gamma$  1.47862 at 19.9°, can only be prepared from 1:1-dimethylcyclohexan-2-one and magnesium methyl iodide, the chlorinated ketone reacting in an anomalous manner with the Grignard reagent.

1:1-Dimethylcyclohexan-3-ol (Crossley and Renouf, T., 1905, 87, 1494; 1907, 91, 70) has  $D_4^{19.7}$  0.9089,  $n_a$  1.45655,  $n_D$  1.45893,  $n_B$  1.46476, and  $n_\gamma$  1.46964 at 19.7°, 1:1-Dimethylcyclohexan-3-one (Crossley and Renouf, *loc. cit.*) has  $D_4^{18.6}$  0.9068,  $n_a$  1.44513,  $n_D$  1.44763,  $n_B$  1.45352, and  $n_\gamma$  1.45851 at 18.6°.

Comparisons of the m. p.'s, b. p.'s, densities, and molecular refractions and dispersions of the preceding substances do not permit any characteristic generalisations to be made. C. S.

**Action of Ammonia on  $\omega$ -Bromoacetophenone.** S. GABRIEL (*Ber.*, 1913, 46, 3859—3861).—It has been shown previously (A., 1908, i, 464) that the yellowish-red, crystalline substance, obtained by the action of alcoholic ammonia on  $\omega$ -bromoacetophenone, yields, on treatment with hydrochloric acid,  $\omega$ -aminoacetophenone hydrochloride, diphenacylamine hydrochloride and 2:5-diphenylpyrazine, and the conclusion was therefore drawn that the crystals contained a mixture of 2:5-diphenyldihydropyrazine and diphenacylamine.

In view of the work of Tutin (T., 1910, 97, 2571), who has shown that diphenacylamine reacts with ammonia, yielding 2:6-diphenyldihydropyrazine, the author now considers it probable that the red substance, obtained from ammonia and  $\omega$ -bromoacetophenone, consists of a mixture of 2:5-diphenyldihydropyrazine and 2:6-diphenyldihydropyrazine, the formation of diphenacylamine hydrochloride from the latter compound by the action of hydrochloric acid being represented thus:



(I.)

This view is supported by the isolation of considerable quantities of ammonium chloride, in addition to diphenylpyrazine,  $\omega$ -aminoaceto-



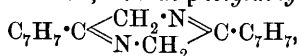
phenone hydrochloride, and diphenacylamine hydrochloride, from the product of the action of hydrochloric acid on the original red substance.

2 : 6-*Diphenyldihydropyrazine* (I) has been prepared by the action of alcoholic ammonia on diphenacylamine hydrochloride in the absence of air. It crystallises in orange-yellow needles, m. p. 139—140°, and is readily oxidised on exposure to air to 2 : 6-diphenylpyrazine. On treatment with hydrochloric acid, it yields diphenacylamine hydrochloride.

F. B.

*p*-Tolacylamine. KURT RÜDENBURG (*Ber.*, 1913, **46**, 3555—3564).—In extension of the work of Gabriel (*A.*, 1908, **i**, 464) on  $\alpha$ -aminoacetophenone, the author has investigated *p*-tolyl aminomethyl ketone (*p*-tolacylamine), for which a new method of preparation is described.

Phthalylglycyl chloride was treated in toluene solution with aluminium chloride with production of tolacylphthalimide which was hydrolysable in two stages (compare Gabriel and Colman, *A.*, 1908, **i**, 274) to the hydrochloride of *p*-tolyl aminomethyl ketone. When this substance is treated in aqueous solution with an equivalent quantity of ammonia with exclusion of air, 2 : 5-*di-p*-tolyldihydropyrazine,

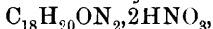


is obtained as orange-yellow crystals, m. p. 185°, which in a moist condition are unstable in the air; *hydrochloride*, iodine-coloured needles, m. p. 178—180° (decomp.). A solution of ditolyldihydropyrazine in warm acetic acid or alcohol, when treated with a little nitric acid or hydrogen peroxide, gives a deposit of 2 : 5-*di-p*-tolylpyrazine,



lemon-yellow needles, m. p. 202—203°, which is, however, most conveniently obtained by atmospheric oxidation of the alcoholic solution.

If *p*-tolyl aminomethyl ketone hydrochloride is shaken with potassium hydroxide in aqueous solution in an atmosphere of hydrogen, polymerisation is effected to  $\alpha\gamma$ -diamino- $\beta$ -hydroxy- $\beta\delta$ -*di-p*-tolylbutan- $\delta$ -one (*bistolacylamine*),  $\text{NH}_2\cdot\text{CH}_2\cdot\text{C}(\text{C}_7\text{H}_7)(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{C}_7\text{H}_7$ , yellow leaflets, which when rapidly heated had m. p. 120° (decomp.), but when slowly heated, or better when maintained in a vacuum at 100°, eliminated the whole of its oxygen as water (compare Gabriel, *loc. cit.*) with formation of *bisanhydrotolacylamine* (3-amino-2 : 4-*di-p*-tolylpyrrole?),  $\text{C}_{18}\text{H}_{18}\text{N}_2$ , green needles, m. p. 223—225°, which slowly reddens; *hydrochloride*, colourless powder, m. p. 248° (decomp.); *platini-chloride*, orange-yellow needles, unfused at 240°; *benzylidene* derivative, lemon-yellow, hexagonal prisms, m. p. 181—182°. The only indication of the existence of an intermediate anhydrobistolacylamine analogous to the anhydrobisphenacylamine obtained by Gabriel was observed in the formation from the aboveistolacylamine of a *nitrate*,

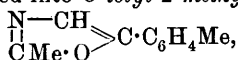


pale yellow, crystalline powder, m. p. 248° (decomp.).

By shaking with benzoyl chloride and anhydrous sodium acetate in acetic acid solution, *p*-tolyl aminomethyl ketone hydrochloride is converted into *p*-tolyl benzoylaminomethyl ketone,  $\text{NH}\cdot\text{Bz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ ,

colourless needles, m. p. 118—119°, which when heated in intimate mixture with phosphorus pentachloride at 100° gives 2-phenyl-5-tolyl-oxazole,  $\begin{array}{c} \text{N}-\text{CH} \\ || \\ \text{C} \cdot \text{Ph} \cdot \text{O} \end{array} \gg \text{C} \cdot \text{C}_6\text{H}_4\text{Me}$ , colourless needles, m. p. 81—82°; *picrate*, yellow needles, m. p. 189—190°. If the above benzoyl derivative is heated at 170° with phosphorus pentasulphide the product is the corresponding 2-phenyl-5-tolylthiazole, brownish-yellow needles, m. p. 120—121°; *picrate*, lemon-yellow spangles, m. p. 168—169°; *hydrochloride*, yellow crystals, m. p. 167—173°.

On heating *p*-tolyl aminomethyl ketone hydrochloride with sodium acetate in acetic anhydride solution, *p*-tolyl acetylaminomethyl ketone,  $\text{NHAc} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Me}$ , almost colourless needles, m. p. 127—128°, is obtained. When heated for a short time with phosphorus pentachloride, this substance is converted into 5-tolyl-2-methyloxazole,



colourless leaflets, m. p. 58—59°; *platinichloride*, prisms with  $2\text{H}_2\text{O}$ , m. p. 195° (decomp.).

The action of phosphorus pentasulphide on *p*-tolyl acetylaminomethyl ketone at 170—180° gives rise to the corresponding 5-*p*-tolyl-2-methylthiazole, almost colourless leaflets, m. p. 81—82°, of characteristic odour; *hydrochloride*, colourless needles with  $\text{H}_2\text{O}$ , m. p. 195—196°; *platinichloride*, orange-yellow needles, m. p. 202—203° (decomp.); *aurichloride*, deep yellow needles, m. p. 129—131°. D F T.

**Preparation of Substitution-products of Phenyl  $\omega$ -Trichloro-*o*-tolyl Ketone.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 267271).—*o*-Chlorophenyl 5-chloro-*o*-tolyl ketone, prepared by condensing *p*-chlorotoluene and *o*-chlorobenzoyl chloride by means of aluminium chloride, is a pale yellow oil, b. p. 225°/12 mm. On chlorination it yields *o*-chlorophenyl  $\omega\omega\omega$ -5-tetrachloro-*o*-tolyl ketone, m. p. 117°. Phenyl 5-chloro-*o*-tolyl ketone is a pale yellow oil, b. p. 210°/30 mm. *o*-Chlorophenyl *m*-xylyl ketone, prepared from *o*-chlorobenzoyl chloride and *m*-xylene, has b. p. 210°/10 mm.; on chlorination it yields *o*-chlorophenyl  $\omega$ -hexachloro-*m*-xylyl ketone as a pale yellow powder. Phenyl *m*-xylyl ketone has b. p. 180°/10 mm., and on chlorination yields phenyl  $\omega$ -hexachloro-*m*-xylyl ketone as a yellow powder.

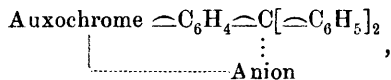
These  $\omega$ -chloro-derivatives are of use in the synthesis of anthraquinone derivatives, to which they may be condensed either directly or through the corresponding carboxylic acids. J. C. C.

**Basic Function of Methoxyl.** HUGO KAUFFMANN and FELIX KIESER (*Ber.*, 1913, 46, 3788—3801).—In order to study the basic and auxochromic action of the methoxyl group a number of derivatives of chalkone and triphenylcarbinol have been investigated, the magnitude of the basic character being determined by titration of the glacial acetic acid-sulphuric acid solution with 75% alcohol.

It is established that the basic character of halochromic compounds is much increased by methoxyl groups in the para-position, only slightly increased when they are in the ortho-position, and hardly altered when they are in the meta-position. This is true also when several methoxyl groups are attached to the same ring. Accordingly,

compounds containing methoxyl groups in resorcinol or phloroglucinol are strongly basic.

These phenomena are explained on the basis of the theory of the distribution of valency, and formulæ are proposed for derivatives of triphenylcarbinol, distyryl ketone and phenyl styryl ketones, such as



which fully express their behaviour (compare Kauffmann, A., 1912, i, 397).

The following substances are described :

2 : 4-Dimethoxyphenyl styryl ketone crystallises in slender, pale yellow needles, m. p. 78°.

2 : 4-Dimethoxyphenyl 4-methoxystyryl ketone forms pale yellow needles, m. p. 88°.

2 : 4-Dimethoxyphenyl 3 : 4-methylenedioxy styryl ketone separates as pale yellow needles, m. p. 135°.

2 : 4-Dimethoxyphenyl 2 : 4-dimethoxystyryl ketone crystallises in pale yellow needles, m. p. 128°.

The isomeric 2 : 4-dimethoxyphenyl 3 : 4-dimethoxystyryl ketone forms yellow crystals, m. p. 89°.

2 : 4-Dimethoxyphenyl 2 : 5-dimethoxystyryl ketone yields lustrous, yellow platelets, m. p. 90.5°.

3 : 4-Dimethoxyphenyl styryl ketone separates in pale yellow platelets, m. p. 85°.

3 : 4-Dimethoxyphenyl 4-methoxystyryl ketone gives stunted, yellow needles, m. p. 90°.

3 : 4-Dimethoxyphenyl 3 : 4-methylenedioxy styryl ketone forms yellow, matted needles, m. p. 144°.

3 : 4-Dimethoxyphenyl 2 : 4-dimethoxystyryl ketone crystallises in minute, pale yellow needles, m. p. 115.5°.

3 : 4-Dimethoxyphenyl 3 : 4-dimethoxystyryl ketone yields slender, pale yellow crystals, m. p. 110°.

3 : 4-Dimethoxyphenyl 2 : 5-dimethoxystyryl ketone forms pale yellow compact crystals, m. p. 81°.

2 : 5-Dimethoxyphenyl 2 : 5-dimethoxystyryl ketone could not be obtained crystalline.

2 : 5-Dimethoxyphenyl 2 : 4-dimethoxystyryl ketone is colourless, m. p. 112°. It does not show halochromism.

2 : 5-Dimethoxyphenyl 3 : 4-dimethoxystyryl ketone forms colourless platelets of silky lustre, m. p. 128°, and shows no halochromism.

3 : 4-Dimethoxyphenyl cinnamylidenemethyl ketone forms minute, citron-yellow needles, m. p. 111°.

3 : 4-Dimethoxyphenyl furfurylidenemethyl ketone yields pale yellow needles, m. p. 81°.

2 : 4 : 6-Trimethoxyphenyl 2 : 4-dimethoxystyryl ketone crystallises in yellow needles, m. p. 127°.

2 : 4 : 6-Trimethoxyphenyl 3 : 4-dimethoxystyryl ketone forms faintly yellow-coloured, microscopic needles, m. p. 118°.

2 : 4 : 6-Trimethoxyphenyl 2 : 5-dimethoxystyryl ketone yields lustrous, yellow platelets, m. p. 137°.

3:5-Dimethoxytriphenylcarbinol forms minute, colourless needles, m. p. 113°.

2:4:6-Trimethoxytriphenylcarbinol separates as slender, colourless crystals, m. p. 110—111°.

2:3:4-Trimethoxytriphenylcarbinol forms stunted crystals, m. p. 139°.

2:4:6:2':4'-Pentamethoxytriphenylcarbinol is characterised by colourless crystals, m. p. 120°. E. F. A.

**Influence of Acid Radicles on the Phenomenon of Halochromism.** HUGO KAUFFMANN and HERMANN BURCKHARDT (*Ber.*, 1913, 46, 3808—3816).—It is pointed out that whereas dimethoxydistyryl ketone gives a deep red coloration with sulphuric acid, *p*:*p*'-tetramethyldiaminodistyryl ketone only gives a yellow. The more powerful auxochrome is the less effective; this is due to the fact that the amino-group is put out of action as it were by the acid, whereas the methoxyl group is unaffected. This is illustrated by the effects caused by the introduction of various acyl radicles in amines in deepening the colours given with concentrated sulphuric acid. Whereas acetyl and benzoyl have relatively little effect, benzenesulphonyl has very considerable influence, the group  $\text{NH}(\text{SO}_2 \cdot \text{C}_6\text{H}_5)$  having an action equivalent to methoxyl or hydroxyl.

$\beta$ -Aminoanthraquinone and its acetyl derivative give a greenish-yellow, the benzoyl derivative gives a yellow, and the benzenesulphonyl compound a red coloration with sulphuric acid. The benzoyl derivative forms yellow crystals, m. p. 227—228°, whilst the benzenesulphonyl derivative crystallises in yellow plates, m. p. 271°.

*p*:*p*'-Diaminobenzylideneazine, like its acetyl and benzoyl derivatives, dissolves in sulphuric acid with a yellow coloration. The benzenesulphonyl compound gives rise to an orange colour. The diacetyl compound is colourless, m. p. 260—261°; the dibenzoyl compound is somewhat yellow, m. p. above 285°, and the dibenzenesulphonyl compound is likewise yellow, m. p. 250°.

Similarly, the benzenesulphonyl derivative of phenyl *p*-aminostyryl ketone is orange, whereas the amino-compound, its acetyl and benzoyl derivatives are colourless. The acetyl derivative forms yellow crystals, m. p. 178°; the benzoyl derivative crystallises in pale yellow leaflets, m. p. 181°, whilst the benzenesulphonyl compound is yellow, m. p. 183—184°.

The compounds from *m*-aminostyryl methyl ketone show a similar range, the benzenesulphonyl compound being orange-red instead of yellow. The acetyl compound forms colourless, matted crystals, m. p. 119—120°, whereas Rupe and Porai-Koschitz (*A.*, 1906, i, 754) give m. p. 104°. The benzoyl compound separates in almost colourless crystals, m. p. 135°, whilst the benzenesulphonyl compound is colourless, m. p. 127°.

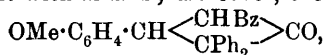
All these derivatives of *m*-aminostyryl methyl ketone are orange-coloured of about equal intensity. Their solutions in concentrated sulphuric acid have a green fluorescence.

*m*-Nitrodistyryl ketone, prepared by condensation of *m*-nitrobenzaldehyde with styryl methyl ketone, forms bright yellow crystals, m. p. 140°. It is reduced to *m*-aminodistyryl ketone, an intense yellow

compound, m. p. 114°. The *acetyl* derivative forms yellow, matted needles, m. p. 150°; the *benzoyl* derivative is yellow, m. p. 150—151°, and the *benzenesulphonyl* derivative has m. p. 140°.

With *m*:*m'*-diaminodistyryl ketone the increase in colour of the acyl derivatives is marked, the benzenesulphonyl compound being orange. *m*:*m'*-Diaminodistyryl ketone, prepared by reduction of the dinitro-compound, is pale yellow, m. p. 161°. The *diacetyl* derivative forms yellow crystals, m. p. 243°; the *dibenzoyl* compound has m. p. 233°, and the *dibenzenesulphonyl* compound is also yellow, m. p. 196°. E. F. A.

**Ketens. VI. Formation of  $\delta$ -Lactones from Diphenylketen.** H. STAUDINGER and R. ENDLE (*Annalen*, 1913, 401, 263—292. Compare A., 1911, i, 876).—The paper deals more fully with the constitution and properties of the  $\delta$ -lactones obtained additively from diphenylketen and phenyl styryl ketone or similar  $\alpha\beta$ -unsaturated ketones (*loc. cit.*). The addition of diphenylketen to, for example, phenyl *p*-methoxystyryl ketone can yield theoretically six substances, two each according as the addition occurs at the carbonyl group, at the double linking, or in the 1:4-position (*loc. cit.*). Three of the formulæ are excluded, because the additive product readily yields an acid by treatment with alkalis; moreover, the formula



is untenable, because the substance does not react with ferric chloride or yield a pyrazole derivative with phenylhydrazine (compare A., 1910, i, 46). Finally, the substance cannot be a  $\beta$ -lactone, because it yields, not a  $\beta$ -hydroxy-acid, but an unsaturated ketonic acid by treatment with an alkali. The formula, therefore, of the additive product must be  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\left\langle\begin{array}{c}\text{CH}\cdot\text{CPh} \\ \text{CPh}_2\cdot\text{CO}\end{array}\right\rangle\text{O}$ , and it has been confirmed in several ways.

[With A. VON KARATEEW.]—The reaction between phenyl styryl ketone and diphenylketen-quinoline is effected best at 130—140° in an atmosphere of carbon dioxide. The warm product is dissolved in ether and the solution by inoculation yields the *lactone*,  $\text{CHPh}\left\langle\begin{array}{c}\text{CH}\cdot\text{CPh} \\ \text{CPh}_2\cdot\text{CO}\end{array}\right\rangle\text{O}$ , m. p. 189—190° (previously supposed to be 3-benzoyl-1:1:2-triphenyl-4-cyclobutanone, A., 1910, i, 46). The lactone is not hydrolysed by concentrated hydrochloric acid on the water-bath, but is converted by ethyl alcoholic potassium hydroxide into  $\gamma$ -benzoyl- $\alpha\alpha\beta$ -triphenylbutyric acid,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ , m. p. 145—147°. The  $\delta$ -lactone is converted by methyl alcoholic potassium hydroxide into the *methyl ester*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{CO}_2\text{Me}$ , m. p. 135—136° (*oxime*, m. p. 197—198°; *phenylhydrazone*, m. p. 150—152°), at the ordinary temperature and into phenyl styryl ketone and diphenylacetic acid by warming. The methyl ester and the acid itself are decomposed in a similar manner by heating above their m. p.'s.

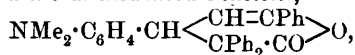
The  $\delta$ -lactone forms a *bromo-derivative*,  $\text{C}_{29}\text{H}_{21}\text{O}_2\text{Br}$ , m. p. 165—166°, is converted into the  $\delta$ -*lactam*,  $\text{CPh}_2\left\langle\begin{array}{c}\text{CHPh}\cdot\text{CH} \\ \text{CO}\text{—NH}\end{array}\right\rangle\text{CPh}$ , m. p.

215—217°, by methyl alcoholic ammonia at 150°, and decomposes slowly at 206°, yielding carbon dioxide and  $\alpha\alpha\beta\delta$ -tetraphenylbutadiene (m. p. 146—148°), the reaction being unimolecular.

It has been shown (*loc. cit.*) that the  $\beta$ -lactone, which is also produced during the reaction between diphenylketen and phenyl styryl ketone, decomposes at 130° into carbon dioxide and the butadiene derivative. The explanation of the preceding remarkable property of the  $\delta$ -lactone, of behaving like a  $\beta$ -lactone in yielding carbon dioxide and the butadiene derivative by heating, is probably that the  $\delta$ -lactone decomposes at the higher temperature into its generators; these re-unite to form the unstable  $\beta$ -lactone, which immediately decomposes into carbon dioxide and  $\alpha\alpha\beta\delta$ -tetraphenylbutadiene. The temporary formation of diphenylketen during the decomposition of the  $\delta$ -lactone is proved by heating with aniline, whereby diphenylacetanilide is obtained.

The reaction between phenyl methoxystyryl ketone and diphenylketen-quinoline at 130—140° yields  $\alpha\alpha\beta$ -triphenyl- $\delta$ -anisylbutadiene,  $\text{CPh}_2\cdot\text{CPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 130—131°, faintly yellow prisms, and the unsaturated  $\delta$ -lactone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}\cdot\text{CPh} \\ \text{CPh}_2\cdot\text{CO}\end{smallmatrix}\right\rangle\text{O}$ , m. p. 179—180°, derived from  $\gamma$ -benzoyl- $\alpha\alpha$ -diphenyl- $\beta$ -anisylbutyric acid. The  $\delta$ -lactone does not react with phenylhydrazine, and is comparatively stable towards oxidising agents. Its transformations are quite similar to those recorded above.  $\gamma$ -Benzoyl- $\alpha\alpha$ -diphenyl- $\beta$ -anisylbutyric acid,  $\text{C}_{30}\text{H}_{26}\text{O}_4$ , crystals containing  $\text{MeOH}$ , m. p. 113—114° (decomp.), regenerates the  $\delta$ -lactone by boiling with thionyl chloride and ether, and decomposes into diphenylacetic acid and phenyl methoxystyryl ketone at 250°. The methyl ester,  $\text{C}_{31}\text{H}_{28}\text{O}_4$ , m. p. 159—160°, decomposes quantitatively at 250° into methyl diphenylacetate and phenyl methoxystyryl ketone, and forms an *oxime*, m. p. 169—170°, and *phenylhydrazone*, m. p. 150—153°, faintly red, crystalline powder, which is changed during recrystallisation to a faintly yellow substance, m. p. 100—102°. The  $\delta$ -lactone is converted by methyl-alcoholic ammonia at 150° into the  $\delta$ -lactam,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}\cdot\text{CPh} \\ \text{CPh}_2\cdot\text{CO}\end{smallmatrix}\right\rangle\text{NH}$ , m. p. 230—231°, forms a bromo-derivative,  $\text{C}_{30}\text{H}_{23}\text{O}_3\text{Br}$ , m. p. 159—160°, colourless crystals (a violet intermediate product is formed in the solution), and decomposes into carbon dioxide and  $\alpha\alpha\beta$ -triphenyl- $\delta$ -anisylbutadiene at 206°.

[With  $\text{KON}$ .]—Diphenylketen-quinoline and phenyl *p*-dimethylaminostyryl ketone react at 130—140° to form  $\alpha\alpha\beta$ -triphenyl- $\delta$ -*p*-dimethylaminophenylbutadiene,  $\text{CPh}_2\cdot\text{CPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , m. p. 138°, yellow crystals, and the unsaturated  $\delta$ -lactone,



m. p. 199—200° (decomp.), derived from  $\gamma$ -benzoyl- $\alpha\alpha$ -diphenyl- $\beta$ -*p*-dimethylaminophenylbutyric acid. The acid itself is too unstable to be isolated, but the methyl ester,  $\text{C}_{32}\text{H}_{31}\text{O}_3\text{N}$ , m. p. 165°, is obtained by warming the  $\delta$ -lactone with methyl-alcoholic potassium hydroxide for fifteen minutes; if the heating is prolonged, the ester decomposes into diphenylacetic acid and phenyl *p*-dimethylaminostyryl ketone. The

$\delta$ -lactone forms a *bromo-derivative*,  $C_{31}H_{26}O_2NBr$ , m. p. 213—214°, colourless crystals (an intermediate, comparatively stable, bluish-violet, crystalline *substance* is formed), and decomposes at 206° into carbon dioxide and  $\alpha\beta$  triphenyl- $\delta$ -*p*-dimethylaminophenylbutadiene. C. S.

**Ketens. VII. Experiments with Diethylketen.** H. STAUDINGER and J. MAIER (*Annalen*, 1913, 401, 292—303).—Diethylketen resembles dimethylketen in its general behaviour, but reacts very much more slowly, not only with substances such as water, *p*-benzoquinone, and distyryl ketone, but also in its rate of polymerisation. This is anomalous because diethylketen is the more highly coloured of the two, and experience has shown that the more intense is the colour of a keten the more rapidly does it polymerise.

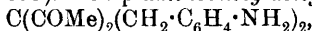
After being heated for about six days in the water-bath, diethylketen is completely polymerised to 2 : 2 : 4 : 4-*tetraethylcyclobutane-1 : 3-dione*,  $CO \begin{smallmatrix} \text{CEt}_2 \\ \text{CEt}_2 \end{smallmatrix} CO$ , m. p. 23—24°, b. p. 95—97°/15 mm., colourless crystals with an odour of camphor, which is converted by 10% sodium hydroxide at 150° into carbon dioxide and *s*-tetraethylacetone, a little  $\alpha$ -ethylbutyric acid also being formed. After keeping for ten days with ethereal benzylideneaniline, diethylketen is converted into the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenyl- $\alpha\alpha$ -diethylpropionic acid,  $CHPh \begin{smallmatrix} \text{CEt}_2 \\ \text{NPh} \end{smallmatrix} CO$ , m. p. 72—73°; the *anilino-acid*,  $C_{19}H_{23}O_2N$ , has m. p. 115—116°.

*Diethylketen-quinoline*,  $C_6H_4 \begin{smallmatrix} \text{CH:CH}\cdot\text{C}\cdot\text{CEt}_2\cdot\text{CO} \\ \text{N-CO-CEt}_2 \end{smallmatrix}$ , m. p. 76—77°, prepared by keeping the keten and quinoline in dry ether for five days, is comparatively stable. Diethylketen and *p*-benzoquinone do not react in ether to form a  $\beta$ -lactone, but by heating in benzene at 100° for three days yield the polymeride, carbon dioxide, and a viscous *substance*, b. p. 98—105°/0 mm. The keten and distyryl ketone at 100° yield, after six days, a viscous *substance*, b. p. 140°/0 mm.

An extremely explosive, colourless *peroxide* is obtained by the action of oxygen on ethereal diethylketen at -20°. An ethereal suspension of the peroxide decomposes quietly at the ordinary temperature, the products being carbon dioxide, diethyl ketone, and *diethylketen oxide*,  $(O \begin{smallmatrix} \text{CEt}_2 \\ \text{CO} \end{smallmatrix})_x$ , m. p. 158—160°; the last *substance* is amorphous, and is more readily obtained by the action of oxygen on diethylketen at 0°.

C. S.

**The Products of Condensation of Nitrobenzyl Chlorides with Acetylacetone, Methylacetylacetone, and the Cyanoacetic Esters.** H. MECH (*Compt. rend.*, 1913, 157, 941—943. Compare A., 1907, i, 63; 1908, i, 655).—*Di-p-aminobenzylacetylacetone*,



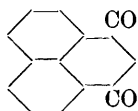
is obtained as a white powder, m. p. 126°, by the reduction of the corresponding nitro-compound (compare *loc. cit.*) with zinc and hydrochloric acid. It gives a *platinichloride*, a reddish-brown powder, and can be diazotised and coupled with phenols. *p*-Nitrobenzyl chloride on condensation with sodiummethylacetylacetone does not yield

the expected compound, but its product of hydrolysis, *a-p-nitrophenyl-β-methylbutan-γ-one*, as a white, crystalline powder, m. p. 54°, giving an *oxime*, m. p. 121°, and a *semicarbazone*, m. p. 199°.

*o*- and *p*-Nitrobenzyl chlorides have been condensed with methyl cyanoacetate (compare A., 1903, i, 260; A., 1905, i, 435), yielding respectively *methyl cyanodi-p-nitrobenzylacetate*, m. p. 161°, and *methyl cyanodi-o-nitrobenzylacetate*, m. p. 103°, each of which on hydrolysis with sulphuric acid yielded the corresponding acid (compare Reissert, A., 1894, i, 626; 1896, i, 371). Ethyl cyanodi-*p*-nitrobenzylacetate is easily reduced in acetic acid solution by a solution of stannous chloride in hydrochloric acid, and the diamine can be diazotised and coupled with phenols and amines.

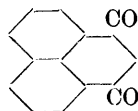
W. G.

**Derivatives of *peri*-Naphthindantrione.** IV. G. ERRERA and F. SORGES (*Gazzetta*, 1913, 43, ii, 625—631) — 2-Anilino-2-hydroxyperinaphthindan-1:3-dione (annexed formula), obtained by the action of aniline on the hydrate or alcoholate of *perinaphthindantrione* (A., 1913, i, 985), forms radiating groups of crystals decomposing at about



130° or. on prolonged heating, at a considerably lower temperature.

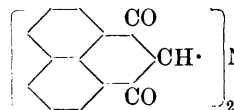
When heated in solution in a solvent of high boiling point, such as xylene, it yields: (1) 2-Phenyliminoperinaphthindan-1:3-dione (formula I), which



forms bluish-black needles with metallic lustre, m. p. 250—259°; (2) *diperinaphthindandionylaniline* (formula II), which

forms stellate aggregates of reddish-brown needles, decomposing at about 300°.

When boiled in water acidified with hydrochloric acid, anilino-hydroxyperinaphthindandione gives a small yield of a faintly acid compound,  $C_{19}H_{13}O_4N$  or  $C_{19}H_{15}O_4N$ , which forms brown laminæ or needles, m. p. 222—225° (decomp.), and is



probably of the structure  $CO \langle C_{10}H_6 \rangle C(OH) \cdot CO \cdot NHPh$ .

2-m-Nitroanilino-2 hydroxyperinaphthindan-1:3-dione,  $C_{19}H_{12}O_5N_2$ , forms brown, microscopic laminæ, blackening slightly at 320°.

2-p-Toluidino-2-hydroxyperinaphthindan-1:3-dione,  $C_{20}H_{15}O_3N$ , forms minute, yellow needles, decomposing at just above 100°.

Condensation of *perinaphthindantrione* with carbamide in acetic acid solution yields the compound,  $C_{10}H_6 \langle CO \rangle C:N \cdot CO \cdot NH_2$  or

$C_{10}H_6 \langle CO \cdot C(OH) \cdot NH \rangle CO$ , which separates as an almost colourless crust decomposing at about 250°.

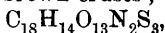
T. H. P.

**The Bohn-Schmidt Reaction in the Benzene Series and the Estimation of Nitrogen in Nitro-compounds by Kjeldahl's Method.** ALFRED ECKERT (*Monatsh.*, 1913, 34, 1957—1964)—It has already been shown that the action of fuming sulphuric acid,

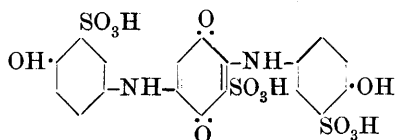


containing dissolved sulphur, on nitro-compounds of the anthraquinone and naphthalene series gives rise to valuable dyes, which owe their formation to the intermediate production of hydroxylamino-derivatives, and the subsequent transformation of the latter into hydroxylamino-compounds. The present paper deals with the behaviour of nitrobenzene, and it is shown that the reaction proceeds in a very similar manner to that occurring in the anthracene and naphthalene series.

When a solution of nitrobenzene in sulphuric acid is added slowly to a solution of sulphur in fuming sulphuric acid, the temperature being maintained below  $20^{\circ}$ , the following compounds are produced: (1) *p*-aminophenol; (2) *p*-aminophenol-2-sulphonic acid; (3) nitrobenzenesulphonic acid; (4) thionol,  $\text{NH} \langle \text{C}_6\text{H}_3(\text{OH}) \rangle \text{S}$ , the barium salt of which forms brown crusts; (5) a substance,



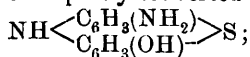
which forms greenish-blue crystals, and dissolves in alkalis, yielding blue salts. It liberates iodine from hydriodic acid, and when treated with stannous chloride and hydrochloric acid, or when boiled with alkali hydroxides, is converted into *p*-aminophenol-2-sulphonic acid. The



compound is considered to have the annexed constitution, but attempts to synthesise it by the condensation of benzoquinonesulphonic acid with *p*-aminophenol-2-sulphonic acid were unsuccessful; (6) amor-

phous, blackish-green, emeraldine-like condensation products, derived from *p*-aminophenol and its 2-sulphonic acid.

With respect to the formation of the above compounds, the author assumes that the nitrobenzene is first reduced to phenylhydroxylamine and then transformed by the action of sulphuric acid into *p*-aminophenol, which is then partly converted into thionoline,



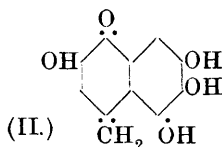
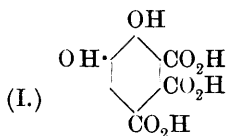
under the influence of sulphuric acid, the latter compound is converted into thionol.

In view of the ease with which the nitro-group is reduced by a solution of sulphur in fuming sulphuric acid, the author has carried out a series of experiments in order to determine whether this acid mixture is suitable for the determination of nitrogen by Kjeldahl's method, and finds that although aromatic nitro-compounds give good results, in the case of aliphatic nitro-compounds and inorganic nitrates the percentage of nitrogen found was invariably too low. F. B.

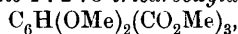
**Purpurogallin.** J. HERZIG (*Ber.*, 1913, 46, 3601—3602).—Polemical. A reply to Nierenstein and Spiers (*A.*, 1913, i, 1367). Purpurogallin contains four free hydroxyl groups. Tetra-acetyl-purpurogallin is colourless. E. F. A.

**Purpurogallin.** II. H. F. DEAN and M. NIERENSTEIN (*Ber.*, 1913, 46, 3868—3879. Compare *A.*, 1913, i, 1367).—When dissolved

in aqueous potassium hydroxide and submitted to the action of air for twenty-four hours, purpurogallin is oxidised to pyrogallolcarboxylic (2 : 3 : 4-trihydroxybenzoic) acid ; oxidation with dilute nitric acid gives rise to dihydroxyhemimellitic acid (I). From these results the conclusion is drawn that purpurogallin is a 2 : 5 : 6 : 7-tetrahydroxy-1 : 4-naphthaquinomethane of the constitution represented in (II).

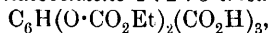


*Dihydroxyhemimellitic* (4 : 5-dihydroxybenzene-1 : 2 : 3-tricarboxylic) acid crystallises with  $5\text{H}_2\text{O}$  in long needles, m. p.  $106-107^\circ$  (decomp.), which loses water at  $50^\circ$  under diminished pressure, and then has m. p.  $194^\circ$  (decomp.). It forms a very explosive *silver* salt,  $\text{C}_9\text{HO}_8\text{Ag}_5$ , and a *phenylhydrazine* salt,  $\text{C}_9\text{H}_6\text{O}_8 \cdot \text{C}_6\text{H}_5\text{N}_2$ , crystallising in lustrous scales, m. p.  $193-194^\circ$  (decomp.). It gives a green coloration with ferric chloride, and yields a green, fluorescent condensation product when heated with resorcinol and zinc chloride. On titration with sodium hydroxide or sodium carbonate, it behaves as a pentabasic acid. With diazomethane in ethereal solution, it yields *methyl 4 : 5-dimethoxybenzene-1 : 2 : 3-tricarboxylate*,



which crystallises in lustrous scales, m. p.  $56-57^\circ$ , and is completely hydrolysed by warm dilute hydrochloric acid to the original dihydroxyhemimellitic acid.

On treatment with ethyl chloroformate in the presence of quinoline it forms 4 : 5-diethylcarbonatobenzene-1 : 2 : 3-tricarboxylic acid,



silky needles, m. p.  $121-123^\circ$  (decomp.); the *dibenzoyloxy-acid*,  $\text{C}_6\text{H}(\text{OBz})_2(\text{CO}_2\text{H})_3$ , prepared by the pyridine method, crystallises in needles or flakes, m. p.  $95-96^\circ$ .

When heated with acetic anhydride under diminished pressure, dihydroxyhemimellitic acid is converted into diacetylnor-*m*-hemipinic [4 : 5-diacetoxyphtalic] anhydride (annexed formula), which crystallises in small cubes, m. p.  $184-185^\circ$  with previous sintering at  $162-164^\circ$ , and is transformed into *m*-hemipinic (4 : 5-dimethoxyphthalic) acid by the action of methyl sulphate and potassium hydroxide in alcoholic solution. When heated with zinc dust and acetic anhydride, it loses two carboxyl groups and gives rise to 3 : 4-diacetoxybenzoic acid, which was not isolated, but converted by hydrolysis with dilute sulphuric acid into protocatechuic acid.

Bromination of purpurogallin in glacial acetic or moist carbon tetrachloride solution yields a *dibromo*-compound,  $\text{C}_{11}\text{H}_6\text{O}_6\text{Br}_2$  (compare Perkin and Steven, T., 1903, 85, 197). This crystallises in deep red needles, m. p.  $204-206^\circ$  (or  $206-208^\circ$ , when slowly heated), yields with acetic anhydride a *tetra-acetyl* derivative, m. p.  $204-205^\circ$ , and on treatment with diazomethane in ethereal solution forms a *monomethyl*

derivative,  $C_{11}H_2O_2Br_2(OH)_3 \cdot OMe$ , crystallising in yellow needles, m. p. 169—171°; it is oxidised by dilute nitric acid to dihydroxy-hemimellitic acid. When brominated in glacial acetic solution, the tetra-acetyl derivative of purpurogallin gives rise to a *dibromomonoacetyl* derivative,  $C_{11}H_2O_2Br_2(OH)_3 \cdot OAc$ , which forms light yellow needles, m. p. 214°, and is converted by the action of acetic anhydride into the tetra-acetyl derivative, mentioned above.

Bromination of purpurogallin in dry carbon tetrachloride solution yields an unstable *dibromo*-derivative of the composition  $C_{11}H_6O_5Br_2$ , crystallising in deep red needles, m. p. 184—186°. F. B.

**Preparation of Bromoaminoanthraquinones.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 266563. Compare A., 1913, i, 1366).—The elimination of the sulphonic group, without bringing about the migration of the bromine atom, by heating bromoaminoanthraquinonesulphonic acids with sulphuric acid can be effected by employing sulphuric acid of 60° Bé. without the addition of mercury or its salts, and heating the mixture only until the sulphonic group is just eliminated. Thus 1-bromo-2-aminoanthraquinone is produced by heating potassium 1-bromo-2-aminoanthraquinone-3-sulphonate with sulphuric acid of the above strength at 150—160° for five to ten minutes. J. C. C.

**Preparation of 1-Aminoanthraquinone-2-carboxylic Acids and Their Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 267211. Compare A., 1912, i, 979; 1913, i, 476).—The esters of 1-substituted anthraquinone-2-carboxylic acids with aromatic alcohols are particularly adapted to the reaction with bases described in the earlier patents. The new esters are easily hydrolysed, even dissolving in cold sulphuric acid. For example, 100 parts of *benzyl 1-chloroanthraquinone-2-carboxylate*, obtained by boiling the potassium salt with benzyl chloride, yellow needles, m. p. 135—136°, are heated with 2:5-dichloroaniline (40 parts), nitrobenzene (120 parts), fused sodium acetate (30 parts), and cupric oxide (1.5 parts) for three hours at 185—190°. The cold product is diluted with alcohol, when *benzyl 1:2':5'-dichloroanilinoanthraquinone-2-carboxylate* crystallises in yellowish-red needles. It forms a yellow solution in sulphuric acid, from which water precipitates the free acid in red flakes. J. C. W.

**Preparation of Aldehydes of the Anthraquinone Series.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 267081).—Aldehydes of the anthraquinone series are prepared by oxidising the corresponding methylanthraquinones with manganese dioxide in sulphuric acid solution. 4-Chloro-1-aldehydoanthraquinone has m. p. 210°. J. C. C.

[Preparation of Phenoxy-derivatives of Anthraquinones.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 263423).—3-Chloro-1:4-diamino-2-phenoxyanthraquinone, crystallising from chlorobenzene in leaflets, is obtained when 2:3-dichloro-1:4-diamino-

anthraquinone (50 parts) is fused with 75 parts of sodium phenoxide and 250 parts of phenol; if the foregoing reaction is carried out energetically, both chlorine atoms are replaced with the formation of 1:4-diamino-2:3-diphenoxyanthraquinone.

1-Amino-4-*p*-toluidino-2-phenoxyanthraquinone is prepared in a similar manner from 2-bromo-1-amino-4-*p*-toluidinoanthraquinone, whilst analogous compounds are also obtained from (1) sodium 2-bromo-1-amino-4-*p*-toluidinoanthraquinonesulphonate, (2) 2:6-dibromo-1:5-diamino-4:8-di-*p*-toluidinoanthraquinone, (3) sodium 3-bromo-1:5-diamino-4:8-dihydroxyanthraquinone-7-sulphonate; and 3:7-dibromo-1:5-diamino-4:8-dihydroxyanthraquinone gives rise to 1:5-diamino-4:8-dihydroxy-3:7-diphenoxyanthraquinone, which is obtained in leaflets. The foregoing derivatives on sulphonation give rise to the corresponding *sulphonic acids*, which dye wool in blue shades.

F. M. G. M.

**Preparation of Condensation Products of the Anthraquinone Series.** FARBE-FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 264290).—The following highly-coloured compounds (iminazole derivatives) prepared by the condensation of diaminoanthraquinones with ketones furnish the corresponding *sulphonic acids*, which are of tinctorial value: (1) 1:2:4-triaminoanthraquinone with acetone in the presence of zinc chloride; (2) the same with acetophenone, glistening, metallic needles; (3) with benzophenone, glistening, metallic crystals; (4) with anthrone, glistening, metallic needles, and (5) 1:2:4:5:6:8-hexaminoanthraquinone with anthrone.

F. M. G. M.

**Preparation of Sulphur Derivatives of Anthraquinone.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 266952. Compare D.R.-P. 248171; A., 1912, i, 1013).—In the earlier patent, the formation of dyes by the condensation of 2-amino-1-thiolanthraquinone with 1:2-dihalogenoanthraquinones was described. Similar products are also obtained when either 1-halogenoanthraquinones or derivatives in which methoxyl, carboxyl, aldehyde, or amino-groups occupy position 2 are employed. The substances are simply heated together in nitrobenzene, pyridine, or naphthalene. The dyes impart to cotton in the vat much more brilliant shades than do the isomerides from 1-amino-2-thiolanthraquinone.

J. C. W.

**Preparation of Sulphinic Acids of the Anthraquinone Series, and their Salts.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 263340).—When anthraquinonesulphonyl chlorides are reduced in aqueous solution with alkali sulphides, they give rise to the corresponding sulphinic acids.

*Anthraquinone-2-sulphinic acid*, colourless crystals, m. p. 215°, yields characteristic calcium and lead salts; *anthraquinone-1-sulphinic acid*, decomp. over 200°, has similar properties, whilst *anthraquinone-2:6-* and *-2:7-disulphinic acids* have also been prepared.

2-Chloroanthraquinone-7-sulphonyl chloride gives rise to 2-chloroanthraquinone-7-sulphinic acid, m. p. 215°; 1-*p*-toluidinoanthraquinone-sulphonyl chloride is a brown, amorphous powder, and furnishes the

corresponding *acid*, brown flakes, whilst *αβ-naphthanthraquinone-sulphinic acid*, yellow crystals, m. p. 220°, is obtained from the corresponding *chloride*, m. p. 260°; the *sodium* salt gives a yellow solution.

F. M. G. M.

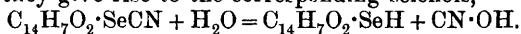
**Preparation of Selenophenols and Diselenides of the Anthraquinone Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264941).—Selenols and diselenides of the anthraquinone series can be obtained by the action of sodium or potassium selenide at about 80° on negatively substituted anthraquinone derivatives.

*2-Selenolanthraquinone*, obtained from 2-chloroanthraquinone, crystallises in yellow needles, and on oxidation (with nitric acid) furnishes a colourless, crystalline *selenic acid*, whilst 1-chloroanthraquinone under similar treatment gives rise to a mixture of 1-*selenolanthraquinone*, orange-red leaflets, m. p. 212°, and *anthraquinone-1-diselenide*, yellow, rhombic crystals, which can be separated by the action of alkali hydroxides, in which the latter compound is insoluble.

The *compound* obtained from potassium 1-chloro-4-nitroanthraquinone-8-sulphonate separates in small, violet needles, whilst the free *acid* forms reddish-violet flakes.

F. M. G. M.

[Conversion of Selenocyanoanthraquinones into Selenolanthraquinones.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264940).—When 1-selenocyanoanthraquinones (A., 1913, i, 494) are treated with aqueous or alcoholic solutions of alkali hydroxides they give rise to the corresponding selenols,



*Sodium 1-selenolanthraquinone-5-sulphonate*, red needles, is obtained in this manner from sodium 1-selenocyanoanthraquinone-5-sulphonate, whilst 1-selenocyanoanthraquinone gives rise to 1-selenolanthraquinone. These compounds are employed therapeutically and in the preparation of dyes.

F. M. G. M.

**Preparation of Compounds of Valeric or Bromovaleric Acid and Therapeutically Active Alcohols or Phenols.** J. D. RIEDEL (D.R.-P. 263018).—The menthyl, bornyl, and *isobornyl* esters of valeric or bromovaleric acid are tasteless, odourless, crystalline substances which find therapeutic employment.

*Bornyl bromoisovalerylcabamate*, prepared from bromo-β-methylbutyryl bro nide and bornyl cabamate in the presence of dimethyl-aniline, has m. p. 138°; *isobornyl bromoisovalerylcabamate*, m. p. 155°; *menthyl bromoisovalerylcabamate*, m. p. 146—147°; *thymyl bromoisovalerylcabamate*, m. p. 137°, and *bornyl isovalerylcabamate*, m. p. 100°.

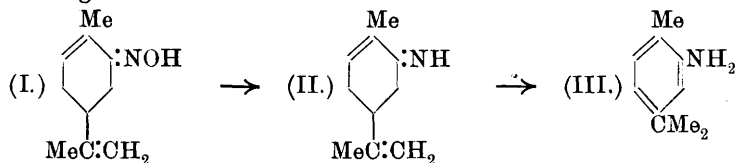
F. M. G. M.

**Specific Rotatory Power of Camphor in 90% Alcohol.** HENRI MALOSSE (*J. Pharm. Chim.*, 1913, [vii], 8, 505—506).—The specific rotatory power of camphor dissolved in 90% alcohol may be calculated from the formula  $[\alpha]_D^{20} = 38.7 + 0.1532c$  or  $38.7 + 0.1344p$  or  $52.14 - 0.1344q$ , where  $c$  = grams of camphor in 100 c.c. of solution,  $p$  = grams of camphor in 100 grams of solution, and  $q$  = grams of solvent in 100 grams of solution.

T. A. H.

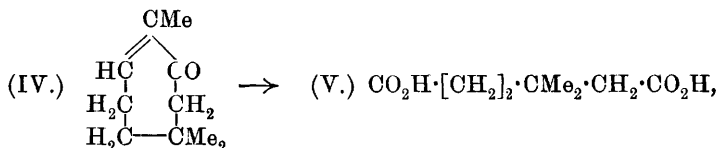
**Behaviour of Carvoxime and Eucarvoxime Towards Hydrogen in Presence of Colloidal Palladium.** O. WALLACH [with ALAN R. ALBRIGHT and RUD. KLEIN] (*Chem. Zentr.*, 1913, ii, 1144—1146; from *Nachr. K. Ges. Wiss. Göttingen*, 1913, 236—248).—The catalytic reduction of carvoxime and eucarvoxime is described.

When the supply of hydrogen was not limited in the reduction of carvoxime, I, the nitroso-group was attacked, as well as the side-chain, and tetrahydrocarvone and carvacrylamine, III, were isolated. The latter is probably the result of the rearrangement of the imide, II, according to the scheme:



By working in dilute methyl alcoholic solution, with gum arabic as a protective-colloid (Skita's modification of Paal's method) and using only one molecular proportion of hydrogen, a new *modification* of carvotanacetoxime,  $\text{C}_{10}\text{H}_{16}\text{:N}\cdot\text{OH}$ , was obtained in transparent prisms, m. p. 66—67°,  $[\alpha]_D + 18.66^\circ$  (4.5% solution in methyl alcohol). The ketone was liberated by hydrolysis; it had b. p. 229.5°,  $D_{20} 0.9376$ ,  $n_D 1.4813$ , and gave the usual oxime, m. p. 75—76°, and the expected semicarbazone. The dihydrocarvoxime was further reduced under the same conditions with more hydrogen, smoothly to tetrahydrocarvoxime.

Similarly, eucarvoxime gave a new *modification* of tetrahydro-eucarvoxime,  $\text{C}_{10}\text{H}_{18}\text{:N}\cdot\text{OH}$ , in woolly needles, m. p. 56—57°. The regenerated tetrahydroeucarvone had b. p. 207°,  $D_{20} 0.906$ ,  $n_D 1.4553$ , and could not be re-converted into the above oxime. Moderated reduction of eucarvoxime led to *dihydroeucarvoxime*,  $\text{C}_{10}\text{H}_{16}\text{:N}\cdot\text{OH}$ , m. p. 122—123°. This was hydrolysed and the ketone purified by the intervention of the *semicarbazone*, m. p. 195—197°. This dihydro-eucarvone had b. p. 213—214°,  $D_{21} 0.9325$ ,  $n_D 1.4790$ , values which differ from those of von Beyer (A., 1894, i, 536). Since it yields dimethyladipic acid (V) on oxidation with chromic acid, it has the formula (IV):



whereas a different constitution was assigned to the ketone obtained by reducing eucarvone with sodium and alcohol (A., 1905, i, 450).

J. C. W.

**New Investigations of Santenone.** I. ENRICO RIMINI (*Chem. Zentr.*, 1913, ii, 1390—1392; from *R. I. Lombardo Sci. Lett. Estr. Rend.*, 1913, 46, 787—796\*).—In extension of the work of Angeli and Rimini on the action of nitrous acid on fenchone- or campher-oxime

\* and *Gazzetta*, 1913, 43, ii, 522—531.

(A., 1897, i, 88, 90, 360), the author has similarly treated the oxime of santenone. Concentrated sulphuric acid converts the pernitroso-derivative into a saturated compound, *isosantenone*, which yields a monobasic acid when oxidised by warm permanganate and an  $\alpha$ -ketonic acid when the cold agent is employed. For these and other reasons, it is probable that *isosantenone* contains an acetyl group and a 5 membered-ring.

Synthetic santenone forms, in contrast to the liquid oxime from the natural product, an *oxime*,  $C_9H_{15}ON$ , which crystallises in leaflets, m. p. 80—81°. Either modification yielded a blue oil,  $C_9H_{14}ONCl$ , b. p. 113—116°/91 mm., when treated in hydrochloric acid solution with nitrous acid. This oil became colourless, even in ethereal solution, in a few days, and yielded *santenonesemicarbazone* when treated with the requisite reagent. A mixture containing about 30% of the pernitroso-derivative was prepared by the method employed in the case of tanacetone (A., 1900, i, 555). When it was treated with concentrated sulphuric acid, a pale yellow oil was produced, which, with semicarbazide, gave *santenonesemicarbazone*, sparingly soluble, m. p. 224° (decomp.), and *isosantenonesemicarbazone*,  $C_{10}H_{17}ON_3$ , fairly soluble needles, m. p. 172—175°. The latter was decomposed by concentrated sulphuric acid or phthalic anhydride, followed by steam distillation, when *isosantenone* was obtained. This was purified by oxidising an impurity with cold 2% permanganate, condensing with semicarbazide, and decomposing the pure product as above. Pure *isosantenone*,  $C_9H_{14}O$ , is a colourless, stable oil, b. p. 180—186°, smelling of peppermint. It forms a syrupy *oxime*, b. p. 155—164°/28 mm., from which, in contrast to *santenoneoxime*, the ketone can be easily regained by hydrolysis with dilute sulphuric acid, and also a *dibromide*,  $C_9H_{12}OBr_2$ , which crystallises in leaflets, m. p. 47—48°, and incites to tears.

The syrupy ketonic acid obtained by oxidising *isosantenone* in the cold, formed a *semicarbazone*,  $C_{10}H_{15}O_3N_3$ , m. p. 196°. The saturated acid,  $C_7H_{11}CO_2H$ , obtained when warm alkaline permanganate was used, had m. p. 38—39°, and an odour resembling that of valeric acid. It was also obtained when the ketone or dibromo*isosantenone* was oxidised by sodium hypobromite, bromoform and carbon tetrabromide being the by-products.

J. C. W.

**Alkylation of Thujone [Tanacetone] and *iso*Thujone by means of Sodamide.** A. HALLER (*Compt. rend.*, 1913, 157, 965—968. Compare A., 1905, i, 602).—Under suitable conditions three alkyl groups can be introduced into tanacetone, whilst with *iso*thujone only two can be introduced. The following derivatives have been prepared by the action of sodamide, followed by the alkyl iodide in ethereal or toluene solution, this process being repeated once or twice.

*Dimethyltanacetone*,  $C_8H_{14} \begin{smallmatrix} \text{CMe}_2 \\ | \\ \text{CO} \end{smallmatrix}$ , a colourless liquid, b. p. 92—94°/12 mm.;  $D_4^{15}$  0.916;  $[\alpha]_D - 19^\circ 45'$ . It does not combine with hydroxylamine, but is decomposed on heating with sodamide in sealed tubes at 208°, giving a substance containing nitrogen and soluble in sulphuric

acid. All attempts to prepare a trimethyl derivative were unsuccessful.

*Diallyltanacetone*,  $C_8H_{14} \begin{smallmatrix} \diagup C(C_3H_5)_2 \\ \diagdown CO \end{smallmatrix}$ , colourless liquid, b. p. 147.5—148.5°/18 mm. (corr.),  $D_4^{20}$  0.9352;  $n_D^{20}$  1.4850. A considerable amount of tarry matter is formed in its preparation.

*Triallyltanacetone*,  $C_{19}H_{28}O$ , a viscous liquid, b. p. 173—175°/21 mm. (corr.),  $D_4^{20}$  0.9467;  $n_D^{20}$  1.5016.

*Dimethylisothujone*,  $C_{12}H_{20}O$ , b. p. 120—122°/19 mm. (corr.). It yields no amide with sodamide in boiling xylene, but a small quantity of a product soluble in dilute sulphuric acid.

*Allylisothujone*,  $C_{13}H_{20}O$ , is difficult to obtain, the yield being very poor, condensation taking place and tarry matters being formed. It is a viscous liquid, b. p. 144—146°/18 mm. (corr.);  $D_4^{20}$  0.9280;  $n_D^{20}$  1.4930.

Tanacetone resembles menthone in that its methylation can only be carried to the dimethyl stage and its allylation to the triallyl stage. *iso*Thujone on alkylation tends to form chiefly condensation products. From these results it appears that tanacetone contains a complex,  $\cdot\dot{C}H\cdot CO\cdot CH_2\cdot$ , whilst *isothujone* contains the grouping  $\cdot\dot{C}\cdot CO\cdot CH_2\cdot$ .

W. G.

[Essential Oils.] SCHIMMEL & Co. (*Semi-Annual Report*, October, 1913, pp. 19—111. Compare A., 1913, i, 743).—*Achasma Walang* leaves yielded 0.25% of oil having  $D^{16}$  0.850,  $\alpha_D$  -0°34', acid number 10.1, saponification number 70, aldehydes 97%; the stalks gave 0.2% of oil, having  $D^{16}$  0.860,  $\alpha_D$  -0°58', acid number 26, saponification number 75.6, saponification number after acetylation 285.6, aldehydes 96%; the roots yielded 0.15% of oil having  $D^{16}$  0.856,  $\alpha_D$  -0°30', acid number 18.9, saponification number 70, saponification number after acetylation 285.6, aldehydes 96% (*Jaarb. dep. Landb. Ned. Ind.*, 1911, 45).

*Acronychia laurifolia* leaves gave 0.06% of oil having  $D^{27}$  0.909,  $\alpha_D$  +9°4', acid number 0.8, saponification number 14 (*loc. cit.*, p. 47).

*Alpinia malaccensis* leaves gave 0.16% of oil having  $D^{26}$  1.03, saponification number 282.8, and yielding allocinnamic acid on saponification (*loc. cit.*, p. 48, and Abstr., 1901, i, 219).

*Andropogon (Cymbopogon) odoratus* (?) herb gave 0.3% of oil having  $D^{26}$  0.914,  $\alpha_D$  -34°44', saponification number 33.6, saponification number after acetylation 98.9. *A. procerus* (?) yielded 0.11% of oil,  $D^{26}$  0.960,  $\alpha_D$  -11°, acid number 1, saponification number 14, saponification number after acetylation 86.8 (*loc. cit.*, p. 44).

*Amomum Cardamomum* oil, distilled in Java, had  $D^{26}$  0.909,  $\alpha_D$  0°20', acid number 0.8, saponification number 14, and contained 12% of cineole (*loc. cit.*, p. 48).

*Michelia Champaca* leaves yielded 0.04% of oil,  $D$  0.922,  $\alpha_D$  +12°30', acid number 1.9, saponification number 25.2, saponification number after acetylation 63.5, having an odour recalling that of *Champaca* flowers (*loc. cit.*, p. 46).

The comparison of various methods for the assay of citronella oil referred to in the previous report (A., 1913, i, 744) is continued.



*Elionurus tripsacoides* grass yields 0.1% of a yellow oil,  $D_{20} 0.976$ ,  $n_D - 10^\circ$ , ester number 10.5, saponification number after acetylation 42, and having an odour recalling that of vetiver oil. The oil boils from  $275^\circ$  to  $325^\circ$ , and is chiefly composed of a sesquiterpene, with a phenol (eugenol?). It gives a reddish-violet coloration with ferric chloride (*Perf. Record*, 1913, 4, 98).

*Eryngium foetidum* oil, prepared in Java, had  $D_{26} 0.905$ ,  $n_D + 0.42'$ , acid number 29.5, saponification number 65, saponification number after acetylation 327 (*Jaarb. dep. Landb. Ned. Ind.*, 1911, p. 46).

Geranium oils from Réunion and Africa yield on hydrolysis considerable quantities of tiglic acid, which is probably present in the form of esters of geraniol, citronellol, and  $\beta$ -phenylethyl alcohol. Geranyl tiglate has  $D_{15} 0.9279$ ,  $n_D \pm 0^\circ$ , b. p.  $149-151^\circ/7$  mm. Citronellyl tiglate has  $D_{15} 0.9090$ ,  $n_D + 2.6'$ , b. p.  $144-145^\circ$ . Phenylethyl tiglate has  $D_{15} 1.0257$ ,  $n_D \pm 0^\circ$ , b. p.  $139-140^\circ$ . All three esters have pleasant, but weak odours.

*Lantana Camara* flower oil had  $D_{15} 0.9274$ ,  $n_D + 14.50'$ , acid number 0.9, ester number 24.3, and contained a paraffin.

*Lophanthus anisatus* herb, grown in Marseilles, gave 0.11% of a brownish-green oil,  $D_{15} 0.9640$ ,  $n_D^{20} 1.51655$ , acid number 2.8, ester number 14.0, soluble in 0.5 to 1 vol. or more of 90% alcohol and possessing a pleasant anise-like odour. The principal constituent is methylchavicol.

*Nigella sativa* seeds gave 0.5% of a brown oil,  $D_{15} 0.8855$ ,  $n_D + 2.52'$ ,  $n_D^{20} 1.48378$ , acid number 1.9, ester number 31.6, ester number after acetylation 73.0, soluble in 2 or more vols. of 90% alcohol.

*iso*Pulegol, prepared by the action of acetic anhydride on citronellal, when treated with sodium ethoxide in alcohol at  $210^\circ$  in a closed vessel was partly converted into methylcyclohexanol (yield 10%) and citronellol (yield 15%).

*Piper aduncum* herb gave 0.1% of oil,  $D_{27} 0.856$ ,  $n_D + 5.40'$ , acid number 1.2, saponification number 8.4, saponification number after acetylation 48.7 (*loc. cit.*, p. 47).

*Prostanthera cinsolifera* herb gives 0.71% of a yellow oil,  $D_{15} 0.9204$ ,  $n_D^{20} 1.4711$ , containing carvacrol, thymol, cuminaldehyde, *p*-cymene, pinene(?), and cineole, the latter forming about 61% of the oil. On saponification the oil yields some acetic acid (Baker and Smith, A., 1913, i, 1142).

*Ravensara aromatica* wood yields an oil, which appears to consist mainly of a terpene, with a small amount of oxygenated substance.

Spanish verbena oil had  $D_{15} 0.9239$ ,  $n_D - 5.25'$ ,  $n_D^{20} 1.49047$ , and was soluble in 1 vol. or more of 80% alcohol. Apart from citral and verbenone, already known to occur in Spanish verbena oil, this oil was found to contain *l*-limonene, cineole (traces), methylheptenone, *d*-citronellol, an alcohol resembling that of cypress oil (A., 1913, i, 744), and 40 to 45% of sesquiterpene (caryophyllene?) and sesquiterpene alcohol, taken together.

*Lavandula Burmanni* flowers yielded an oil,  $D_{15} 0.9309$ ,  $n_D + 1.40'$ , acid number 1.9, ester number 115.7, soluble in 1.5 or more vols. of 80% alcohol, which was pale brown in colour and contained fenchone. The leaf oil had  $D_{15} 0.9131$ ,  $n_D - 0.40'$ , acid number 9.9,

ester number 36.3, was soluble in 1.5 or more vols. of 70% alcohol, and had an odour recalling that of citral.

The Report also contains a résumé of recent work on the chemistry, pharmacology, etc., of essential oils and their constituents.

T. A. H.

**Constituents of Ethereal Oils. Constituents of Oil of Calamus.** F. W. SEMMLER and K. E. SPORNITZ (*Ber.*, 1913, 46, 3700—3708).—A calamus oil of Russian origin having  $D_{20}^{20}$  0.9633,  $n_D$  1.50710,  $\alpha_D$  +26°12', has been separated into its constituents by fractional distillation, and the following products identified: Pinene, camphene, and camphor, which occur in the fraction b. p. 50—100°/9 mm., and were identified by conversion into the nitroso-chloride, isoborneol, and oxime respectively.

The fraction b. p. 115—135°/12 mm., after distillation over sodium, and subsequent oxidation with potassium permanganate, yielded a sesquiterpene hydrocarbon,  $C_{15}H_{24}$ , which the authors propose to term *calamene*, a name already assigned by Thoms and Beckström (*A.*, 1901, i, 395; 1902, i, 809, 810) to the hydrocarbon  $C_{15}H_{22}$  isolated by them from oil of calamus.

Calamene has b. p. 123—126°/10.5 mm.,  $D_{19}^{20}$  0.9224,  $\alpha_D$  +5°,  $n_D$  1.50572, forms a liquid *monohydrochloride*, and is reduced by hydrogen in the presence of platinum to *tetrahydrocalamene*,  $C_{15}H_{28}$ , b. p. 123—125°/10 mm.,  $D_{19}^{20}$  0.8951,  $n_D$  1.48480. It is probably a bicyclic sesquiterpene of the naphthalene series.

The main constituent of the fraction b. p. 150—160°/13 mm.,  $D_{23}$  0.96115,  $n_D$  1.5098, is a sesquiterpene alcohol,  $C_{15}H_{24}O$ , for which the name *calamenenol* is suggested. The alcohol forms a *sodium* derivative,  $C_{15}H_{23}ONa$ , and loses water so readily that attempts to prepare esters by the action of acetic and phthalic anhydrides were unsuccessful. The removal of water is best accomplished by heating the alcohol with formic acid or potassium hydrogen sulphate. After purification by distillation over sodium and subsequent treatment with potassium permanganate, the resulting hydrocarbon,  $C_{15}H_{22}$ , which the authors term *calamenene*, has b. p. 136—143°/15 mm.,  $D_{19}^{20}$  0.9324,  $n_D$  1.52317,  $\alpha_D$  +6°, and is converted by reduction with hydrogen in the presence of platinum into the tetrahydrocalamene described above. It is identical with the calamene of Thoms and Beckström (*loc. cit.*).

In a preliminary investigation, a specimen of calamus oil, having b. p. 55—170°/12.5 mm.,  $D_{20}$  0.9569,  $n_D$  1.5070,  $\alpha_D$  +20°, gave a fraction b. p. 150—160°/13 mm.,  $D_{20}$  0.9688,  $n_D$  1.51263,  $\alpha_D$  +8°, consisting essentially of an *alcohol*,  $C_{15}H_{24}O$ , which differs from the isomeric calamenenol mentioned above, in that it yields an *acetyl* derivative, b. p. 155—163°/12 mm.,  $D_{17}$  0.9727,  $n_D$  1.51004,  $\alpha_D$  +4°, when heated with acetic anhydride and sodium acetate.

F. B.

**Transformation of the Essential Oil of Citrons into the Essential Oil of Roses.** PH. BARBIER and R. LOCQUIN (*Compt. rend.*, 1913, 157, 1114—1118).—In support of their view that *d*-citronellol and *l*-rhodinol are not merely optical but position isomerides, the authors have succeeded in converting *d*-citronellol into

*d*-rhodinol, the latter having all the properties, including perfume of natural rhodinol as obtained from roses and pelargonias, but being opposite in its optical activity.

*d*-Citronellol,  $\text{CH}_3\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , in the form of its acetate gives a bromohydrin with hydrogen bromide in acetic acid solution, and this on heating with sodium acetate in acetic acid for one hour at  $160^\circ$  and saponifying the product yields rhodinol and  $\gamma\eta$ -dimethyloctan- $\alpha\eta$ -diol.

*d*-Citronellal is converted through its oxime and nitrile into the corresponding acid, which on warming with thionyl chloride in benzene and pouring the product into alcohol yields *ethyl*  $\xi$ -chloro- $\beta\xi$ -dimethyloctoate, b. p.  $137\text{--}140^\circ/15$  mm. This ester on heating with sodium acetate in acetic acid loses hydrogen chloride, giving ethyl rhodinate, which is reduced by sodium in absolute alcohol to *d*-rhodinol.

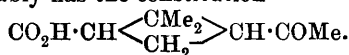
Citronellic acid on esterification with sulphuric acid in alcohol yields *ethyl*  $\xi$ -hydroxy- $\beta\xi$ -dimethyloctoate,  $\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $139\text{--}142^\circ/13$  mm., which on reduction with sodium in absolute alcohol gives  $\gamma\eta$ -dimethyloctane- $\alpha\eta$ -diol, this alcohol being also obtained from *d*-citronellol by shaking it with 30% sulphuric acid. This glycol on boiling for two to three hours with 5% sulphuric acid gives pure *d*-rhodinol, this treatment being useful for purifying *l*-rhodinol itself.

Both natural *l*-rhodinol and the *d*-rhodinol prepared as above, on oxidation with chromic acid, yield an unstable aldehyde, the oxime of which on treatment with acetic anhydride yields, not a nitrile, but acetylmenthoneoxime. The oxime of *d*-citronellal, on the other hand, when similarly treated yields only a nitrile and no trace of acetylmenthoneoxime.

The odour, characteristic of both the rhodinols, is ascribed by the authors to the grouping  $\cdot\text{CMe}_2$ . W. G.

**Constituents of Oil of Frankincense.** EMIL FROMM and EMIL AUTIN (*Annalen*, 1913, **401**, 253—262).—Olibanum oil [oil of frankincense] free from terpenes, b. p.  $70^\circ/12$  mm.,  $D_{20}^{15}$  0.9685,  $n_D^{20} + 20.48'$ , yields by distillation a small fraction, b. p. about  $150^\circ$ , two chief fractions, b. p.  $210\text{--}211^\circ$  and  $260^\circ$  respectively, and a viscous residue. The fraction b. p.  $210\text{--}211^\circ$  has been examined. It contains a substance,  $\text{C}_{10}\text{H}_{16}\text{O}$ , which is called *olibanol*. Olibanol is certainly not an ether. It reduces ammoniacal silver oxide slightly, yields hydrogen by treatment with sodium, and does not form a crystalline acetyl or benzoyl derivative, phenylhydrazone, oxime, or semicarbazone, so it is doubtful whether the substance is an alcohol, aldehyde, or ketone.

By oxidation with neutral, concentrated potassium permanganate in the cold, olibanol yields unidentified neutral products and acid products. From the latter a ketonic acid,  $\text{C}_9\text{H}_{14}\text{O}_3$ , m. p.  $130^\circ$ , has been isolated, which is converted by sodium hypobromite into bromoform and norpinic acid, and therefore, probably has the constitution



The ketonic acid is identical with the acid obtained from verbenone by Kerschbaum (m. p. of the mixed semicarbazones), and is very probably identical with pinonic acid. [Haensel (A., 1908, i, 665) separated from oil of frankincense, an alcohol,  $C_{26}H_{44}O$ , b. p.  $205-212^\circ$  (later the b. p. was given as  $217^\circ/20$  mm.,  $333-334^\circ/757$  mm.), which he termed olibanol.] C. S.

**Ravensara Oil.** FERRAUD and BONNAFOUS (*Chem. Zentr.*, 1913, ii, 1302—1303; from *Bull. Sci. Pharmacol.*, 1913, 20, 403—405).—A eucalyptus-like oil has been obtained from the leaves and young twigs of the Madagascar tree, *Ravensara aromatica*, order *Lauraceae*. It consisted chiefly of a terpene,  $C_{11}H_{20}$ , b. p.  $171-172^\circ$ ,  $D^{15}_D$  0.8809,  $n^{20}_D$  1.4616, which would scarcely be freed from a trace of an oxygen compound, and also an oil which had b. p.  $260-280^\circ$ , a marked eucalyptus odour, and green fluorescence. J. C. W.

**The First-runnings of Finnish Turpentine Oil (II.).** Theory of the Distillation of Wood. OSSIAN ASCHAN (*Zeitsch. angew. Chem.*, 1913, 26, 709—713. Compare A., 1907, i, 947).—The further investigation of the first-runnings obtained below  $60^\circ$  has proved the presence of acetaldehyde, propaldehyde, a hydrocarbon,  $C_5H_{10}$ , and furan. Homologues of acetylene, including isoprene, were absent.

The melting point of acetaldehyde-ammonia is found to be  $92-94^\circ$ .

The theory deals with the method by which a number of the products isolated from turpentine oil may be considered to be built up from the decomposition products of acetic acid, which itself results from the decomposition of the cellulose and carbohydrates present in the wood. T. S. P.

**The Leaf Oil of Douglas Fir.** A. W. SCHORGER (*J. Amer. Chem. Soc.*, 1913, 35, 1895—1897. Compare Brandel and Sweet, *Pharm. Review*, 1908, 26, 326).—The oil, D 0.8727—0.8759, obtained from the Douglas firs (*Pseudotsuga taxifolia* Britt.) of California, commenced to boil at  $157.3^\circ$ , the main portion distilling at  $160-170^\circ$ .

The chief constituent was  $\beta$ -pinene (48%), and was accompanied by  $\alpha$ -pinene (25%), dipentene, probably together with *l*-limonene (6%), borneol (6.5%), bornyl acetate (6.1%), and a green oil (5%), probably a sesquiterpene. The remainder is accounted for by loss through polymerisation. The first fraction gave a decided reaction for furfuraldehyde. D. F. T.

**Analysis of the Resin from the Cedar of Lebanon.** LOUIS REUTER [and SCHWEINFURTH] (*Chem. Zentr.*, 1913, ii, 1303; from *Schweiz. Woch. Chem. Pharm.*, 1913, 51, 472—473).—A faintly aromatic resin with m. p.  $95.5-97^\circ$ , saponification and ester numbers 54.5—58.6, acid number 0, has been examined. It responded to reactions for caoutchouc and cholesterol. The steam-distillate of an alkaline suspension contained a colourless oil,  $D^{15}_D$  0.8802,  $[\alpha]_D -13.36^\circ$ ,  $n^{20}_D$  1.48567, which became yellow in the air and also deposited borneol. From the alkaline residue, *cedric acid*,  $C_{10}H_{16}O_2$ , a brownish-yellow

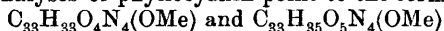
powder, and *cedrenolic acid*,  $C_{54}H_{86}O_5$ , a semi-liquid resin, were isolated. The cedar resin also contained an unsaponifiable, neutral ingredient which had the properties of a resin. J. C. W.

**Analysis of the Resin from Pistacia Terebinthus var., Palästina.** LOUIS REUTTER (*Chem. Zentr.*, 1913, ii, 1303—1304; from *Schweiz. Woch. Chem. Pharm.*, 1913, 51, 537—540).—An aromatic resin with m. p. 70—71°, acid number 126.16—130.54, saponification number 235.87—241.14, ester number 106.7—110.6, containing numerous pointed crystals and responding to the cholesterol tests, has been investigated. The steam-distillate contained an oil,  $D_0^{20} 0.8516$ ,  $[\alpha]_D -17^\circ 18'$ ,  $n_D 1.4622$ , which deposited borneol. The following were isolated from the residue: *pistacic acid*,  $C_{18}H_{26}O_3$ , amorphous, m. p. 104°; *pistacolic acid*,  $C_{24}H_{42}O_3$ , colourless crystals, m. p. 148—148.5°;  $\beta$ -*pistacolic acid*,  $C_{21}H_{34}O_3$ , white powder, m. p. 148—149.5°, acid number 101.08—101.12;  $\alpha$ -*pistacolic acid*,  $C_{19}H_{30}O_3$ , white powder, m. p. 91.5—92.4°, acid number 61.77—62.15; *pistacinolic acid*,  $C_{22}H_{38}O_3$ , yellowish-white crystals, m. p. 138°;  $\alpha$ -*pistacinolic acid*,  $C_{18}H_{30}O_2$ , white powder, m. p. 103—104°;  $\alpha$ -*terpentinic acid*,  $C_{26}H_{44}O_3$ , large, colourless crystals, m. p. 110—111°;  $\beta$ -*terpentinic acid*,  $C_{21}H_{26}O_3$ , white powder, m. p. 82.5—84°, acid number 78.6—78.89;  $\alpha$ -*pistaciaresen*,  $C_{29}H_{48}O_3$ , white crystals, m. p. 103—104°;  $\beta$ -*pistaciaresen*,  $C_{18}H_{26}O_3$ , amorphous, m. p. 96—97.5°; *terpentinorenen*,  $C_{19}H_{27}O_3$ , amorphous, m. p. 79—81.5°. J. C. W.

**Biochemical Synthesis of Glucosides of Multivalent Alcohols:  $\alpha$ -Glucosides of Glycerol and Glycol.** EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1913, 157, 1024—1027. Compare A., 1913, i, 1080).—The formation of glucosides by the action of bottom yeast on solutions of dextrose in aqueous solutions of glycerol or ethylene glycol containing varying percentages of these multivalent alcohols has been followed in each case and allowed to proceed until the rotation became constant. In the first case the amount of combined dextrose at the end of the reaction increased steadily with the concentration of the glycerol up to 94% glycerol. In the case of glycol, a similar increase was noted up to 60% of glycol, beyond which little or no action took place. Glycol at a concentration of above 60% thus apparently destroys  $\alpha$ -glucosidase, its toxicity coming between that of the univalent alcohols and the tervalent alcohol, glycerol. W. G.

**Chlorophyll. XVIII. Phyllocyanin and Phylloxanthin.** H. MALARSKI and L. MARCHLEWSKI (*Biochem. Zeitsch.*, 1913, 57, 112—124).—The preparation of phyllocyanin by the action of concentrated hydrochloric acid on chlorophyllan and its purification by Willstätter and Mieg's process are described. By treatment with 1% aqueous potassium hydroxide, phyllocyanin is converted into anhydro- $\beta$ -phyllotaonin and a second substance not closely related to it.

Numerous analyses of phyllocyanin point to the formulæ



for the substance dried at 110° and air-dried respectively. These formulæ are in harmony with the formation of anhydro- $\beta$ -phyllotaonin

from phyllocyanin by the loss of methyl alcohol and with the conversion of neochlorophyllan into phyllocyanin by the elimination of the phytlyl group.

The absorption spectrum of a 0.04% solution of phyllocyanin in chloroform has been measured. Its comparison with those of neochlorophyllan and  $\beta$ -phyllotaonin indicates that the phytlyl group has very little, the methoxy-group a very marked, influence on the optical properties.

The work on the identity of phylloxanthin and *allochlorophyllan* has been already recorded (A., 1912, i, 203).

The paper concludes with some criticisms of Willstätter's work on the degradation of chlorophyll by alkalis (A., 1913, i, 1214). C. S.

**The Chlorophyll Group. XIX. Variation in the Chlorophyll Quotient in Leaves and its Biological Significance.** H. BOROWSKA and L. MARCHLEWSKI (*Biochem. Zeitsch.*, 1913, 57, 423—429).—The methods devised by Jacobson and Marchlewski (A., 1912, ii, 705) for the determination of the relation of neo- to *allo*-chlorophyll have been subjected to critical revision, and their accuracy is upheld. It is proved that both chlorophyllans are completely extracted from leaves. The chlorophyll quotient is found not to be constant as claimed by Willstätter, but to vary both from one species to another and in the same species under different external conditions. In support of this view, quotations are given from Max Wagner (*Allgem. Forst und Jagdzeit*, 1913), who shows that the breadth of the absorption band varies both from plant to plant and with species, and that the band consists of two portions, the boundaries between which were not constant, but are altered almost daily as the plants develop. There is an alteration both in the composition of the leaf-green and in the breadth of the absorption band.

The relation between the character of the soil, the absorption of light, and consequent growth is expressed as follows: the absolute and relative quantities of the bluish-green neochlorophyll produced depend on the character of the soil; the amount of the pigment regulates the power of the plant to absorb light of suitable wavelength, and this in turn governs the synthesis of organic matter.

E. F. A.

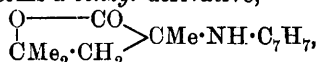
**The Composition of the Lake which is Formed on Cotton Fibre in Dyeing with Basic Dyes.** A. SANIN (*Kolloid. Zeitsch.*, 1913, 13, 305—310).—The author describes experiments which have been made in order to elucidate the nature of the changes which are involved in the successive treatment of cotton fibre with solutions of tannin, potassium antimonyl tartrate, and basic dyes. Previous observations have shown that the interaction of the two former substances leads, under certain conditions, to the formation of a definite compound of the composition  $(C_{14}H_9O_9)_2SbOH$ . The behaviour of this substance towards a number of basic dyes has now been examined. The antimony tannin compound was suspended in water, and to this was added an excess of an aqueous alcoholic solution of the

dye, the mixture being then boiled for twenty minutes, and afterwards filtered through a cotton-wool filter. After washing and drying, the solid residue was examined by estimation of the antimony and the nitrogen. The products obtained with chrysoidine, magenta, crystal-violet, safranin, and Victoria-blue, afford strong evidence in support of the view that a definite chemical compound is formed by combination of the basic dye with the antimony tannin compound. It is supposed that the free hydroxyl group of the antimony tannin compound is thereby eliminated.

H. M. D.

**Reactions of Lactones.** MORITZ KOHN [and, in part, with H. HOLZINGER] (*Monatsh.*, 1913, **34**, 1729—1740).—An account of the action of organo-magnesium compounds on 4-hydroxy-5-keto-2:2:4-trimethyltetrahydrofuran (A., 1909, i, 599) and 4-amino-5-keto-2:2:4-trimethyltetrahydrofuran (A., 1908, i, 819). The hydroxy-compound reacts with magnesium methyl iodide (3 mols.) in ethereal solution, yielding  $\beta\gamma\epsilon$ -trimethylhexane- $\beta\gamma\epsilon$ -triol (Richard and Langlais, A., 1910, i, 455; Bouveault and Levallois, A., 1911, i, 3); with magnesium bromide it forms the *anhydride* of *aa*-diphenyl- $\beta\gamma$ -dimethylpentane- $\alpha\beta\delta$ -triol (4-hydroxy-5:5-diphenyl-2:2:4-trimethyltetrahydrofuran), b. p. 205°/12 mm., m. p. 113°, 
$$\begin{array}{c} \text{O} \\ | \\ \text{CPh}_2 \\ | \\ \text{CMe}_2 \cdot \text{CH}_2 \end{array} > \text{CMe} \cdot \text{OH}.$$

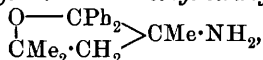
4-Amino-5-keto-2:2:4-trimethyltetrahydrofuran combines with chloroacetic acid (1 mol.) in ethereal solution, yielding a *chloroacetate* as a leafy, white mass, m. p. 167—170°. When heated with benzyl chloride it forms a *benzyl* derivative,



which yields a *picrate*, m. p. 184°, and a *nitroso*-compound, crystallising in needles, m. p. 92—94°.

It reacts with magnesium methyl iodide, yielding  $\gamma$ -amino- $\beta\gamma\epsilon$ -trimethylhexane- $\beta\epsilon$ -diol,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CMe}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ . This has b. p. 157—160°/30 mm., m. p. 64—65°, and forms a *chloroacetate*, m. p. 142—144°.

4-Amino-5:5-diphenyl-2:2:4-trimethyltetrahydrofuran,



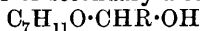
prepared by the action of magnesium phenyl bromide on 4-amino-5-keto-2:2:4-trimethyltetrahydrofuran and warming the resulting product with 45% sulphuric acid, crystallises from alcohol in white needles, m. p. 108°.

4-Methylamino-2-phenyl-1:4-dimethoxy-5-pyrrolidone (A., 1908, i, 829) combines with chloroacetic acid in alcoholic solution, yielding a *dichloroacetate*,  $\text{C}_{15}\text{H}_{18}\text{ON}_2 \cdot 2\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ , which crystallises in transparent plates, m. p. 131—133°.

F. B.

**Action of Mixed Organo-magnesium Derivatives on the Bimolecular Polymeride of Crotonaldehyde.** ROGER DOURIS (*Compt. rend.*, 1913, **157**, 943—945).—In support of Delépine's

formula for this polymeride (compare A., 1910, i, 219), the author has prepared from it a number of secondary alcohols of the type



by the action of magnesium alkyl haloids (1.25 mols.) on the aldehyde (1 mol.) in ethereal solution. From these the corresponding acetic esters have been prepared.

The *alcohol*,  $C_7H_{11}O \cdot CHMe \cdot OH$ , has b. p. 107—109°/14 mm.;  $D_4^0$  1.0144;  $D_4^{15}$  1.0098; and gives an *acetate*, b. p. 109—112°/15 mm.;  $D_4^0$  1.0243;  $D_4^{20}$  1.0068.

With an excess of magnesium methyl iodide, the alcohol is not obtained, but the *compound*,  $C_7H_{11}O \cdot CH \cdot CH_3$ , with a strong odour of camphor, having b. p. 59—63°/18 mm.;  $D_4^0$  0.9200;  $D_4^{20}$  0.8983, and unacted on by acetic anhydride.

The *alcohol*,  $C_7H_{11}O \cdot CHEt \cdot OH$  (compare *loc. cit.*), is a viscid, pale yellow liquid, b. p. 125—130°/21 mm.;  $D_4^0$  1.0004;  $D_4^{17}$  0.9987, giving an *acetate*, b. p. 129—130°/23 mm.;  $D_4^0$  1.0168;  $D_4^{20}$  0.9992.

The *alcohol*,  $C_7H_{11}O \cdot CHPr^{\beta} \cdot OH$ , b. p. 118—125°/22 mm.;  $D_4^0$  1.0022;  $D_4^{17}$  0.9970, giving an *acetate*, b. p. 119—122°/13 mm.;  $D_4^0$  0.9974;  $D_4^{17}$  0.9827.

The *alcohol*,  $C_7H_{11}O \cdot CH(OH) \cdot C_4H_9^{\beta}$ , b. p. 127—133°/13 mm.;  $D_4^0$  0.9729;  $D_4^{16}$  0.9619, furnishing an *acetate*, b. p. 130—132°/14 mm.;  $D_4^0$  0.9818;  $D_4^{17}$  0.9680.

The *alcohol*,  $C_7H_{11}O \cdot CH(OH) \cdot C_5H_{11}^{\beta}$ , b. p. 144—150°/15 mm.;  $D_4^0$  0.9678;  $D_4^{15}$  0.9543, giving an *acetate*, b. p. 143—145°/13 mm.;  $D_4^0$  0.9716;  $D_4^{17}$  0.9592. W. G.

**Condensation of Phloroglucinol with Aldehydes. I. F. WENZEL** (*Monatsh.*, 1913, 34, 1915—1955).—[With L. FINKELSTEIN.]—An examination of the condensation products of phloroglucinol with a number of simple aliphatic and hydroxy-aldehydes shows that, although their composition is in agreement with the view (compare Counciler, A., 1895, i, 164) that the condensation takes, according to the scheme, 3 mols. phloroglucinol + 2 mols. aldehyde — 2 mols. water, the products really consist of mixtures of two substances, the composition of which may be represented as follows:

(a) 1 Mol. phloroglucinol + 1 mol. aldehyde —  $1H_2O$ .

(b) 2 Mols. phloroglucinol + 1 mol. aldehyde —  $1H_2O$ .

$\beta$ -Hydroxybutaldehyde and formaldehyde show an exceptional behaviour, in that they undergo condensation with phloroglucinol in one direction only, yielding products of the type (a) and (b) respectively.

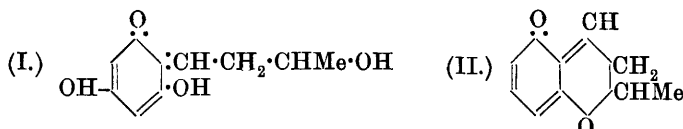
The course of the condensation depends both on the temperature and on the nature of the condensing agent employed, the best results being obtained by the use of sulphuric acid.

The initial condensation products are amorphous, colourless substances, but, when kept in contact with the mother liquor, slowly lose water and give rise to red substances.

When  $\beta$ -hydroxybutaldehyde dissolved in a little water is added to a solution of phloroglucinol in 4—5% sulphuric acid (by volume) and the temperature of the mixture maintained at about 6°, a *substance*,  $C_{10}H_{12}O_4$ , is rapidly deposited in snow-white flocks. The substance



forms a pale yellow powder when dry, gives a blood-red coloration with strong sulphuric acid, and yields with acetic anhydride and anhydrous sodium acetate a colourless, amorphous *triacetyl* derivative. When kept in contact with the sulphuric acid solution in which the condensation was carried out, the substance gradually acquires a red colour, and is transformed into the *compound*,  $C_{10}H_{10}O_3$ . The original colourless condensation product is considered to have the formula (I), whilst the red compound has the structure (II):



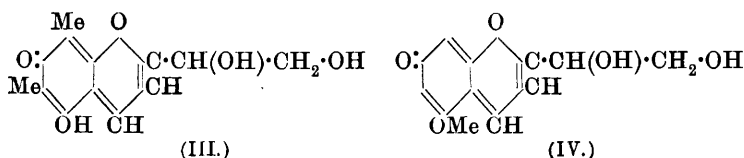
The condensation products of phloroglucinol with formaldehyde, acetaldehyde, propaldehyde, valeraldehyde,  $\beta$ -hydroxypropaldehyde, acetopropionaldol, and propionaldol are also described. Glycollaldehyde and glyceraldehyde undergo condensation with phloroglucinol with much greater difficulty than the aldehydes already mentioned. On the other hand, acraldehyde readily condenses with phloroglucinol, yielding a lilac-coloured substance, which differs from the condensation products derived from the saturated and hydroxy-aldehydes in that it cannot be acetylated, and in undergoing no change in colour when kept in contact with the solution in which the condensation was carried out.

[With EUGEN LÁZÁR.]—The condensation of *l*-arabinose and *l*-xylose with phloroglucinol by means of hydrochloric acid has also been examined. It is found that the velocity of condensation depends to a very great extent both on the concentration of the hydrochloric acid employed and on the temperature at which the reaction is carried out.

The condensation proceeds much more readily with *l*-xylose than with *l*-arabinose, and in both cases is accelerated by the addition of ethyl or amyl alcohol.

Dimethylphloroglucinol (2:4:6-trihydroxy-*m*-xylene) condenses with furfuraldehyde in the presence of hydrochloric acid, yielding a *substance*,  $C_{21}H_{22}O_7$ , which forms a light brown powder and becomes dark olive-green on exposure to air.

The condensation *product* of dimethylphloroglucinol with *l*-xylose forms a deep brownish-red powder; it chars without melting, and is considered to have the constitution represented in III:

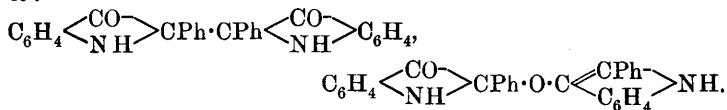


The *product* (formula IV), formed by condensing phloroglucinol monomethyl ether with *l*-xylose in the presence of hydrochloric acid, separates as the *hydrochloride* in slender, deep red needles which

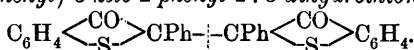
are transformed into a light brown, amorphous powder by washing with water.

[With L. FINKELSTEIN.]—In the presence of hydrochloric acid, vanillin condenses with phloroglucinol, yielding a colourless, amorphous substance,  $C_{14}H_{12}O_5$ ; if sulphuric acid is used as a condensing agent, a mixture of the compounds  $C_{14}H_{12}O_5$  and  $C_{20}H_{18}O_8$  is obtained as light rose-coloured flocks which suddenly become light yellow when washed with water F. B.

**3-Hydroxy-2-phenylthionaphthen and 2:2'-Diphenylthioindigo White.** LUDWIG KALB and JOSEPH BAYER (*Ber.*, 1913, 46, 3879—3885. Compare Apitzsch, A., 1913, i, 1341).—In a previous paper (A., 1912, i, 726) the authors have described a compound, obtained by the oxidation of phenylindoxyl or the reduction of 2-phenylindone, which dissociates when heated in indifferent solvents into phenylindoxyl and 2-phenylindone, but they were unable to determine which of the two following structures should be assigned to it:



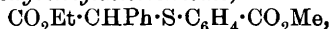
With the object of throwing further light on this point the authors are undertaking an examination of the behaviour of a number of 2:2'-substitution products of indigoid compounds, the present paper dealing with ("2:2'-diphenylthioindigo white") 2(3'-*keto*-2'-phenyl-2':3'-*dihydrothionaphthenyl*)-3-*keto*-2-phenyl-2:3-*dihydrothionaphthen*,



This substance dissolves in the more volatile solvents, yielding almost colourless solutions which at their b. p. acquire a greenish-yellow colour. Its solutions in xylene, nitrobenzene, and other less volatile solvents have a yellowish- to emerald-green colour, the intensity of which depends on the temperature; on cooling, the colour practically disappears.

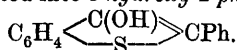
This change in colour is considered to be due to the dissociation of the compound into free radicles as indicated by the dotted line. The green solutions decolorise bromine, oxidise quinol to *p*-benzoquinone, and when boiled for some time, acquire a yellow colour; on evaporation, the yellow solutions yield a substance, m. p. above  $350^\circ$ , which gives a yellowish-red coloration with sulphuric acid. The free radicle is not so sensitive towards atmospheric oxygen as the triarylmethyls, for the green solutions can be shaken with air without undergoing appreciable change; oxidation, however, ensues when oxygen is passed into the ethyl benzoate solution at  $150^\circ$ , the green colour giving place to brown. The greater stability of the radicle towards oxygen as compared with the triarylmethyls is referred to the presence of the carbonyl group.

*Methyl o- $\alpha$ -carbethoxybenzylthiolbenzoate,*



prepared by the interaction of ethyl phenylbromoacetate and the potassium

salt of methyl *o*-thiolbenzoate in alcoholic solution, crystallises in prismatic plates, m. p. 62—63°, and on treatment with ethyl-alcoholic sodium ethoxide is converted into 3-hydroxy-2-phenylthionaphthen,



This forms clusters of colourless needles, m. p. 103—104°, develops a yellowish-brown coloration with sulphuric acid, and yields a *benzoyl* derivative crystallising in prisms, m. p. 115—116°. Its solution in aqueous sodium hydroxide is oxidised by potassium ferricyanide to 2(3'-keto-2'-phenyl-2':3'-dihydrothionaphthenyl)-3-keto-2-phenyl-2:3-dihydrothionaphthen, which forms yellow prisms having a faint greenish tinge, m. p. 231°.

F. B.

**Hydrogenation of Organic Compounds.** VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.-P. 267306).—The catalytic hydrogenation of organic compounds can be easily effected by treating the substance with finely divided metals of the platinum group and formic acid. The acid is catalytically decomposed into carbon dioxide and hydrogen, the former being evolved, and the latter acting on the organic substance present. Examples are given illustrating the preparation of hydroquinine from quinine (using colloidal or spongy palladium), and of  $\beta$ -phenylpropionic acid from cinnamic acid (using spongy palladium).

J. C. C.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT (*Chem. Zentr.*, 1913, ii, 1310; from *Apoth. Zeit.*, 1913, 28, 667. Compare A., 1912, i, 644; 1913, i, 750).—Whereas *l*-ephedrine is converted into *d*- $\psi$ -ephedrine on heating with 25% hydrochloric acid in a tube at 100°, and vice versa, the hydrochlorides are stable towards water at 200—205°.

J. C. W.

**Physostigmine [Eserine].** I. FRITZ STRAUS (*Annalen*, 1913, 401, 350—376. Compare Salway, T., 1912, 101, 978; 1913, 103, 351).—Little is known about eserine beyond the facts that it has the formula  $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_3$ , contains the group  $\cdot\text{CO}\cdot\text{NHMe}$ , and yields methylindoles by distillation with zinc dust, eseroline by treatment with potassium hydroxide in the absence of air, and rubreserine, eserine-brown and eserine-blue by atmospheric oxidation.

The authors now find that eserine decomposes when heated at 150° in an absolute vacuum, and yields eseroline, which can then be distilled at 240° without any change, even in the magnitude of its rotation. Eseroline, therefore, as been selected as the starting-point in this investigation. The picrate is apparently dimorphous; usually the m. p. is 167—168°, but on one occasion 190—191° was observed (Salway gives 195°). The *benzoate*,  $\text{C}_{20}\text{H}_{24}\text{O}_3\text{N}_2$ , m. p. 155—156°,  $[\alpha]_D - 108.7^\circ$  in 38.4% methyl alcohol, stout leaflets, prepared by the addition of solid benzoic acid to an ethereal solution of eseroline, is very characteristic and is useful for the identification and isolation of the base.

Eseroline methiodide (*picrate*, m. p. 184—185° [decomp.]) is converted by aqueous silver sulphate and sulphuric acid into methyl-eserolinium sulphate, which reacts with barium carbonate to give a

solution of *methyleserolinium carbonate*. This solution reacts with sodium picrate to give a picrate identical with that above, and yields by evaporation in a vacuum, ultimately in a current of hydrogen at 80—90°, a viscous residue which is completely freed from water at 100° in a vacuum, leaving a reddish-brown, amorphous substance, m. p. about 170° (decomp.). The amorphous substance is heated under reduced pressure at 190—200° (whereby it undergoes a distinct change), and, finally, under greatly reduced pressure (oil-pump) at 200—235°. An ethereal solution of the solid distillate is separated by hydrochloric acid into a basic *substance* (which has not been examined, but reasons are given for the belief that it has the constitution  $\text{OH} \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{NMe} \\ \text{CH}(\text{CH}:\text{CH}_2) \end{array} \right\rangle \text{C}:\text{CH}_2$ ) and a phenolic *substance*,  $\text{C}_{11}\text{H}_{11}\text{ON}$ , m. p. 107·5—108°, colourless needles, which is called *physostigmol*. The latter dissolves extremely easily in very dilute sodium hydroxide, but not in sodium carbonate, is soluble in concentrated hydrochloric acid, develops a green coloration with ferric chloride, reduces ammoniacal silver oxide and alkaline potassium permanganate, condenses with diazobenzenesulphonic acid, and forms a *picrate*, m. p. 161—162°, long, dark red needles. *Physostigmol* probably has the constitution  $\text{OH} \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{NMe} \\ \text{C}(\text{CH}:\text{CH}_2) \end{array} \right\rangle \text{CH}$ , although it does not respond to the pine-shaving test; it is optically inactive.

The volatile bases obtained in the preparation of *physostigmol* contain trimethylamine and dimethylamine. *Ethylamine aurichloride* and *dimethylamine aurichloride* have m. p. 194—196° and 195—198° respectively; the m. p. of the mixture is 172°.

Eserine forms an *aurichloride*,  $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_3 \cdot 2\text{HAuCl}_4$ , m. p. 163—165° (decomp.), yellow leaflets, and *platinichloride*,  $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_3 \cdot \text{H}_2\text{PtCl}_6$ , decomp. about 180°, orange-yellow needles. C. S.

**Preparation of Hydrastinine from Dihydrohydrastinine.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 267272).—An alcoholic solution of dihydrohydrastinine is treated with an alcoholic or ethereal solution of iodine in the presence of anhydrous potassium acetate. The hydrastinine hydriodide which separates out has m. p. 233—234°. J. C. C.

**Extractives of Muscle. Creatosine, a New Base from Meat Extract.** R. KRIMBERG and LEONID IZRAÏLSKY (*Zeitsch. physiol. Chem.*, 1913, 88, 324—330).—A base, *creatosine*, forming an *aurichloride* of the composition  $\text{C}_{11}\text{H}_{28}\text{O}_4\text{N}_3\text{Au}_2\text{Cl}_8$  has been isolated from two different preparations of Liebig's meat extract. It crystallises in yellow needles, m. p. 128—130°. A second base forming an *aurichloride* with 43·7% of gold is under investigation. E. F. A.

**Strychnos Alkaloids. XVIII. Some Non-Acid Products of the Oxidation of Strychnine.** HERMANN LEUCHS and GEORG SCHWAEBEL (*Ber.*, 1913, 46, 3693—3699. Compare A., 1908, i, 563).—In addition to strychninonic and dihydrostrychninonic acids the

oxidation of strychnine in chloroform solution by an acetone solution of potassium permanganate at 15–20° yields small quantities of the following neutral or basic substances :

(1) A neutral *substance*,  $C_{19}H_{20}O_4N_2$ , crystallising in transparent prisms, which becomes brown at 290° and has m. p. 320° (decomp.).

(2) A *hydrochloride* (or *methochloride*),  $C_{18}H_{18}O_3N_2 \cdot HCl \cdot H_2O$  or  $C_{17}H_{16}O_3N_2 \cdot CH_3Cl \cdot H_2O$ , which crystallises in very slender, felted needles or in rectangular or pentagonal leaflets. It becomes brown at 270° and has m. p. 296–300° (decomp.). The free *base* is soluble in water.

(3) A *substance*,  $C_{21}H_{22}O_5N_2$ , crystallising in very slender, colourless leaflets, m. p. 252–255° (decomp.), with previous sintering at 247°. For details of the separation of the above substances, all of which give the Otto reaction for strychnine, the original should be consulted.

F. B.

**Preparation of Readily Soluble Xanthine Derivatives.** FARBEFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 264389).—A crystalline *substance*, which is a molecular mixture of theophylline and sodium 2-methylquinoline-6-carboxylate, is obtained when an aqueous solution of sodium theophylline (202 parts) and 190 parts of 2-methylquinoline-6-carboxylic acid is heated and the filtered solution evaporated to dryness under diminished pressure.

Caffeine and sodium 2-phenylquinoline-4-carboxylate furnish a similar crystalline *substance*.

F. M. G. M.

**Preparation of a Ferrous Salt of 2-Pyrrolidone-5-carboxylic Acid.** F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 264391).—When an aqueous solution containing 15 parts of 2-pyrrolidone 5-carboxylic acid is boiled during five hours with iron powder (5 parts) in the presence of an inert gas, filtered, and the filtrate subsequently evaporated, it furnishes a red *compound*,  $(C_5H_6O_3N)_2Fe$ , which is stable in a dry condition.

F. M. G. M.

**Methylpiperidinecarboxylic Acid.** ERNST SCHMIDT (*Chem. Zentr.*, 1913, ii, 1310; from *Apoth. Zeit.*, 1913, 28, 667).—Starting with dibromopimelic ester and methylamine, a mixture of two isomeric methylpiperidinecarboxylic acids has been obtained. One of them is apparently identical with the acid which was isolated during the oxidation of scopoline (A., 1909, i, 173).

J. C. W.

**Pyrrole Group. X. Alkylation of Pyrroles. I. Direct Synthesis of Homopyrroles.** BERNARDO ODDO and ROMUALDO MAMELI (*Gazzetta*, 1913, 43, ii, 504–517. Compare A., 1912, i, 804).—The action of methyl iodide on magnesium pyrrol bromide yields principally 3-methylpyrrole, together with small proportions of 2-methylpyrrole, both dimethylpyrroles,  $C_4NH_3Me_2$ , and a base, which is apparently 1 : 2-dihydropyridine.

T. H. P.

**Derivatives of Isatin and Dioxindole.** MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1913, **34**, 1741—1750).—Isatin-3-oxime is very readily prepared by gradually adding 10% aqueous potassium hydroxide to an equimolecular mixture of isatin and hydroxylamine hydrochloride until a clear yellow solution is obtained, and then acidifying with a mineral acid. With acetic anhydride it forms a *diacetyl* derivative,  $\text{NAc} \langle \text{C}_6\text{H}_4 \rangle_{\text{CO}} \text{C:N} \cdot \text{OAc}$ , which crystallises in pointed needles of a light brown colour, m. p. 174—175°, with previous softening at 165°.

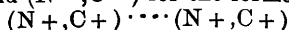
On treatment with barium hydroxide in hot aqueous solution, 1-methylisatin yields a *barium* salt,  $\text{Ba}(\text{C}_9\text{H}_8\text{O}_3\text{N}_2)_2$ , crystallising with  $2\text{H}_2\text{O}$  in clusters of intensely yellow needles, which lose their water at 125°, and then have an orange-yellow colour. The barium salts react with hydroxylamine hydrochloride to form 1-methyl-2-isatoxime. This has m. p. 189—192° with previous softening (compare Colman, T., 1889, **55**, 5), and yields an *acetyl* derivative, crystallising in short, dark yellow columns, softening at 135°, m. p. 154—155°.

The *barium* salt of 5-bromo-1-methylisatin crystallises with  $2\text{H}_2\text{O}$ , and on treatment with hydroxylamine hydrochloride gives rise to 5-bromo-1-methylisatin-3-oxime,  $\text{NMe} \langle \text{C}_6\text{H}_3\text{Br} \rangle_{\text{CO}} \text{C:N} \cdot \text{OH}$ , m. p. 228°, with previous darkening and softening at 205° and 215° respectively.

The addition of magnesium phenyl bromide in ethereal solution to a benzene solution of 1-methylisatin yields 3-phenyl-1-methyldioxindole,  $\text{NMe} \langle \text{C}_6\text{H}_4 \rangle_{\text{CO}} \text{CPh} \cdot \text{OH}$ , which forms white, leafy crystals, m. p. 139°, and reacts with methyl sulphate and aqueous potassium hydroxide to form a 3-phenyl-1-methyldioxindole methyl ether, identical with that obtained by the direct methylation of 3-phenyldioxindole (compare A., 1912, i, 50).

3-*Naphthyl*-1-methyldioxindole, prepared from 1-methylisatin and magnesium  $\alpha$ -naphthyl bromide, crystallises in bright, greyish-brown, microscopic needles, m. p. 152—153°. F. B.

**Stereoisomerism of Inactive Ammonium Salts containing Asymmetric Nitrogen and Asymmetric Carbon.** E. WEDEKIND and K. BANDAUF (*Annalen*, 1913, **401**, 326—349).—It has already been shown (A., 1912, i, 501; 1913, i, 893) that asymmetric ammonium or di-ammonium salts containing an active carbon atom can be separated into two stereoisomerides represented by the schemes  $(\text{N}^+, \text{C}^-)$  and  $(\text{N}^-, \text{C}^-)$  for the former, and



and  $(\text{N}^-, \text{C}^+) \cdots (\text{N}^-, \text{C}^+)$  for the latter, salts. The present paper is an extension of the work and deals with the stereoisomerism of inactive ammonium salts containing asymmetric nitrogen and asymmetric carbon. The inactive ammonium salt, therefore, contains the four stereoisomerides,  $(\text{C}^+, \text{N}^+)$ ,  $(\text{C}^+, \text{N}^-)$ ,  $(\text{C}^-, \text{N}^+)$ , and  $(\text{C}^-, \text{N}^-)$ . It has been separated by the authors' solubility method into the inactive pairs,  $\left\{ \begin{smallmatrix} \text{C}^+, \text{N}^+ \\ \text{C}^-, \text{N}^- \end{smallmatrix} \right\}$  and  $\left\{ \begin{smallmatrix} \text{C}^+, \text{N}^- \\ \text{C}^-, \text{N}^+ \end{smallmatrix} \right\}$ . Attempts to resolve

each of these inactive salts into their active components by means of the *d*-camphorsulphonates or *d*-bromocamphorsulphonates have been unsuccessful, possibly because the salts examined belong to the tetrahydroisoquinolinium series (no inactive member of this series has ever been resolved into its active components).

1:2-Diethyl-1:2-dihydroisoquinoline,  $C_{13}H_{17}N$ , b. p. 145—150°/15 mm., prepared in the usual manner from magnesium ethyl iodide and isoquinoline ethiodide (compare Freund and Bode, A., 1909, i, 514), reacts readily with benzyl iodide to form 2-benzyl-1:2-diethyl-1:2-dihydroisoquinolinium iodide. Although this salt, by fractional crystallisation, shows evidence of being separated into two components, salts of this type are in general not suited to the authors' purpose on account of their decomposability. Very successful results, however, are obtained with the salts of the tetrahydroisoquinolinium bases, which are quite stable and crystallise well. By reduction with tin and hydrochloric acid, 1:2-diethyl-1:2-dihydroisoquinoline is converted into 1:2-diethyl-1:2:3:4-tetrahydroisoquinoline,  $C_{13}H_{19}N$ , b. p. 122°/18 mm., the *picrate* of which, decomp. 106—108°, pale yellow, triclinic crystals ( $a:b:c=1.2062:1.13652$ ;  $\alpha=92^\circ13\frac{1}{2}'$ ,  $\beta=113^\circ35\frac{1}{2}'$ ,  $\gamma=91^\circ32'$ ), is proved crystallographically to be individual.

A mixture of the tetrahydro-base and benzyl bromide solidifies after some days to form 2-benzyl-1:2-diethyl-1:2:3:4-tetrahydroisoquinolinium bromide,  $C_{20}H_{26}NBr$ , decomp. 208°, which is separated by fractional crystallisation from alcohol into a sparingly soluble  $\alpha$ -salt, decomp. 215°, monoclinic needles, and an easily soluble  $\beta$ -salt, decomp. 195°, monoclinic (?) crystals. The *d*-camphorsulphonate and *d*-bromocamphorsulphonate of the  $\alpha$ -base have decomp. 168—170° and 185—187° respectively, whilst the corresponding salts of the  $\beta$ -base have decomp. 105° and 213° respectively.

The following salts have been prepared by methods similar to the preceding: 2-Benzyl-1:2-diethyl-1:2:3:4-tetrahydroisoquinolinium iodide, decomp. 195°, is separated by crystallisation from alcohol and subsequent sorting into an  $\alpha$ -iodide (also obtained from the  $\alpha$ -bromide, decomp. 215°, through the *d*-camphorsulphonate), decomp. 195°, rhombic crystals ( $a:b:c=0.9035:1:1.0323$ ), and a  $\beta$ -iodide (also prepared from the  $\beta$ -bromide, decomp. 195°), decomp. 195°, monoclinic crystals ( $a:b:c=1.8921:1:4.8609$ ;  $\beta=93^\circ53'$ ), which differ only slightly in solubility. The  $\alpha$ - and the  $\beta$ -chlorides, prepared from the respective iodides and silver chloride, have decomp. 223—224° and exhibit no appreciable differences; the same is true of the *platini-chlorides*, decomp. 194°.

1:2-Diethyl-2-allyl-1:2:3:4-tetrahydroisoquinolinium iodide is separated by fractional crystallisation from alcohol into a sparingly soluble  $\alpha$ -iodide,  $C_{16}H_{24}NI$ , decomp. 192°, monoclinic crystals, and a soluble  $\beta$ -iodide,  $C_{16}H_{24}NI$ , decomp. 153°, felted crystals.

2-Ethyl-1-propyl-1:2:3:4-tetrahydroisoquinoline,  $C_{14}H_{21}N$ , b. p. 143°/15 mm. (the *picrate*, decomp. 109—110°, monoclinic prisms, is individual), reacts at 40° with benzyl bromide after many days to form 2-benzyl-2-ethyl-1-propyl-1:2:3:4-tetrahydroisoquinolinium bromide,  $C_{21}H_{28}NBr$ , which is separated by alcohol into an  $\alpha$ -bromide, decomp. 204—205°, and a more soluble  $\beta$ -bromide, decomp. 187—190°.

The corresponding  $\alpha$ -iodide,  $C_{21}H_{28}NI$ , decomposes at  $174^\circ$ , and the more soluble  $\beta$ -iodide decomposes at  $165$ — $166^\circ$ , both being obtained by the fractional crystallisation of 2-benzyl-2-ethyl-1-propyl-1:2:3:4-tetrahydroisoquinolinium iodide.

2-Ethyl-1-propyl-2-allyl-1:2:3:4-tetrahydroisoquinolinium iodide,  $C_{17}H_{26}NI$ , is separated by alcohol into an  $\alpha$ -iodide, decomp.  $165$ — $167^\circ$ , monoclinic crystals [ $a:b:c=1.5435:1:0.5973$ ;  $\beta=94^\circ39'$ ], and a  $\beta$ -iodide, decomp.  $165$ — $167^\circ$ , monoclinic crystals

[ $a:b:c=1.0638:1:0.4599$ ;  $\beta=103^\circ14\frac{1}{2}'$ ],

the latter being about three times as soluble as the former in 50% alcohol.

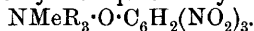
1-Ethyl-2-propyl-1:2:3:4-tetrahydroisoquinoline,  $C_{14}H_{21}N$ , b. p.  $140^\circ/25$  mm. (picrate, decomp.  $150$ — $152^\circ$ ), reacts somewhat rapidly with allyl iodide to form 1-ethyl-2-propyl-2-allyl-1:2:3:4-tetrahydroisoquinolinium iodide, decomp.  $170$ — $172^\circ$ , which is easily soluble in alcohol and has not been separated into its  $\alpha$ - and  $\beta$ -components.

1:2-Dipropyl-1:2:3:4-tetrahydroisoquinoline,  $C_{15}H_{23}N$ , b. p.  $145^\circ/18$  mm., and benzyl bromide yield 2-benzyl-1:2-dipropyl-1:2:3:4-tetrahydroisoquinolinium bromide,  $C_{22}H_{30}NBr$ , decomp.  $187^\circ$ , which also is very easily soluble in alcohol and in acetone; the same is true of the iodide,  $C_{22}H_{30}NI$ , decomp.  $176^\circ$ . 1:2-Dipropyl-2-allyl-1:2:3:4-tetrahydroisoquinolinium iodide is separated by dilute alcohol comparatively easily into an  $\alpha$ -iodide,  $C_{18}H_{28}NI$ , decomp.  $174$ — $175^\circ$ , monoclinic crystals ( $a:b:c=0.7806:1:1$ ;  $\beta=95^\circ4'$ ), and  $\beta$ -iodide,  $C_{18}H_{28}NI$ , decomp.  $165$ — $167^\circ$ , monoclinic crystals

( $a:b:c=1.4108:1:1.7274$ ;  $\beta=92^\circ15'$ ).

Transformation of an  $\alpha$ -salt into the  $\beta$ -isomeride, or vice versa, has not been observed. In order to prove that the isomeric phenomena quoted above are actually referable to the asymmetry of the nitrogen, 1:2:3-triethyl-1:2:3:4-tetrahydroisoquinolinium iodide,  $C_{16}H_{24}NI$ , decomp.  $162$ — $164^\circ$ , has been fractionally crystallised from alcohol containing a little ether; all the fractions have the same crystalline form, solubility, and decomposition temperature as the original iodide, which is therefore individual. C. S.

**Behaviour of Trinitroanisole Towards Tertiary Bases.** MORITZ KOHN and FRITZ GRAUER (*Monatsh.*, 1913, **34**, 1751—1755).—2:4:6-Trinitroanisole reacts with tertiary amines either at the ordinary temperature or in warm alcoholic solution, yielding picrates of the corresponding methylated quaternary bases,



The following compounds have been prepared in this manner: Tetramethylammonium picrate from the trimethylamine, m. p.  $318$ — $320^\circ$  (Lossen, this Journ., 1876, ii, 629, gives  $312$ — $313^\circ$ ). Methyltriethylammonium picrate from triethylamine, m. p.  $266^\circ$ .

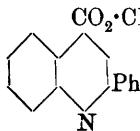
Methylpyridinium picrate from pyridine has m. p.  $107$ — $110^\circ$ , and is identical with the picrate obtained by the successive action of silver oxide and picric acid on pyridinium methiodide (Ostermeyer, *Ber.*, 1885, **18**, 592, gives  $34^\circ$ ).

Methylquinolinium picrate has m. p.  $162$ — $164^\circ$ .



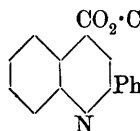
*Methylcinchonine picrate*,  $C_{19}H_{22}ON_2Me \cdot O \cdot C_6H_2(NO_2)_3$ , forms woolly crystals, m. p. 239—241°, with previous darkening. F. B.

**Preparation of Esters of 2-Phenylquinoline-4-carboxylic Acid and its Homologues.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 267209).—When the salts of certain substituted quinoline-4-carboxylic acids are heated with halogenoacetones they are converted into acetol esters, which are easily hydrolysed, and have the beneficial influence of the free acid on the elimination of uric acid, with the advantage that they are tasteless.



*Acetylcarbiny 2-phenylquinoline-4-carboxylate* (annexed formula) forms white needles, m. p. 104°. *Acetylcarbiny 2:3-diphenylquinoline-4-carboxylate* has m. p. 170°; *acetylcarbiny 6-methyl-2-phenylquinoline-4-carboxylate* has m. p. 197—198°, and *acetylcarbiny 2-p-anisylquinoline-4-carboxylate* has m. p. 180—181°. J. C. W.

**Preparation of Esters of 2-Phenylquinoline-4-carboxylic Acid.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 267208).—When the sodium salt of 2-phenyl-



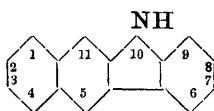
quinoline-4-carboxylic acid is heated under pressure with halogen-substituted acetic esters, new esters of the annexed type are formed. They may receive application as liniments.

*Ethyl 2-phenylquinoline-4-carboxyloacetate*, from ethyl chloroacetate, has m. p. 60° and forms a faintly yellow oil, which dissolves in olive oil as well as in the common solvents. The *menthyl* ester is a viscous oil. J. C. W.

**Preparation of Carbazoledicarboxylic Acids.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 263150. Compare A., 1912, i, 512).—When potassiocarbazole is heated with carbon dioxide at 240—250° for twenty to twenty-five hours under a pressure of 10 atmospheres, it furnishes a mixture of carbazole-mono- and -di-carboxylic acids, separable by treatment with cold sodium hydrogen carbonate, in which the former is insoluble, but the latter dissolves.

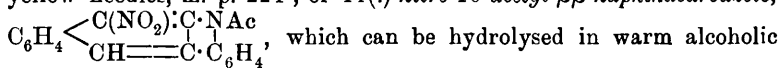
*Carbazolecarboxyl chloride* has m. p. 175°. *Carbazoledicarboxylic acid*, a colourless powder, m. p. above 340° (decomp.), furnishes a *dichloride*, m. p. 242°. If this reaction is carried out at a slightly lower temperature, the monocarboxylic acid is the chief product, whilst at 240—270° for twenty-five to thirty hours the dicarboxylic acid predominates. F. M. G. M.

**Derivatives of 2:3-Benzocarbazole [ $\beta\beta$ -Naphthacarbazole] and of 3:4-Benzocarbazole [ $\alpha'\beta'$ -Naphthacarbazole].** F. KEHRMANN, A. OULEVAY, and F. REGIS (*Ber.*, 1913, 46, 3712—3723).—



$\beta\beta$ -Naphthacarbazole (annexed formula) readily undergoes acetylation when heated with excess of acetic anhydride and a little zinc chloride on a water-bath; the *acetyl* derivative exists in two forms, small, opaque needles, m. p. 117°, and

long, transparent needles, m. p. 121° (compare Graebe and Knecht, A., 1880, 663), which are interconvertible by recrystallisation. The acetyl derivative can be nitrated in solution in acetic acid at the ordinary temperature by nitric acid (D 1·4), giving after twelve hours yellow needles, m. p. 224°, of 11(?)*-nitro-10-acetyl-ββ-naphthacarbazole*,



which can be hydrolysed in warm alcoholic suspension by sodium hydroxide producing 11(?)*-nitro-ββ-naphthacarbazole*, yellowish-red needles, m. p. 248°. Reduction of the nitro-compound by tin and hydrochloric acid in alcoholic solution yielded a sparingly soluble *zincichloride* of an easily oxidisable 11(?)*-amino-ββ-naphthacarbazole*, which by direct treatment with sodium acetate and acetic anhydride was converted into stable *acetyl-amino-ββ-naphthacarbazole*, colourless, silky needles, m. p. 250°; this in sulphuric acid gives a yellow solution with a green fluorescence, and in alcohol yellow with a blue fluorescence.

Although the above nitration yields only a mononitro-derivative, direct nitration of *ββ-naphthacarbazole* in acetic acid with an acetic acid solution of the theoretical quantity of nitric acid, D 1·4, gives an almost immediate formation of *dinitro-ββ-naphthacarbazole*, brownish-red needles, which decompose near 300° without definite m.p. When heated with a mixture of stannous chloride, tin, hydrochloric acid, acetic acid, and alcohol for three to four hours a granular, yellow *zincochloride* of an oxidisable *diamino-ββ-naphthacarbazole* is obtained, which was directly converted into *diacetyldiamino-10-acetyl-ββ-naphthacarbazole*, yellow needles, decomp. near 300°, without definite m. p.

By heating *ββ-naphthacarbazole* or its nitro-derivatives described above with a mixture of sulphuric and nitric acids, golden-yellow leaflets of *pentanitro-ββ-naphthacarbazole*, m. p. near 256°, are obtained; the substance possesses acidic properties, producing a red *aniline* salt and dissolving in dilute aqueous alkalis to red solutions. The corresponding *amins* is so easily oxidisable that even the preparation of the acetyl derivative from the *zincochloride* could not be effected.

[With F. REGIS.]—When a solution of a diazo-salt diluted with acetic acid is introduced as a thin stream into a boiling acetic acid solution of *ββ-naphthacarbazole*, condensation takes place; the result is most satisfactory with diazo-compounds derived from the nitro-anilines; 11-*p-nitrobenzeneazo-ββ-naphthacarbazole* forms reddish-violet needles with a metallic lustre, m. p. approx. 300°; 11-*m-nitrobenzeneazo-ββ-naphthacarbazole*, violet-red needles with feeble metallic lustre, m. p. 224°, which on reduction yield the same amino-compound as was obtained by the reduction of the above mononitro-derivative of *ββ-naphthacarbazole*.

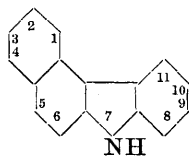
A re-examination of the destructive distillation of 3-phenyl-*ββ-naphthaisotriazole*,  $\begin{array}{c} \text{CH}-\text{C}_6\text{H}_4-\text{C}-\text{N}=\text{N} \\ | \quad \quad | \quad \quad | \\ \text{CH} \quad \quad \text{C} \quad \quad \text{NPh} \end{array}$ , shows that the decomposition gives rise to *ββ-naphthacarbazole* in addition to the *α'β'*-isomeride (compare Ullmann, A., 1898, i, 591); the decomposition of phenyl-*β-naphthylamine* (Graebe and Knecht, *loc. cit.*) produces only the *ββ*-derivative without any of the *α'β'*-isomeride.

$\beta\beta$ -Naphthacarbazole-5:11-quinone,  $C_6H_4$   $\begin{matrix} \diagup & \text{CO} & \text{C} & \text{NH} \\ & | & || & | \\ \diagdown & \text{CO} & \text{C} & \text{C}_6\text{H}_4 \end{matrix}$  (Graebe

and Knecht, *loc. cit.*), treated in warm alkaline solution with hydroxylamine hydrochloride, gives rise to yellow needles of the sodium salt of  $\beta\beta$ -naphthacarbazole-5:11-quinone-11-oxime, from which acetic acid separates the free oxime as golden-yellow needles, decomp. near  $260^\circ$ ; the free oxime dissolves in sulphuric acid with a red colour; it regenerates the quinone when warmed with hydrochloric acid in alcoholic solution, and successfully resisted attempts to convert it into a dioxime. Reduction of the oxime by gradually introducing a concentrated alcoholic solution into a warm solution of stannous chloride in concentrated hydrochloric acid produced the yellow, crystalline zincchloride of 11-amino-5-hydroxy- $\beta\beta$ -naphthacarbazole; again the free base is very sensitive to oxidation by the atmosphere, and the double salt was directly converted into the diacetyl derivative, yellow needles with a green fluorescence, m. p. near  $250^\circ$  (decomp.), soluble in alcohol and in acetic acid to yellow solutions with a strong blue fluorescence. If the zinc chloride double salt is submitted to atmospheric oxidation in alcoholic solution, there is produced a compound of equimolecular proportions of  $\beta\beta$ -naphthacarbazole-5:11-quinone with  $\beta\beta$ -naphthacarbazole-5:11-quinone-11-imide, brown needles, m. p. near  $290^\circ$ , together with a small quantity of a green substance; addition of hydrochloric acid to an alcoholic solution of the brown needles gives a blood-red colour, presumably of a hydrochloride, which slowly disappears with formation of  $\beta\beta$ -naphthacarbazole-5:11-quinone. Prolonged heating of the naphthacarbazolequinone with stannous chloride, hydrochloric acid, and alcohol gives a yellow solution of 5:11-dihydroxy- $\beta\beta$ -naphthacarbazole, which, on account of its ready atmospheric oxidation to a green quinhydrone compound, was separated as the diacetyl derivative, needles with a green fluorescence, m. p.  $244^\circ$ , by heating the naphthacarbazolequinone with sodium acetate, acetic anhydride, acetic acid, and zinc dust for three-quarters of an hour. The diacetyl derivative is easily hydrolysed by alcoholic sodium hydroxide, and is oxidised by ferric chloride to the original quinone.

$\alpha'\beta'$ -Naphthacarbazole (annexed formula) (acetyl derivative, m. p.  $144^\circ$ ; compare Japp and Maitland, T., 1903, 83, 272; Schöpf, A., 1896, i, 243) was converted into 10-nitro- $\alpha'\beta'$ -naphthacarbazole, orange-red needles, m. p.  $223^\circ$ , by nitration of the acetyl derivative to 10-nitro-7-acetyl- $\alpha'\beta'$ -benzocarbazole, lemon-yellow needles or leaflets, m. p.  $238^\circ$ , with subsequent hydrolysis by warm alcoholic sodium hydroxide.

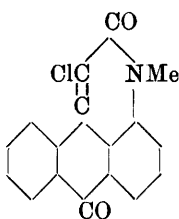
Direct nitration of  $\alpha'\beta'$ -naphthacarbazole produces the same nitro-compound, together with other substances not further examined. By reduction of the above nitroacetyl- $\alpha'\beta'$ -naphthacarbazole with an alcoholic solution of stannous chloride and hydrochloric acid, the zincchloride of 10-amino- $\alpha'\beta'$ -naphthacarbazole was obtained in the form of colourless needles or leaflets, which on treatment with aqueous ammonia gave the free base as clear crystals, m. p.  $225^\circ$ . The base



is stable towards the atmosphere, gives an alcoholic solution with a blue fluorescence, and forms an *acetyl* derivative, colourless needles, m. p. 283°.

D. F. T.

**Preparation of Chloroanthrapyridones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264010. Compare A., 1908, i,



456; 1909, i, 256, 524).—*Chloroanthrapyridone* (annexed formula), glistening yellow needles, m. p. 256—257°, is obtained in quantitative yield when the calculated amount of chlorine is passed through an acetic acid solution of *N*-methylantrapyridone at 80—100°; the chlorine atom is very reactive, for when this compound is heated with alcoholic sodium sulphide it gives rise to the corresponding *thiophenol*; or with aniline furnishes an *anilide*, and

with potassium hydroxide a *phenol* which exhibits a green fluorescence in alkaline solution. If 4-bromo-1-*N*-methylantrapyridone is subjected to the action of chlorine it furnishes a *chlorobromoanthrapyridone*, long needles, m. p. 287—288°, whilst the chlorinated compounds obtained from 1-*N*-*p*-tolylantrapyridone, and from the two anthrapyridones prepared from diacetyl-1:5-dimethyldiaminoanthraquinone and acetyl-1-aminoanthraquinone respectively, are also described.

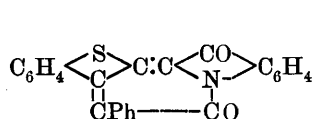
F. M. G. M.

**Preparation of Anthraquinonethiazoles.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 264943).—When 2-aminoanthraquinones containing a free ortho-position are heated with sulphur, hydrogen sulphide, or metallic sulphides and benzotrichloride in the presence of a suitable solvent they furnish thiazoles which are employed in the preparation of dyes. Thus when naphthalene (120 parts), 2-aminoanthraquinone (30 parts), benzotrichloride (40 parts), and sulphur (20 parts) are boiled together for two to three hours they furnish a thiazole identical with that obtained from 2-amino-1-thiolanthraquinone and benzaldehyde or benzotrichloride.

3-Bromo-2-aminoanthraquinone in a similar manner gives rise to the corresponding *bromoanthraquinonethiazole*, whilst the *anthraquinonethiazoles* obtained from 2:3-, 2:6-, and 2:7-diaminoanthraquinone are also described.

F. M. G. M.

**Preparation of Red Condensation Products of the Indigo Series.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P.



263470. Compare A., 1913, i, 763).—The compound (annexed formula), red crystals, is obtained when 2-thionaphthen-2-indole (20 parts) and phenylacetyl chloride (80 parts) are boiled together in xylene solution; the mixture becomes

coloured orange-red, and the product separates from the filtered solution on cooling; the *sulphonic acid* dyes wool in orange tints.

F. M. G. M.

**Preparation of isoSelenazoles of the Anthraquinone Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264139. Compare A., 1910, i, 338).—*Anthraquinoneselenazole*,  $C_{14}H_7ONSe$ , fine needles, m. p. 203, is obtained when 3.1 parts of 1-selenocyananthraquinone (yellow needles, m. p. 249°, obtained by heating 1-diazoanthraquinone with potassium selenocyanate) are heated at 120–160° with concentrated ammonium hydroxide (38 parts) during four to five hours; whilst *potassium 1-selenocyano-5-anthraquinone-sulphonate* (yellow needles), when left in contact with ammonium hydroxide during several days, gives rise to *anthraquinoneselenazole-sulphonic acid*, green needles. These compounds are of therapeutic value. F. M. G. M.

[Preparation of Derivatives of *p*-Phenylenediaminesulphonic Acid.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 263655).—The compounds are obtained by condensing *p*-aminodiphenylaminesulphonic acids or their substitution products with 4-chloro-1:3-dinitrobenzene.

5-op-Dinitroanilino-2-*p*-toluidinobenzenesulphonic acid,  $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_3(SO_3H) \cdot NH \cdot C_6H_4Me$ , is prepared in this way from sodium 4-amino-2-*p*-toluidinobenzene-2-sulphonate. The substances, of which this is an example, dye wool in yellow to brown shades. J. C. C.

**Preparation of 1-Halogen-2:3-naphthisatins and their  $\alpha$ -1'-Halogen-naphthaloids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264265).—It has been shown (A., 1904, i, 832, 893) that  $\beta$ -hydrocyanocarbodinaphthylimides are converted into  $\beta$ -naphthisatin derivatives by means of concentrated sulphuric acid, and this

reaction has now been carried out with its chloro-derivatives by the action of aluminium chloride.

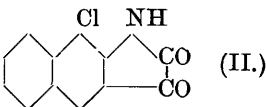
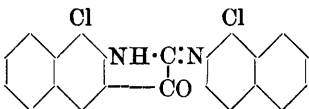
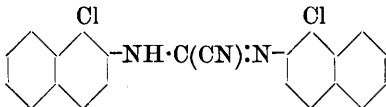
1:1'-Dichloro-2:2'-hydrocyanocarbodinaphthylimide (annexed formula), yellow needles, m. p. 201°, is prepared by the action of sulphuryl chloride on 2:2'-hydrocyanocarbodinaphthylimide; when this compound is suspended in dry benzene and slowly treated with aluminium chloride at 30–35°, the mixture becomes bluish-black, and after treatment with water and removal of the solvent, furnishes

1-chloro-2:3-naphthisatin- $\alpha$ -1'-chloronaphthalide (formula I), dark brown needles, m. p. 280°, which, on

hydrolysis with dilute sulphuric acid, gives rise to 1-chloro-2:3-naphthisatin (formula II), red needles, m. p. 258–259°; and this when treated with phosphorus pentachloride furnishes an  $\alpha$ -chloro-derivative, which can be reduced to a dichloro-

*naphthindigotin* or other indigoid derivative.

On further halogenation the foregoing compound gives rise to a 1-chlorobromo-2:3-naphthisatin, m. p. 313°, and a dichloro-2:3-naphthisatin, m. p. 258–259°.



1 : 1'-*Dibromo-2 : 2-dinaphthylthiocarbamide*, colourless crystals, m. p. 185°, is obtained from 1-bromo-2-naphthylamine by means of a carbon disulphide (compare Braun, A., 1907, i, 123); this when treated with lead carbonate and potassium cyanide is converted into 1 : 1'-*dibromohydrocyanocarbo-2 : 2'-dinaphthylimide*, yellow needles, m. p. 203°, which successively furnishes 1-bromo-2 : 3-naphthisatin- $\alpha$ -1'-bromo-naphthalide (glistening, coppery, dark violet needles, m. p. 254°) and 1-bromo-2 : 3-naphthisatin, red needles, m. p. 256°. *Dibromo-2 : 3-naphthisatin* has m. p. 295°.

F. M. G. M.

**Preparation of  $\alpha$ -Substituted Indoles.** WALTER MADELUNG (D.R.-P. 262327).—When aromatic monoacylamino-compounds which contain a methyl group in the ortho-position are heated at 340—380° with alkaline earth oxides or alkali ethoxides, they furnish  $\alpha$ -substituted derivatives of indole.

2 : 2'-*Di-indyl* (annexed formula), yellow crystals, m. p. 300° (decomp.), is obtained when oxalo-*o*-toluidide is heated at 360° with sodium amyloxide; it forms a *picrate*, violet-brown needles, m. p. 178° (decomp.), which contains 2 mols. of picric acid combined with 1 mol. of di-indyl.

The preparation of 2-methylindole from aceto-*o*-toluidide, of 2-phenylindole from benzo-*o*-toluidide, of 2 : 5-dimethylindole from *m*-4-xylidine, and of indole-2-carboxylic acid from potassium *o*-tolylloxamate is also described.

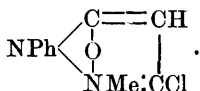
F. M. G. M.

**Constitution of "Anilipyryne."** E. COMANDUCCI (*Boll. chim. farm.*, 1913, 52, 717—718. Compare A., 1913, i, 296, 903).—Polemical. A reply to Zampolli, A., 1913, i, 1101.

R. V. S.

**3- and 5-Monochloro-1-phenyl-2-methylpyrazolone.** A. MICHAELIS and ERNST KIRSTEIN (*Ber.*, 1910, 46, 3603—3611).—3-Chloro-1-phenyl-5-pyrazolone (Michaelis and Roemer, A., 1899, i, 234), when heated with methyl sulphate, is converted into

3-chloro-1-phenyl-2-methyl-5-pyrazolone,  $\text{NPh} \begin{matrix} \text{CO} \text{---} \text{CH} \\ \diagdown \quad \diagup \\ \text{NMe} \cdot \text{CCl} \end{matrix}$  or

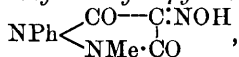


This separates in long needles or monoclinic, twin crystals, m. p. 67°. The *hydrochloride* forms short, yellowish-white crystals, m. p. 177°, which diliquesce on exposure. The *platinichloride* crystallises in yellowish-red prisms, m. p. 216° (decomp.). The *aurichloride*,



forms bright yellow crystals, m. p. 121°. The *picrate* separates in long, yellow needles, m. p. 130°.

4-Oximino-1-phenyl-2-methyltetrahydropyrazole-3 : 5-dione,



prepared by the action of sodium nitrite on 3-chloro-1-phenyl-2-methyl-

pyrazolone, crystallises in deep red needles, m. p. 180° (decomp.). It is easily converted into the corresponding 4-amino-1-phenyl-2-methyltetrahydropyrazole-3:5-dione, which is characterised by lustrous colourless platelets, m. p. 181° (decomp.), to a brownish-red liquid. The hydrochloride forms colourless platelets.

3-Chloro-1-phenyl-2-methyl-5-pyrazolone forms a 4-bromo-derivative, separating in lustrous, colourless crystals, m. p. 152°. The 4-iodo-derivative, m. p. 182°, is very similar.

2:3:5-Trichloro-1-phenyl-2-methylpyrazole,  $\text{NPh} \begin{array}{l} \text{NMeCl}:\text{CCl} \\ \text{CCl}=\text{CH} \end{array}$ , has m. p. 155—158°. The corresponding methiodide forms colourless crystals, m. p. 166—167°. On heating this with silver oxide and water, 5-chloro-1-phenyl-2-methyl-2:3-pyrazolone,  $\text{NPh} \begin{array}{l} \text{NMe}\cdot\text{CO} \\ \text{CCl}=\text{CH} \end{array}$ , is obtained in monoclinic needles, m. p. 117°. The 4-bromo-derivative forms colourless prisms, m. p. 112°.

5-Chloro-1-phenyl-2-methyl-3(or 2:3)-thiopyrazolone, prepared by the action of sodium sulphide on the methiodide of dichloropyrazole, forms colourless crystals without lustre, m. p. 123°.

3:5-Dichloro-4-bromo-1-phenylpyrazole forms a methosulphate,  $\text{C}_9\text{H}_5\text{N}_2\text{Cl}_2\text{Br}\cdot\text{Me}_2\text{SO}_4$ , crystallising in colourless prisms, m. p. 210°, which is converted by potassium iodide into a methiodide,  $\text{NPh} \begin{array}{l} \text{CCl}=\text{CBr} \\ \text{NIMe}:\text{CCl} \end{array}$ , characterised by colourless, matted needles, m. p. 178°. Sodium sulphide converts it into the 4-bromo-derivative of the above thiopyrazolone, which crystallises in large, colourless prisms, without lustre, m. p. 185°. The methiodide forms tiny matted needles, m. p. 173°, that of the unbrominated thiopyrazolone being a crystalline powder, m. p. 190°.

5-Anilino-1-phenyl-3-anilopyrine,  $\text{NPh} \begin{array}{l} \text{NMe}\cdot\text{NPh} \\ \text{C}=\text{CH} \end{array} \text{C}\cdot\text{NHPh}$ , forms a colourless, voluminous, crystalline powder, m. p. 190°. The hydriodide separates in colourless needles, m. p. 112°; the hydrochloride forms lustrous platelets, m. p. 145°. E. F. A.

**Preparation of  $\omega$ -Methosulphites of Amino-substituted Arylpyrazolones.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 263458).—4-Amino-1-p-tolyl-3-methyl-2-ethyl-5-pyrazolone is obtained by the reduction of the nitroso-derivative of 1-p-tolyl-3-methyl-2-ethyl-5-pyrazolone (m. p. 90°); when warmed with a mixture of formaldehyde and sodium hydrogen sulphite solution it gives sodium 4-amino-1-p-tolyl-3-methyl-2-ethyl-5-pyrazolone methosulphite, m. p. 90—100°, decomp. 118°.

4-Amino-1-p-phenetyl-3-methyl-2-ethyl-5-pyrazolone, m. p. 67°, is prepared in a similar manner from the nitroso-derivative of 1-p-phenetyl-3-methyl-2-ethyl-5-pyrazolone, m. p. 119—120°, and with formaldehyde and bisulphite furnishes sodium 4-amino-1-p-phenetyl-3-methyl-2-ethyl-5-pyrazolone methosulphite, m. p. 98°, decomp. 115°, whilst sodium 1-p-aminophenyl-3-methyl-2-ethyl-5-pyrazolone methosulphite, sintering at 130° when exposed to air and (when dried over sulphuric acid)

m. p. 262—263°, is prepared from 1-*p*-aminophenyl-3-methyl-2-ethyl-5-pyrazolone, m. p. 225°. F. M. G. M.

**Preparation of a Mercury Derivative of the Pyrazolone Series.** LEON GIVAUDAN and EMIL SCHEITLIN (D.R.-P. 266578. Compare A., 1913, i, 1239).—A compound resembling that previously described, but containing 66% of mercury, is obtained by warming a mixture of mercuric oxide and 4-sulphamo-1-phenyl-2:3-dimethyl-5-pyrazolone with the addition of sodium hydrogen sulphite as reducing agent. J. C. C.

**Methylphenazonium Iodide.** A. HANTZSCH (*Ber.*, 1913, 46, 3588—3589).—A reply to Kehrmann and Havas, who have stated (A., 1913, i, 1241) that confirmation has been obtained of the quinhydrone nature of the green methylphenazonium iodide (compare Hantzsch, *ibid.*, i, 393, 903). D. F. T.

[Preparation of Derivatives of Perimidine.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 264292, 264293).—Compounds obtained by the fusion of nitro- or amino-perimidines with polysulphides have previously been described, and the reaction has now been extended to the case of the parent substance and other derivatives.

Perimidine (20 parts), crystalline sodium sulphide (180 parts), sulphur (50 parts), and copper (10 parts) are heated together at 200—250° during eight to ten hours; the *product* dyes cotton in brown shades.

*Perimidinesulphonic acid*, a pale yellow, crystalline powder, is obtained by heating 1:8-naphthylenediamine-4-sulphonic acid with formic acid; *perimidine-5:8-disulphonic acid*, yellow crystals, is prepared in a similar manner from 1:8-naphthylenediamine-3:6-disulphonic acid, whilst ethyl-1:8-naphthylenediamine gives rise to *ethylperimidine*. These compounds, and those described below, also furnish colouring matters when heated with sulphur and sodium sulphide.

II. Describes the preparation of similar *compounds* from the fusion of 1:8-naphthylenethiocarbamide derivatives with polysulphides.

1:8-Naphthylenethiocarbamide-3:6-disulphonic acid, yellowish-white leaflets, is prepared by the action of carbon disulphide on 1:8-naphthylenediamine-3:6-disulphonic acid.

Dinitro-1:8-naphthylenethiocarbamide, a yellowish-brown powder, is prepared by the action of nitric acid (2 mols.) on an acetic acid suspension of naphthylenethiocarbamide; mononitrothiocarbamide is a greyish-brown powder, and 1:8-naphthylenethiocarbamide-4-sulphonic acid forms greyish-white leaflets. F. M. G. M.

[Preparation of Phthaloperinone Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 263903).—An account of the preparation and tinctorial properties of *compounds* prepared by the fusion with polysulphides of (1) phthaloperinone, (2) phthaloperinone-sulphonic and (3) -disulphonic acids.



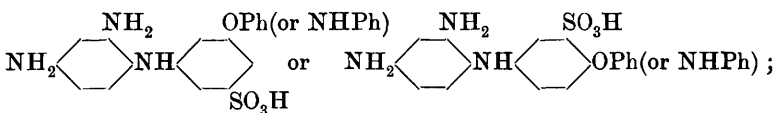
*Perimidyl-5 : 8-disulphonyl-o-benzoic acid*, orange leaflets, is obtained by the condensation of 1 : 8-naphthylenediamine-3 : 6-disulphonic acid with phthalic anhydride in aqueous solution ; when heated at 180—200°, it loses water and gives rise to *phthaloperinone-5 : 8-disulphonic acid*, a brownish-red powder.  
F. M. G. M.

[Preparation of Halogenated Compounds of the Rosaniline Series.] LEOPOLD CASSELLA & Co. (D.R.-P. 264942).—Halogenated compounds of the rosaniline series can be prepared by heating *o*-halogenated primary or secondary aromatic amines with *p*-aminobenzaldehyde and arsenic acid either in the presence or absence of zinc chloride.

*Dichloropararosaniline*, a metallic green, microcrystalline, glistening powder, is obtained when a mixture of *p*-aminobenzaldehyde (12 parts), *o*-chloroaniline (22·5 parts), and arsenic acid (44 parts) is heated first at 105° and then at 140—145° for five to six hours.

*Dibromopararosaniline hydrochloride*, an olive-green, crystalline powder, is obtained in a similar manner from *o*-bromoaniline, whilst *o*-chlorotoluidine gives rise to *dichlorodimethylpararosaniline*, a green, glistening, metallic powder.  
F. M. G. M.

[Preparation of Derivatives of Diaminodiphenylamine-sulphonic Acids.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 265197).—A description of the tinctorial properties of compounds of general formulæ :



they are obtained by condensing amino-*m*-sulphophenyl ethers or aminodiphenylamine-*m*-sulphonic acids with 4-chloro-1 : 3-dinitrobenzene and subsequent reduction of the condensation products.

The condensation of 4-phenoxy-2' : 4'-diaminodiphenylamine-3-sulphonic acid and of 4-anilino-2' : 4'-diaminodiphenylamine-3-sulphonic acid with 4-chloro-1 : 3-dinitrobenzene is also described.  
F. M. G. M.

[Preparation of Anthrimides.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 262788).—*Tetra-anthrimide* (1<sup>2</sup> : 1<sup>3</sup>-dianthraquinonyl-4 : 4'-diamino-1 : 1'-dianthrimide), a dark violet powder, is obtained when 4 : 4'-diamino-1 : 1'-dianthrimide (1 mol.) is condensed with 1-chloroanthraquinone (2 mols.) ; when fused at 260—270° with aluminium chloride it furnishes a grey powder, which dyes cotton in olive-grey shades.

*Penta-anthrimide* (*tetra-a-anthraquinonyl-1 : 4 : 5 : 8-tetra-aminoanthraquinone*), a black powder, is prepared by the condensation of 1-aminoanthraquinone (4 mols.) with 1 : 4 : 5 : 8-tetrachloroanthraquinone (1 mol.), and furnishes similar dyes when heated with aluminium chloride.  
F. M. G. M.

**Pyrimidone Chloride and 4-Aminoantipyrine Chloride.**

A. MICHAELIS and BRUNO STAU (*Ber.*, 1913, **46**, 3612—3615).—*Pyrimidone chloride* or the *methochloride* of 5-chloro-4-dimethylamino-

1-phenyl-3-methylpyrazole,  $\text{NPh} \begin{array}{c} \text{CCl}=\text{C}\cdot\text{NMe}_2 \\ \text{NMeCl}\cdot\text{CMe} \end{array}$ , crystallises in well formed, colourless platelets, m. p. 102°. The *methiodide*,

$\text{C}_{12}\text{H}_{14}\text{N}_3\text{Cl}\cdot\text{CH}_3\text{I}$ , forms tiny, colourless crystals, m. p. 220°.

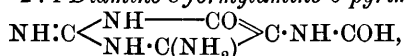
On heating pyrimidone chloride, 5-chloro-4-dimethylamino-1-phenyl-3-methylpyrazole,  $\text{NPh} \begin{array}{c} \text{CCl}\cdot\text{C}\cdot\text{NMe}_2 \\ \text{N}=\text{CMe} \end{array}$ , is obtained as a colourless, viscid

oil, b. p. 189—190°/35 mm. The *hydrochloride* forms monoclinic plates; the *methiodide* is characterised by long, colourless needles, m. p. 169°, and contains the methyl iodide attached to the dimethylamine residue in position 4. The *methochloride* of 5-chloro-4-amino-

1-phenyl-3-methylpyrazole,  $\text{NPh} \begin{array}{c} \text{CCl}=\text{C}\cdot\text{NH}_2 \\ \text{NMeCl}\cdot\text{CMe} \end{array}$ , prepared by the

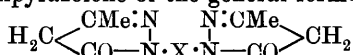
action of phosphoryl chloride on benzylideneaminoantipyrine, forms tiny, colourless crystals, m. p. 201° (decomp.). The *methiodide* crystallises in long needles. E. F. A.

**Preparation of 2:4-Diamino-5-formylamino-1-methyl-6-pyrimidone.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 264009).—2:4-Diamino-5-formylamino-6-pyrimidone,



decomposes without fusion on heating and is obtained by heating 2:4:5-triamino-6-pyrimidone with 70% formic acid for three to four hours at 100°; when methylated it gives 2:4-diamino-5-formylamino-1-methyl-6-pyrimidone, which crystallises from water in long needles containing 1 mol. of solvent of crystallisation; when heated at 290—295° it is converted into 1-methylguanine. F. M. G. M.

[Preparation of Dipyrazolone Derivatives.] ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 264287).—When 2 mols. of a diazosulphodiphenyl ether or its substitution products are combined with 1 mol. of a dipyrazolone of the general formula



(where X is an aromatic residue), *compounds*, are obtained which dye wool in greenish-yellow shades.

The *dipyrazolone* obtained by the condensation of 4:4'-dihydrazinodi-*m*-tolylmethane with acetoacetic ester is a colourless powder with indefinite m. p. The analogous *compounds* from 3:3'-dichloro-4:4'-diaminodiphenylmethane, and from 4:4'-diamino-2:5:2':5'-tetramethyldiphenylmethane are colourless, and that from 4:4'-diamino-3:3'-dimethylbenzophenone is yellow.

The tinctorial properties of *compounds* obtained from the condensation of these with diazotised aminodiphenyl ether or its derivatives are described. F. M. G. M.

**Methylation of Guanine and New Syntheses of Paraxanthine, Heteroxanthine, and 1-Methylxanthine.** WILHELM TRAUBE and HAROLD W. DUDLEY (*Ber.*, 1913, 46, 3839—3852).—When guanine is methylated by means of methyl chloride in presence of sodium hydroxide a mixture of the 7-methylguanine and 1:7-dimethylguanine previously described by Fischer (*A.*, 1898, i, 98) is obtained.

To obtain 1-methylguanine, 
$$\begin{array}{c} \text{NMe} \cdot \text{CO} - \text{C} \cdot \text{NH} \\ | \qquad \qquad | \\ \text{C}(\text{NH}_2) : \text{N} - \text{C} - \text{N} \end{array} \geq \text{CH}, 3:4:5\text{-triamino-6-pyrimidone}$$
 is warmed with dilute formic acid for a short time and treated with methyl sulphate. On boiling the *formyl-2:4:5-triamino-1-methyl-6-pyrimidone* so obtained with concentrated formic acid, it is converted into 1-methylguanine. The constitution of this is established by its conversion under the influence of nitrous acid into the known 1-methylxanthine.

Further methylation of 1-methylguanine converts it into 1:7-dimethylguanine, which forms a crystalline *methiodide* and *methochloride*, and is converted by nitrous acid into paraxanthine. In a similar manner, 7-methylguanine is converted into 7-methylxanthine (heteroxanthine). Higher methylated xanthines could not be prepared.

The *formyl* derivative of 2:4:5-triamino-6-pyrimidone crystallises in thin, colourless, lustrous platelets; it decomposes slowly when heated. The *sodium* salt crystallises in long needles. The 1-methyl derivative crystallises in long, slender needles, which are converted into 1-methylguanine when heated. 1-*Methylguanine* forms a heavy, colourless, crystalline powder; on heating it chars without melting. The *sodium* salt separates in thin platelets. Other salts described are the *hydrochloride*, crystallising in long, thin plates; the *sulphate*, which forms a mixture of thin plates and bent needles; the *nitrate*, which crystallises in well formed prisms; the *platinichloride*, which separates in stout, yellow needles, aggregated in lumps, and the *double salt* with silver nitrate crystallising in rosettes of slender or bent needles.

1:7-*Dimethylguanine methiodide* crystallises in lustrous, large, colourless plates, m. p. 330—333°. The corresponding *methochloride* forms thin platelets, m. p. 297—300°.

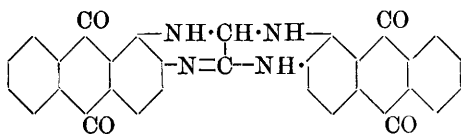
*Trimethylguanine methiodide* crystallises in colourless, slender needles, m. p. 295—300° (decomp.). The corresponding *methochloride* forms long needles, m. p. 267—271°.

E. F. A.

**Formation of Complexes in Solutions of Uric Acid and Urates.** RUDOLF KOHLER (*Zeitsch. physiol. Chem.*, 1913, 88, 259—271).—Polemical (compare Kohler, *A.*, 1911, i, 243, 690; Ringer, *A.*, 1911, i, 1044). Solubility measurements made at 37° and 70° confirm those originally made at 18°, and prove that quadriurates do not exist. Even by electrical conductivity methods their presence in solution could not be established.

E. F. A.

[Preparation of Derivatives of Anthraquinone.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 264043).—When an acetic acid



solution of 1:2-diaminoanthraquinone (2 mols.) is boiled with glyoxylic acid (1 mol.), it furnishes the compound (annexed formula), a bluish-black powder, in-

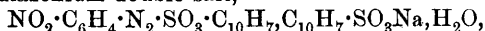
soluble in the ordinary organic solvents, but crystallisable from quinoline.

Similar compounds from 2:3-diaminoanthraquinone and 1:2:3-triaminoanthraquinone are described; this experiment can also be conducted in alcoholic solution in the presence of sulphuric acid.

F. M. G. M.

**The Constitution of "Aged" and of "Bichromate" Aniline-blacks.** II. A. G. GREEN and W. JOHNSON (*J. Soc. Dyers*, 1913, 29, 338—343; *Ber.*, 1913, 46, 3769—3779).—See P., 1913, 29, 276.

**Preparation of Stable Nitrobenzenediazonium Double Salt.** OTTO N. WITT (D.R.-P. 264268).—A stable non-explosive nitrobenzenediazonium double salt,



is obtained when two molecular proportions of naphthalene-2-sulphonic acid are added to a solution of *p*-nitrobenzenediazonium chloride; it forms glistening, citron-yellow needles, which give a neutral reaction in aqueous solution.

F. M. G. M.

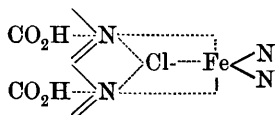
**Benzoyl Compounds of Proteins.** F. BLUM and TH. UMBACH (*Zeitsch. physiol. Chem.*, 1913, 88, 285—323).—Proteins are preferably benzoylated with benzoyl chloride in sodium hydrogen carbonate solution. The products obtained were insoluble in all solvents, and represented a colourless or yellow powder of granular or sometimes crystalline character. On heating they become brown about 115°, and decompose as the temperature is increased.

Analytical details are given of the products from a number of proteins. The blood globulin preparations from different animals show definite differences after benzoylation.

E. F. A.

**Constitution of Hæmin.** WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1913, 88, 377—388).—A criticism of the recent conclusions of Willstätter (*A.*, 1913, i, 1251).

There is a marked difference in the behaviour of hæmin and its dimethyl ester to hydrochloric acid, the latter losing more iron than hæmin itself under similar conditions. The position of the iron in the hæmin molecule is accordingly formulated as annexed constitution.



The formula  $\text{C}_{33}$  instead of  $\text{C}_{34}$  for hæmin is not accepted, and it is considered possible that carbon is eliminated in the formation of a etiophyllin.

E. F. A.

**A Nucleic Acid from the Pancreas.** R. FEULGEN (*Zeit.ch. physiol. Chem.*, 1913, 88, 370—376).—It is well known that the pancreas contains a mono-nucleotide (guanylic acid), but other observers have found that it yields also a nucleic acid, which is a polynucleotide, and this has been assumed to be similar to that found in other organs, for instance, the thymus, which yields the usual four bases. In the present paper it is shown that the reactions, elementary composition, and cleavage products of this nucleic acid are different from those of the thymus, and this is due to the fact that it yields three bases only (adenine, cytosine, and thymine), but no guanine.

W. D. H.

**Influence of Some Chemical Substances on Peptic Proteolysis.** MAURICIO CANÓNICA (*Anal. Soc. Quim. Argentina*, 1913, 1, 104—122).—Quantitative data are given of the retarding or accelerating effect of many salts, alcohols, sugars, and organic compounds in varying concentrations on the hydrolysis of egg-albumin by pepsin-hydrochloric acid. Amongst salts, strontium lactate exerts the least, and sodium arsenate the greatest, retarding influence. With benzoic and salicylic acids, the influence of the salt (sodium) in small proportions is equal to that of an equimolecular proportion of free acid, but in larger concentrations (0.5 to 2.0%) the effect of the salt is larger.

The presence of glycerol or of sucrose appears to augment the inhibitory effect of alcohol.

Amongst organic acids, acetic, tartaric, citric, and gallic have little effect; oxalic, benzoic, and *o*-acetoxybenzoic retard, whilst tannic is very prejudicial to the digestion.

Of organic medicaments in general, those of phenolic character cause the greater inhibition. Methylene-blue up to 1%, and caffeine up to 2%, exercise an accelerating influence.

G. D. L.

**Erepsin.** P. RONA and F. ARNHEIM (*Biochem. Zeitsch.*, 1913, 57, 84—94).—The conditions under which erepsin acts are very similar to those of trypsin. Here, also, the anions are the proteolytically active parts of the molecule. The optimal action lies at  $[H^+] = 2.10^{-8}$ , and the acid dissociation constant is  $1.2 \times 10^{-6}$ . The numbers differ slightly, but appreciably, from the corresponding numbers for trypsin. The optimal point of action of erepsin agrees very closely with the hydrogen-ion concentration of the intestinal juice of the dog, as determined by Auerbach and Pick. The methods of experiment and calculation are those that have been repeatedly employed by Michaelis and his pupils.

S. B. S.

**The Conditions of Action of the Maltase of Beer Yeast.** L. MICHAELIS and P. RONA (*Biochem. Zeitsch.*, 1913, 57, 70—83).—Maltase is active and preservable only in the form of its anions. Excess of alkali destroys the ferment with the formation of bivalent anions. Strong acidification also destroys the ferment, with the precipitation of a substance of nucleoprotein-like character. The optimal condition of precipitation is at the isoelectric point of the nucleoprotein, and this is apparently the isoelectric point of the

ferment. Its optimal conditions of action lie between  $p_H=6.1$  and  $p_H=6.8$ , that is, in a solution which is just acid. This differs markedly from the optimal conditions of action of invertase (optimal point  $p_H=4.5$ ), under which, not only is maltase inactive, but is even destroyed. Furthermore, in the case of invertase, only the electrically neutral molecules are active, whereas in the case of maltase, the anions are active. The invertase, also, is soluble in solutions of all hydrogen ion concentrations, whereas the maltase is precipitated at its isoelectric point. Maltase, also, is adsorbed by kaolin, whereas invertase is not.

S. B. S.

**Conditions of Action of Maltase of Beer-yeast. II. The Action of Maltase on  $\alpha$ -Methylglucoside and the Affinity Constant of the Ferment.** P. RONA and L. MICHAELIS (*Biochem. Zeitsch.*, 1913, 58, 148—157).—The ferment exerts its optimal action between  $p_H=5.8$  and  $6.6$ . The conditions of action, as regards the hydrogen ion concentration, are very near to, if not identical with, those of the maltose hydrolysis. The affinity constant of  $\alpha$ -methylglucoside is  $11.1$ , which is markedly lower than the constant of the invertase-sucrose compound. The graphical method of determining the constant is described in detail, and is similar to that employed by Michaelis and his co-workers in determining the affinity constants of other ferments to their substrates.

S. B. S.

**The Action of Radium Emanation on Lipase.** E. K. MARSHALL, jun., and L. G. ROWNTREE (*J. Biol. Chem.*, 1913, 16, 379—384).—No accelerating influence is exerted by radium emanation on the lipase of pig's liver, or of castor oil bean; the change is rather in the direction of inhibition.

W. D. H.

**Studies on Enzyme Action. VIII. The Action of Amino-acids and Castor Bean Lipase on Esters.** MARSTON LOVELL HAMLIN (*J. Amer. Chem. Soc.*, 1913, 35, 1897—1904).—A continuation of the previous investigation (Hamlin, A., 1913, i, 665; Falk and Nelson, A., 1912, i, 593; Falk, A., 1913, i, 664).

The hydrolytic action of various amino-acids on esters has already been investigated, and the effect of alanine, of phenylalanine, and of castor bean lipase towards methyl, ethyl, glyceryl and phenyl acetates, ethyl butyrate, and ethyl and phenyl benzoates has been examined. Castor oil and olive oil also were examined with respect to the effect of the castor bean lipase, and as the experimental conditions were slightly modified, the action of glycine towards the above esters was again studied.

It is found that the behaviour of alanine and phenylalanine is markedly similar to that of glycine. It is shown that under suitable conditions the hydrolysis of methyl acetate in a solution containing glycine, sodium chloride, and hydrochloric acid is not the same as in an isohydric solution of hydrochloric acid, and that in some cases a change in conditions which causes an increase in the hydrolysis of methyl acetate may produce a decrease in the hydrolysis of ethyl butyrate.

D. F. T.

**Studies on Enzyme Action. IX. Extraction Experiments with the Castor Bean Lipase.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, **35**, 1904—1915. Compare A., 1913, i, 303, 433, 664, etc.).—An account of experiments attempting the separation of the lipase preparation into soluble and insoluble fractions, the resulting fractions being examined as to their activity towards ethyl butyrate and glyceryl triacetate.

Extraction experiments with water indicate that about half the effect is reached in the first minute, a limit being practically attained after twenty-four hours' extraction, when about 70% of the active material (tested by ethyl butyrate) has passed into the water. When the hydrolytic activity of the extract is tested by glyceryl triacetate, however, it is found that only 50% of the material active in this direction can be extracted; this is interpreted as indicating the presence of two enzymes, the less soluble of which is more active towards glyceryl triacetate.

The results obtained when a solution of methyl alcohol, sodium fluoride or sodium chloride is used for the extraction confirm the above view of the composite nature of the lipase preparation.

D. F. T.

**The Deamidising Action of Tyrosinase.** R. CHODAT and K. SCHWEIZER (*Biochem. Zeitsch.*, 1913, **57**, 430—436. Compare A., 1913, i, 411).—The authors have already shown that colour reactions are produced when amino-acids are treated in the presence of *p*-cresol or other phenols with tyrosinase in weakly alkaline solutions (lime water). It is now shown that the tyrosinase exerts in these circumstances a deamidising action, and in the case of glycine and some other amino-acids, formaldehyde is also produced. The presence of dextrose inhibits the deamidising action. Chlorophyll in the presence of light and carbon dioxide was found to produce practically no formaldehyde from glycine. It accelerates, however, the production of formaldehyde in the presence of tyrosinase. This accelerating action takes place both in the light and in the dark, even in the absence of lime water. This particular action, therefore, is to be distinguished from the photosynthetical formation of formaldehyde in the presence of chlorophyll, which requires the action of light.

S. B. S.

**Preparation of Phenylarsinic Acid.** CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.P. 264924).—A solution of benzenediazonium nitrate is neutralised with sodium hydroxide and the cooled solution slowly added to a mixture of sodium arsenite, sodium hydroxide and precipitated cuprous oxide; when the evolution of nitrogen has ceased, the solution is reduced alkaline with barium hydroxide, filtered, and the product isolated by the addition of hydrochloric acid.

F. M. G. M.

**Preparation of 2:4-Dinitrophenylarsinic Acid.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 266944).—The formation of aromatic arsinic acids by the action of arsenious acid on diazonium salts usually occurs only in alkaline or neutral solutions. Diazotised

2:4-dinitroaniline, however, only reacts in the presence of mineral acids in excess.

The base is dissolved in concentrated sulphuric acid, diazotised at 25° by means of nitrosylsulphuric acid, and, after dilution with ice, a solution of sodium arsenite is added. The reaction is completed by warming, and then the liquid is clarified and saturated with salt 2:4-Dinitrophenylarsinic acid,  $C_6H_3(NO_2)_2 \cdot AsO_3H_2$ , forms colourless velvety needles, m. p. 199—200°. J. C. W.

**Preparation of a Nitroaminophenylarsinic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 267307).—Contrary to expectation, it was found that 2-nitro-4-acylaminophenylarsinic acids may be hydrolysed by acids or alkalis without affecting the arsinic acid group. Further, it is unnecessary to isolate the acyl derivative when the free amino-compound is required, since the latter may be prepared by adding sodium arsenite to the diazotised nitromonoacyl-*p*-phenylenediamine in acid solution and boiling, after the diazo-reaction is over.

Thus 2-nitro-4-acetylaminophenylarsinic acid, which forms yellow, microscopic needles, yields 2-nitro-4-aminophenylarsinic acid,  $NO_2 \cdot C_6H_3(NH_2) \cdot AsO_3H_2$ , in orange-yellow needles, m. p. 258° (decomp.). J. C. W.

**Preparation of Neutral Derivatives of 3:3'-Diamino-4:4'-dihydroxyarsenobenzene, Soluble in Water.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 263460, 264014. Compare A., 1913, i, 1121).—3:3'-Diamino-4:4'-dihydroxyarsenobenzeneformaldehydesulphoxylic acid is obtained as a yellow precipitate when an aqueous solution of sodium 3-amino- or 3-nitro-4-hydroxyphenylarsinite is warmed at 100° with 2 parts of formaldehyde sulphoxylate.

II. States that the arsinic acids employed in the above reaction can be replaced by the corresponding arsenious oxides, and the preparation of the above compound from 3-nitro- and 3-amino-4-hydroxyphenylarsenious oxides is described. F. M. G. M.

**Arsenostibino- and Arsenobismutho-compounds.** P. EHRLICH and P. KARRER (*Ber.*, 1913, 46, 3564—3569).—The exceptional position occupied by the azo-compounds compared with the compounds of the types  $PR:PR$  and  $AsR:AsR$  in respect to colour and resistance to chemical action, for example, to oxidation, lends a special interest to the synthesis of analogous substances of the types  $AsR:SbR$  and  $AsR:BiR$ , for which the terms arsenostibino- and arsenobismutho- are suggested.

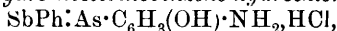
It is already known that arsines can undergo condensation with arsenoxides or dichloroarsines giving arseno-compounds of the structure  $AsR:AsR$ , and a similar condensation has now been effected between arsines and stibinoxides, dichlorostibines, and even inorganic antimony salts; bismuth chloride and bromide will also react with arsines. Condensation in all cases proceeds at the ordinary temperature, conveniently in alcoholic solution, and a wide range of arsines



can be applied. The arsenostibino-compounds are stable, brown substances resembling the corresponding arseno-compounds, but the black arsenobismutho-compounds are very unstable and are decomposed even by boiling water; they also undergo atmospheric oxidation.

The following are described as examples of the new classes of compound :

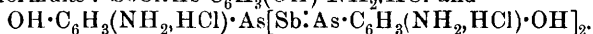
*3-Amino-4-hydroxyarsenostibinobenzene hydrochloride,*



is a brown, amorphous powder obtained by mixing phenyldichlorostibine with 3-amino-4-hydroxyphenylarsine in solution in methyl alcohol containing hydrogen chloride and subsequently adding ether; the sparingly soluble *sulphate* can be precipitated from a solution of the hydrochloride.

*p*-Acetylaminophenyldi-iodostibine,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SbI}_2$ , in solution in acetic acid when treated with a solution of 3-amino-4-hydroxyphenylarsine in methyl alcohol containing hydrogen chloride and subsequently with ether gives *3-amino-4-hydroxy-4'-acetylaminarsenostibinobenzene hydrochloride*,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{Sb}:\text{As}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2\cdot\text{HCl}$ , as a deep brown, amorphous powder readily soluble in water and methyl alcohol.

The product obtained on mixing antimony trichloride and 3-amino-4-hydroxyphenylarsine in solution in methyl alcohol containing hydrogen chloride consisted of a mixture of the substances represented by the formulæ:  $\text{SbCl}:\text{As}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2\cdot\text{HCl}$  and



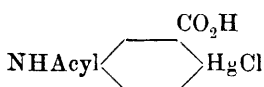
When bismuth chloride and 3-amino-4-hydroxyphenylarsine are mixed in solution in methyl alcohol containing hydrogen chloride with exclusion of air, the addition of ether precipitates a black *substance* of the formula  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{Cl}_3\text{As}_3\text{Bi}_2$ , the constitution probably being analogous to that of the preceding arsenostibino-compound. The substance is easily oxidised, for example, by hydrogen peroxide in alkaline solution, producing 3-amino-4-hydroxyphenylarsinic acid and bismuth pentoxide.

There are, therefore, five other types of substance known which are analogous to the azo-compounds, namely,  $\text{PR}:\text{PR}'$ ,  $\text{AsR}:\text{AsR}'$ ,  $\text{AsR}:\text{SbR}'$ ,  $\text{SbR}:\text{SbR}'$ ,  $\text{AsR}:\text{BiR}'$ . Of these the P:P-group is the weakest chromophore, the colour deepening in the order given; the azo-compounds occupy an abnormal position in connexion with this series. On account of their lack of colour, it is suggested that the substances described earlier as phosphazo-compounds (Michaelis and Schroeter, A., 1904, i, 241) are not of structure analogous to the azo-compounds, but are possibly analogous to the diazonium compounds.

The arsenostibino-compounds exhibit marked medicinal power.

D. F. T.

**Preparation of Derivatives of Aminobenzoic Acid Containing Mercury in the Ring.** VEREINIGTE CHEMISCHE WERKE AKT.-GES. (D.R.-P. 264388).—When the mercury salts of *m*-acylaminobenzoic acid are heated at 150—210° they furnish compounds



of the annexed general formula, and of therapeutic value. These are also obtained by heating the free acids with mercury oxide or the salts with a mercury salt.

*m*-Acetylaminomercuribenzoic acid chloride forms colourless needles, m. p.  $240^\circ$ ; the sodium, barium, lead, and silver salts are colourless powders; the iron salt is brown, and the nickel salt greenish-white.

*m*-Benzoylaminomercuribenzoic acid has m. p.  $220^\circ$ ; the sodium salt is a greyish-white powder; the barium, lead, and silver salts are colourless, and the iron salt is brown.

The corresponding lactyl, propionyl, and butyryl compounds are also mentioned, and on hydrolysis furnish *m*-aminomercuribenzoic acid.

F. M. G. M.

[Preparation of a Mercury-compound of Tyrosine.]  
DR. BAYER & Co. (D.R.-P. 267411, 267412).—When an aqueous solution of tyrosine is heated with freshly precipitated mercuric oxide until the colour of the latter vanishes (1st patent), or with mercuric acetate (2nd patent), a compound is precipitated, having the formula  $\text{C}_9\text{H}_9\text{O}_2\text{NHg}$ . The solution in alkali hydroxides, on neutralisation, yields the substance unchanged. The compound is intended for therapeutic application.

J. C. C.

## Physiological Chemistry.

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**The Composition of the Air in the Tracheal System of Insects.** AUGUST KROGH (*Skand. Arch. Physiol.*, 1913, 29, 29—36).—The tracheal system in the hind legs of the grasshopper can be rapidly and extensively ventilated by the respiratory movements of the insect. About 20% of the contained air can be renewed by one breath. The oxygen percentage of the air of the hind legs is high during rest (16%), but after exhausting muscular exercise it is reduced to 5%. The percentage of carbon dioxide is always much lower than the oxygen deficit, and a large part of the carbon dioxide formed in the tissues must be carried away by other means than through the tracheæ. W. D. H.

**Saline Perfusion of the Respiratory Centre in Frogs; the Effect of Calcium Chloride and Potassium Chloride.** D. R. HOOKER (*J. Pharmacol. expt. Ther.*, 1913, 4, 443—451).—When the respiratory centre is perfused with a suitable salt solution, it continues active for several hours. If the salt solution contains balanced quantities of calcium and potassium, removal of the potassium depresses, and of the calcium excites the centre. Increase of potassium depresses, and decrease excites. Increase of calcium excites, and decrease depresses. W. D. H.

**Chemical and Morphological Investigations on the Importance of Cholesterol in the Organism. IV. The Cholesterol Content of the Blood of Different Animals and the Influence of Cholesterol Intake, especially with the Food.** L. WACKER and W. HUECK (*Arch. expt. Path. Pharm.*, 1913, **74**, 416—441).—Simple shaking of fluids (blood, bile, etc.) with ether, chloroform, etc., for the purpose of extracting lipoids is not free from error, for the other colloid constituents of the fluid are affected. Cholesterol in the blood is contained in the corpuscles in the free state; the white corpuscles contain five times the amount of that in the red corpuscles. The blood fluid contains cholesterol partly free, partly as esters. Defibrination does not affect the cholesterol. The relationship of the free to the combined cholesterol varies in the animals used (rabbit, calf, dog, horse) from 1:1.7 to 1:3.3. It is affected by nutrition, muscular work, breathing, and other factors. By feeding on free cholesterol, the amount of free cholesterol in the blood serum is increased, but that in ester form is still more increased; it may reach twenty-two times the normal. The same result follows subcutaneous administration; the corpuscles are but little affected. In growing animals, cholesterol accelerates growth, leading especially to deposition of fat. The suprarenal cortex is richer in cholesterol and other lipoids. The same is true for other organs (liver, kidney, spleen, etc.). Continued administration leads to disorders of the alimentary canal, and to arterial sclerosis. W. D. H.

**Chemical and Morphological Investigations on the Importance of Cholesterol in the Organism. V. The Cholesterol Content of the Blood of the Dogfish (*Scyllium catulus*) under the Influence of Dyspnoea.** W. HUECK (*Arch. expt. Path. Pharm.*, 1913, **74**, 442—449).—The blood-plasma of *Scyllium* contains very little lipid (0.05%), and about half of this, 0.02%, is cholesterol. The red corpuscles contain only free cholesterol (0.08%); the plasma contains free cholesterol (0.015%), and cholesterol esters (0.005%). In narcosis, and in the dyspnoëic condition which follows exposure to air, the cholesterol esters of the blood quickly rise to tenfold the normal amount, and the free cholesterol is doubled. W. D. H.

**Chemical and Morphological Investigations on the Importance of Cholesterol in the Organism. VI. The Influence of Muscular Work on the Cholesterol Content of the Blood and Suprarenal Bodies.** EDWIN PICARD (*Arch. expt. Path. Pharm.*, 1913, **74**, 450—460).—In dogs, muscular work affects the amount of cholesterol in the blood, and in the suprarenal cortex in opposite directions. If the work is prolonged and increasing, the cholesterol esters of the cortex fall, and of the blood rise. In short, with rapid muscular exercise, the amount increases in the cortex, and slightly falls in the blood. W. D. H.

**The Permeability of Blood-corpuscles for Dextrose.** P. GYÖRGY (*Biochem. Zeitsch.*, 1913, **57**, 441—455).—It has been shown

by Rona and others that the blood-corpuscles of sheep are impermeable to dextrose, whereas those of dog and man are permeable. Experiments were carried out with the corpuscles of sheep to ascertain whether they could be made permeable, either by alteration of the hydrogen ion concentration of the artificial medium, in which the corpuscles were suspended, by means of regulators (phosphate, carbonate, or acetate mixtures), or by the addition of sugar to the whole blood in the presence of hæmolytics (present in quantities below those necessary to produce hæmolysis), and in the presence of various salts, such as those of calcium or aluminium. The results obtained were, however, negative.

S. B. S.

**The Behaviour of the Maltase of the Blood-serum of Fed and Fasting Animals.** T. KUMAGAI (*Biochem. Zeitsch.*, 1913, 57, 375—379).—The hydrolysis of maltose by the blood-serum obtained from fasting dogs takes place more rapidly than by that from fed animals. Quantities of serum which, when obtained from fed animals are inactive, produce distinct hydrolytic action when obtained from fasting animals. The results confirm those previously obtained by Kusumoto (A., 1909, ii, 69).

S. B. S.

**The Gastric Secretion at Birth.** ALFRED F. HESS (*Amer. J. Dis. Children*, 1913, 6, 264—276).—New-born infants secrete a good deal of hydrochloric acid before any food is given; it was found in fifty-one out of fifty-two cases. The amount is variable. The gastric juice in unfed new-born children also contains pepsin, rennin, and lipase.

W. D. H.

**Pancreatic Enzymes in Infants. I.** ALFRED F. HESS (*Amer. J. Dis. Children*, 1912, 4, 205—218).—In infants it is easy to obtain the duodenal contents by a long catheter; the pancreatic juice aspirated off in this way contains all the normal enzymes, but the total secretion is very scanty during the first week of life. Amylase increases in amount with age, so also does the total juice. Even in marasmic children, the amount secreted, although thin, is abundant, and contains all the enzymes, although it is weak in lipase. In these children the gastric juice is scanty.

W. D. H.

**Pancreatic Enzymes in Infants. II. In Acute Intestinal Indigestion.** ALFRED F. HESS (*Amer. J. Dis. Children*, 1913, 5, 268—272).—In acute indigestion (alimentary toxæmia), the lipase of the pancreatic juice is deficient, although the other two enzymes are present in considerable amount. This is not a general characteristic of all febrile conditions. The lack of lipase may be related to fat intolerance, which is often seen in this condition.

W. D. H.

**Fermentation Processes in the Digestive Tract of Ruminants and Pigs.** J. MARKOFF (*Biochem. Zeitsch.*, 1913, 57, 1—69).—The partly digested food was removed from the first stomach of oxen

by means of a stomach-pump, described and figured, and transferred to the lower bulb of a modified Pflüger gas pump. The gastric contents thus obtained were then allowed to ferment, and the gases produced were removed and submitted to analysis in a modified Haldane gas apparatus. The details of the method are fully described, and the apparatus is figured in the text. The carbon dioxide, methane, and hydrogen produced by fermentation were estimated, and also the amount of carbon dioxide which is produced by the direct treatment of the gastric juice with acids. This is derived from the carbonates secreted in the saliva, which in the case of oxen is large in amount. Attention is incidentally called to the fact that diastase is not present in this saliva. The addition of sugar causes increased production of carbon dioxide, due to the formation of organic acids of about the same molecular weight as butyric acid. The contents of the other parts of the alimentary tract than the first stomach of freshly killed animals (oxen and pigs) were also removed, and submitted to fermentation by the above-described methods. In this way the fermentation in different parts of the alimentary tract was examined after ingestion of different kinds of food, and the losses of energy value of the food-stuffs owing to fermentation was thereby determined. The results are illustrated by a large number of gas analyses, which are mainly of technical interest.

S. B. S.

**The Fate of Protein Digestion Products in the Body. III. The Absorption of Amino-acids from the Blood by the Tissues.**

DONALD D. VAN SLYKE and GUSTAVE M. MEYER (*J. Biol. Chem.*, 1913, **16**, 197—212).—The disappearance of amino-acids from the circulation after intravenous injection is rapid, and due to their absorption by the tissues without undergoing any immediate change. In the muscles there is a saturation point beyond which the acids are not absorbed (75 to 80 mg. per 100 grams); the capacity of internal organs is greater (125 to 150). The removal from the blood is never complete; after a fast of several days the blood still contains 0.003—0.008%. At this point the amino-acids of the blood are in equilibrium with those of the tissues. Transference from organ to organ or from mother to foetus may occur. The process is not wholly osmotic, because normally the concentration of amino-acids in the tissues is five to ten times greater than in the blood. Probably the tissues adsorb the acids mechanically, or else a loose compound is formed between the tissue-proteins and the acids.

W. D. H.

**The Fate of Protein Digestion Products in the Body. IV. The Locus of Chemical Transformation of Absorbed Amino-acids:**

DONALD D. VAN SLYKE and GUSTAVE M. MEYER (*J. Biol. Chem.*, 1913, **16**, 213—230).—Not only are amino-acids injected into the blood absorbed by the tissues, but absorbed amino-acids disappear rapidly from the liver. The amino-nitrogen of the liver may be doubled after injection of amino-acids into the blood, but in two hours it returns to normal; in the muscles there is in this time no

appreciable fall; the disappearance from kidney, intestine, pancreas and spleen is also less rapid than from the liver. The decrease in the liver is accompanied by an increase of urea in the blood. This supports the view so long held that the liver is the main organ where catabolism of protein digestion products takes place. The liver being so ready to get rid of absorbed amino-acids maintains indefinitely its power to remove these substances from the circulation; and it is only when the entrance is unnaturally rapid, as in injection experiments, or when the liver is degenerated, that this organ is unable to cope with the supply; the kidney then assists by excreting them unchanged. Each tissue is probably able to synthesise its own proteins from the amino-acids which it absorbs from the blood.

W. D. H.

**The Fate of Protein Digestion Products in the Body. V. The Effects of Feeding and Fasting on the Amino-acid Content of the Tissues.** DONALD D. VAN SLYKE and GUSTAVE M. MEYER (*J. Biol. Chem.*, 1913, 16, 231—234).—The amino-acids not only serve as tissue-building material, but also occur as intermediate breakdown products of the tissue proteins. Starvation therefore would not necessarily mean a disappearance of the tissue amino-acids; it might even increase the amount. This view is supported by experiments on dogs in various degrees of inanition; male dogs only were used to avoid complications due to pregnancy.

The failure to increase the free amino-acid content of the tissues by high protein feeding indicates, furthermore, that when nitrogen is retained in the organism it is not to an appreciable extent stored in the state of digestion-products, but as body protein. W. D. H.

**Endogenous Metabolism of the Pig. I. The Effects of Acid and Basic Salts and of Free Mineral Acids on the Endogenous Nitrogen Metabolism.** E. V. MCCOLLUM and D. R. HOAGLAND (*J. Biol. Chem.*, 1913, 16, 299—316).—Data are presented which show that the endogenous metabolism of the pig reaches its lowest level when the animal has an abundant supply of carbohydrates, together with a salt mixture of an alkaline character. The total output of nitrogen derived from endogenous sources can be greatly increased without changing the output of creatinine. The additional nitrogen excreted on an acid diet is in the form of ammonia. The pig is not able to use the nitrogen of the urea fraction to neutralise the acids of the food, but draws additional nitrogen from the tissues for the production of ammonia.

W. D. H.

**Endogenous Metabolism of the Pig. II. The Influence of Fat Feeding on the Endogenous Nitrogen Metabolism.** E. V. MCCOLLUM and D. R. HOAGLAND (*J. Biol. Chem.*, 1913, 16, 317—320).—If fat is given as the sole source of energy, there is no sustained rise in the nitrogen output of pigs which have been reduced to their lowest level of nitrogen metabolism by long-continued feeding

on starch; but it may lead to a considerable elimination of creatine. The total creatine+creatinine may be greatly increased without a corresponding rise in the total nitrogen output. The possibility of the acid or basic character of the ration influencing creatine production is suggested. W. D. H.

**Endogenous Metabolism of the Pig. III. The Influence of Benzoic Acid on the Endogenous Nitrogen Metabolism.** E. V. MCCOLLUM and D. R. HOAGLAND (*J. Biol. Chem.*, 1913, 16, 321—326). A good deal of the nitrogen which appears as urea in pigs reduced to the lowest level of endogenous protein metabolism may be converted into glycine when benzoic acid is given, and excreted as hippuric acid. Benzoic acid does not raise the total nitrogen excreted unless very large quantities are given; the urea-nitrogen may then be less than 20% of the total; it causes no change in the creatinine output. Endogenous protein metabolism presents two types; one can be stimulated by acids leading to the production of ammonia, or by benzoic acid leading to the production of hippuric acid; the other, measured by creatinine, remains unaffected. W. D. H.

**Formation of Sugar from Fat.** RUDOLF ROUBITSCHKE (*Pflüger's Archiv*, 1913, 155, 68—73).—Adrenaline does not cause glycosuria in the case of dogs completely free from glycogen. Glycosuria sets in immediately, however, when the liver is enabled to make glycogen from the glycerol component of an oil. It is requisite that the oil shall have passed through the intestine and given up its glycerol component. E. F. A.

**The Diet and Metabolism of Eskimos.** AUGUST KROGH and MARIE KROGH (*Meddelelser om Grønland*, 1913, 51, Reprint, 52 pp.).—The normal diet of Eskimos contains an excessive amount of protein (280 grams) and much fat (135 grams), while the quantity of carbohydrate is very small (54 grams), of which more than half is the glycogen of the meat eaten. This diet has no injurious effects whatever; the people are capable of prolonged work, and have great endurance towards cold and other hardships. Uric acid diseases are very rare if they occur at all. The large quantities of seal meat are well absorbed and utilised. The loss of nitrogen in the faeces amounts to 3 to 5 grams per day. Details are given of the composition of the urine in different parts of the day, and of the respiratory exchanges. The "specific dynamic action" of the protein works out as  $8.6 \pm 5\%$  of the calorific value of the protein catabolised. The dietary habits of the Eskimos are very like those of the carnivora, and these people are able to retain a large amount of protein for a certain period exceeding twenty-four hours, and to utilise it as a source of energy with very little loss. W. D. H.

**Metabolism Studies on Cold-blooded Animals. II. The Blood and Urine of Fish.** W. DENIS (*J. Biol. Chem.*, 1913, 16, 389—393).—The non-protein nitrogen, urea, ammonia, uric acid,



and creatinine were estimated by the methods of Folin and his colleagues, and the results stated for numerous fish in a table. In elasmobranch fishes, the urea in the blood is high, but in teleosts it is lower than in mammals. The ammonia fraction of the blood is high. Uric acid is present in elasmobranch blood in the merest traces, but in teleostean blood in moderate amount; the amount in the urine is small in both classes.

The analysis of one composite specimen of urine from the goose fish (*Lophius piscatorius*) is given; this is a representative teleost; the most noteworthy points are the large amount of undetermined nitrogen, and the creatinine is almost entirely replaced by creatine. It is possible that in fishes, nitrogenous waste may be eliminated by some organ other than the kidney. W. D. H.

**Studies on Growth. I. Growth on Vitamine-containing and Vitamine-free Foods.** CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1913, **88**, 352—356).—Young chickens were fed on various diets, and their growth watched. Those fed on ordinary chicken food grew normally; on polished rice they died quickly from beri-beri. On unpolished rice they did not develop disease, but did not grow. On unpolished rice plus yeast they grew comparatively slowly; on unpolished rice plus sarcoma tumour (Rous) they grew more slowly still. In each batch some of the birds were inoculated with the tumour; the inoculated specimens grew more rapidly. From the last-named observations no conclusions are drawn at present; but from the others the conclusion is drawn that the vitamine which prevents beri-beri is a different one from that which stimulates growth. The chemistry of the "growth vitamine" is not yet known. It is suggested that the vitamine undergoes metabolic changes in such organs as the pituitary gland.

W. D. H.

**The Influence of Butter-fat on Growth.** THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, EDNA L. FERRY, and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1913, **16**, 423—437).—The growth-promoting "vitamine" of milk is found in the butter-fat fraction; its chemical nature is not known. The experiments were made on rats.

W. D. H.

**Parenteral Nutrition by Intravenous Injection.** V. HENRIQUES and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1913, **88**, 357—369).—A method is described by which it is possible to keep animals (goats) alive for a considerable time by intravenous injections of a nutritive mixture. The mixture is composed of almost completely cleaved flesh (about 15% of the nitrogen in peptide form), dextrose, sodium acetate, and salts. The animals put on nitrogen. Protein synthesis is therefore possible, without the digested protein products passing through the intestinal wall.

W. D. H.

**The Lipoids of Ancient Egyptian Brains.** W. MAIR (*J. Path. Bact.*, 1913, **17**, 179—184).—Whereas fresh brain contains no

cholesteryl esters, but only free cholesterol, the brains of mummies 3000—4000 B.C., and even of Copts, 500 A.D., contain esters. Thus the free cholesterol in recent brains amounts to 11·3%; of the Coptic brain the total cholesterol is 8·4%, of which 8 is in ester form. In the brains 3000 to 500 B.C., the total is from 0·68 to 0·83%, and that as ester from 0·43 to 0·5. In ancient brain (4000 B.C.), the little cholesterol present (0·04%) is all in the form of esters. Details are also given of nitrogen, phosphorus, ash, etc. The Coptic bodies were packed in salt before burial; the older ones not. The effect of time on chemical reactions is probably the same as the effect of heating. W. D. H.

**Preparation and Saponification of Cholesteryl Esters.** W. MAIR (*J. Path. Bact.*, 1913, 17, 185—190).—Cholesteryl esters occur in areas of brain softening; these are saponifiable by boiling for four hours in a *N*/5-barium hydroxide solution in 90% methyl alcohol. The lipoids in ancient Coptic brains are not saponifiable in this way. Various esters were therefore examined; those with lower fatty acids are saponifiable; those with higher fatty acids are not saponifiable by this method. Lauric, palmitic, and stearic acids, however, form two kinds of ester with cholesterol; if prepared from the chloride the ester is not saponifiable; if prepared from the fatty acid, the ester is saponifiable by the method mentioned, and differs in melting point, solubilities, and crystalline characters from the other. The esters in necrotic brain are either those of the latter class, or are esters of lower acids. W. D. H.

**The Relationship between the Protein and Total Nitrogen and the Hydrogen Ion Concentration in the Cerebrospinal Fluid.** AXEL BISGAARD (*Biochem. Z-itsch.*, 1913, 58, 1—64).—The protein can be conveniently estimated by the method of Roberts and Brandberg, according to which the maximum dilution of the liquid which is still capable of giving a turbidity with nitric acid (Heller's test) is ascertained. The author gives the experimental details of the process. A similar method can be applied when ammonium sulphate is used instead of nitric acid. The physiological limits of the ammonium sulphate reaction lie between the numbers 0 and 2 (dilutions), whereas those of the nitric acid reaction lie between 6 and 20. In cases of *dementia paralytica* there is an increase of total protein in the solution, accompanied by an increased percentage of protein precipitable by half-saturated ammonium sulphate. These increases are absent in cases of cerebral tumour, cerebral syphilis, and acute meningitis. Formalin forms compounds with the proteins, and alters the reaction of the liquid to nitric acid and ammonium sulphate. The total nitrogen was estimated in small quantities in the liquid by a combination of the methods of Kjeldahl and Nessler, which are described in detail by the author. The protein nitrogen, calculated from the nitric acid reaction, amounts to from 10 to 20% of the total. The physiological limits of total nitrogen lie between 0·01 and 0·025%. The residual nitrogen is seldom less than 0·009%. In organic

diseases of the central nervous system, the relationship between protein and total nitrogen increases. The hydrogen ion concentration of the cerebrospinal fluid exceeds the value  $p_H=8.10$ .

S. B. S.

**The Phosphatides of the Heart and Other Organs.** HUGH MACLEAN (*Biochem. Zeitsch.*, 1913, 57, 132—142).—It has been the custom hitherto, in the extraction of lipoids from the heart and other tissues, to extract first with ether and then with alcohol, and it has been generally assumed that the two extracts yield different lipoids. It is now shown by the author that this double extraction is unnecessary, as the alcohol and ether both extract the same lipoids. The alcoholic extract is, however, contaminated with other substances, from which the lipoids cannot be extracted by the methods ordinarily employed (solution in ether, and precipitation from this solution by alcohol, acetone, etc.). The alcoholic extract can be purified by suspending it in water and carefully adding acetone. The lecithin then separates, leaving the nitrogenous impurities in the water. In addition to lecithin and cruorin, the heart muscle contains traces of a diaminomonophosphatide, similar in properties to the substance described by Stern and Thierfelder and by Thudichum. A similar product has been obtained by the author and by Dunham and Jacobson from the kidneys. The substance from the heart muscle may be derived from the nervous tissue contained therein.

S. B. S.

**The Perfused Heart. I. Anæsthetics and Inorganic Salts.** W. BURRIDGE (*Quart. J. expt. Physiol.*, 1913, 7, 145—166).—Anæsthetics produce three kinds of contraction in the frog's ventricle; their depressing action is antagonised by calcium salts; depression of initiation and conduction are similarly antagonised. Damage to the sarcoplasm is believed to underlie an action of anæsthetics, which results in increased amplitude of contraction.

W. D. H.

**The Perfused Heart. II. Action of Acids and Alkalis.** W. BURRIDGE (*Quart. J. expt. Physiol.*, 1913, 7, 167—183).—Alkalis produce in small concentration a type of ventricular contraction which depends on the calcium salts in the perfusing medium; greater concentrations cause "alkali-rigor." Acids also produce two types of contraction; certain organic acids cause a slowly developing rigor which destroys the contractile material; inorganic acids produce a quickly developing contraction. The action of lactic acid is intermediate. Acids act probably by altering the permeability of cell membranes to calcium or potassium salts. This can be neutralised by a phosphate, but not by a bicarbonate.

W. D. H.

**The "Spontaneous" Evolution of Hydrogen Sulphide from the Liver and from White of Egg and the Nature of the Thiol Group.** MAX HAUSMANN (*Biochem. Zeitsch.*, 1913, 58, 65—91).—Fresh minced liver, either after warming or treatment

with alcohol (50—100%) or phenol (4—90%), evolves "spontaneously" hydrogen sulphide, the evolution lasting for several days. This evolution is dependent on the thiol group present in the liver, which can be detected by the sodium nitroprusside reaction. Other animal organs and yeast give a similar reaction and hydrogen sulphide evolution. "Natural" egg-white does not evolve this gas, as it contains no thiol group. Two reactions appear to explain the hydrogen sulphide evolution: (a) the formation of polysulphides from potassium sulphide solutions, especially on addition of phenol; (b) egg-white, after treatment with polysulphides and coagulation by alcohol and phenol, also evolves hydrogen sulphide. As a pre-existing thiol group is absent in egg-white, Heffler's hypothesis for the explanation of hydrogen sulphide on addition of sulphur is not sufficient.

S. B. S.

**Urea Formation in the Liver. A Study of the Urea-forming Function by Perfusion with Fluids Containing (a) Ammonium Carbonate and (b) Glycine.** CYRUS H. FISKE and HOWARD T. KARSNER (*J. Biol. Chem.*, 1913, 16, 399—418).—The surviving liver is able to convert ammonium carbonate perfused through it, partly into urea. Whether any is converted into amino-acids has not been determined. The perfusion of the liver of the cat or rabbit with homologous defibrinated blood containing as much as 44 mg. of nitrogen as glycine per 100 c.c. leads to no increase of urea.

W. D. H.

**Nitrogenous Constituents of Dried Cod (*Gadus Brandtii*).** K. YOSHIMURA and M. KANAI (*Zeitsch. physiol. Chem.*, 1913, 88, 346—351).—One thousand grams of dried cod, containing 17% of water, yielded the following: creatinine, 1.40 grams; betaine (as chloride), 0.44 gram; methylguanidine (as picrate), 0.7 gram; taurine, 13 grams; alanine, 0.5 gram; and a little glutamic acid. Creatine and choline were absent.

E. F. A.

**Carbon Metabolism. The Physiological and Pathological Significance of the Labile Carbon of the Urine.** ENRICO REALE (*Biochem. Zeitsch.*, 1913, 57, 143—155).—The C/N ratio of the urine is markedly increased after administration of carbohydrates. The procentual relationship of the carbon to hydrogen in the three persons investigated was increased on an average by 11.28%. With a normal person on standard diet, the administration of 100 grams of dextrose increased the relationship by a average number of 12.32%, whereas the isodynamic quantity of fat caused an increase of only 6.3%. When the bread of a standard diet is replaced by meat, there is a diminution of the C/N ratio. The effect of diet on the labile carbon (that is, carbon of the urine which can be oxidised by hydrogen peroxide) is still more marked. Whereas the labile carbon on a standard diet is 6% of the total, the administration of dextrose causes a rise to 12%. The administration of fat causes, however, a diminution of this number to 4.58%. After a meat

diet, the amount of labile carbon in the urine on the second day was practically negligible. Thyroid administration caused a diminution of the percentage of labile carbon to 2.76% of the total. Even the administration of 100 grams of dextrose under the influence of thyroid medication did not bring the percentage of labile carbon up to the normal. The presence of labile carbon in the urine appears to indicate incomplete utilisation of the carbohydrates. S. B. S.

**The Influence of Drugs on Uric Acid Excretion.** R. ABL (*Arch. expt. Path. Pharm.*, 1913, 74, 119—163).—Diminution in the excretion of uric acid is brought about by calcium salts, barium sulphate, bismuth subnitrate, and uzara; increase of the action of atophan by calcium salts, barium sulphate, uzara, and atropine. Increase of uric acid excretion is produced by mustard, arsenic, colchicin, thorium-X, sulphur, santonin, glycerol, choline, chloral hydrate, neurine, strontium, piperazine, and other drugs. Important factors in producing an effect are solubility, ease of absorption, and local action in the alimentary canal. There is a parallelism between the flow of blood in the portal system, the secretion of the digestive glands, and the output of uric acid. W. D. H.

**Isolation of Carotene from Ox Gallstones.** HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, 88, 331—333).—A yellowish-red, microcrystalline powder separates from the ethereal extract of ox gallstones. This is identified as carotene, m. p. 178—180°. It is considered to be derived from the food of the animal, and not to have been formed in the body. E. F. A.

**The Formation of Dextrose from Propionic Acid in Diabetes mellitus.** ISIDOR GREENWALD (*J. Biol. Chem.*, 1913, 16, 375—378).—Ringer showed that in phloridzinised dogs the administration of propionic acid is followed by the elimination of "extra dextrose" equal in amount to that capable of being formed by propionic acid if all three carbon atoms are used. In the present observations on severe cases of human diabetes the same is true, but there is, as a rule, no rise in the excretion of the acetone group of substances. W. D. H.

**Membranes and Narcosis. The Colloidal Theory of Narcosis.** S. LOEWE (*Biochem. Zeitsch.*, 1913, 57, 161—260).—The author reviews at length the conception of the cell membrane as a polyphasic gel-like structure, in which the hydrophil colloid is the carrier of the properties influencing the selective permeability, and in which lipoids exist as an essential component. The phenomenon of narcosis produces a change in this system, and it is assumed that the action of the narcotic consists in changing the hydrophil lipid constituent of the colloid into a hydrophobe condition without loss of its water of combination. This causes a change in the permeability of the membrane, and an injury to its normal functions, indicated by a weakening of the bioelectric differences of potential and the loss of selective per-

meability. To test this theory experimentally, the changes of conductivity of the membrane under influence of various narcotics was investigated. It was assumed that the colloid particles which can adsorb the narcotic become surrounded by a non-conducting layer, and are thus no longer effective as regards permeability for electrolytes. If now the hydrophil, previously partly-conducting particles, become non-conducting the addition of narcotics should result in a decrease in the conductivity of the membrane. A method is described for preparing membranes from colloids. A parchment membrane is covered with the lipoid solution in organic solvents and the solvent allowed to evaporate. By an arrangement, the apparatus for which is figured in the text, this membrane is clamped between two parchment papers which cover the ends of two bent tubes, the whole system forming a U-tube. Salt solutions are placed in each limb, and the membrane is allowed to imbibe water. Electrodes at accurately known distances apart are introduced into each limb, and the influence of the addition of narcotics on the conductivity can then be investigated. It can hardly be said, however, that the results of experiment confirm the theory. The author draws attention to the great difficulties of the experimental method employed, and to the great possibilities of error. S. B. S.

**The Relation between Non-protein Nitrogen Retention and Phenolsulphonphthalein Excretion in Experimental Uranium Nephritis.** C. FROTHINGHAM, R. FITZ, OTTO FOLIN, and W. DENIS (*Arch. int. Med.*, 1913, 12, 245—258).—In uranium-nephritis in rabbits, the excretions of phenolsulphonphthalein in the urine and non-protein nitrogen and urea of the blood vary from the normal, and return to the normal as the nephritis heals. The degree of variation is parallel to the amount of kidney injury. During the attack the urinary phenolsulphonphthalein drops, and the non-protein nitrogen and urea of the blood increase. In these experiments both the uranium nitrate and the phenolsulphonphthalein were administered subcutaneously. W. D. H.

**The Action of Univalent Alcohols on the Surviving Mammalian Heart.** YAS. KUNO (*Arch. expt. Path. Pharm.*, 1913, 74, 399—415).—From experiments on the rabbit's heart perfused with Locke's solution to which alcohol was added, the following conclusions are drawn; the action of alcohols on the heart increases with the rise in their boiling points; the effect is never stimulating, but always the reverse. The alcohols dilate the coronary blood-vessels. If a heart is perfused with an alcoholic solution, and then brought back to its former condition by Locke's solution, each successive perfusion with the alcohol produces a smaller effect. W. D. H.

**The Capacity of Carbohydrates to Act as Antigens.** T. KUMAGAI (*Biochem. Zeitsch.*, 1913, 57, 380—413).—The author confirms the results of Weinland, according to whom the repeated subcutaneous injection of sucrose in large quantities into young dogs causes invertase to appear in the serum after 12—15 days.

He was, however, unable to confirm Abderhalden and Kapfberger's statement (A., 1910, ii, 1093) that injections of small quantities of sucrose into fully-grown dogs produces invertase in the serum after a very short interval. On the other hand, he confirms the results of Abderhalden and Brahm (A., 1910, ii, 319), who produced this result when large quantities of sugar were injected. The results of the latter investigators were not, however, constant, but it is now shown that a constant result can be obtained, if a definite interval of some days is allowed to elapse before the serum is investigated. A new property of the antiserum produced by the sucrose "antigen" was also discovered, namely, that it acts also on dextrose and lævulose. The former is converted first into a lævorotatory and then into a dextrorotatory substance, which latter product is also obtained by the action of the antiserum on lævulose. These conversion products have been obtained pure (the details are not given in this paper); the dextrose is first converted into lævulose, and the latter is converted into a dextrorotatory disaccharide. The sucrose immune serum also acts on lactose, and the dextrose thereby produced is also converted into lævulose (and finally a disaccharide). It also hydrolyses soluble starch much more energetically than a normal serum. The serum when perfectly fresh is somewhat inert. On being kept at room temperature for four hours, it becomes very active. The fresh serum appears therefore to contain a pro-amylase. Sucrose immune serum loses its activity as regards sucrose and its hydrolysis products on keeping, but the activity can be restored by the addition of normal serum. The immune serum produces a precipitate with soluble starch.

The immune serum can be produced by the methods both of active and passive immunisation. If the serum of an animal which has been immunised by the injection of sucrose is injected into another animal (even of a different species), the serum of the latter rapidly acquires the properties of an immune serum.

When starch, maltose, and dextrose are injected into animals (employed as antigens), the only effect observed is a larger or smaller increase in the amount of amylase in the serum. When, on the other hand, lævulose, lactose, or galactose is employed as antigen, not only is there an increase in the amylase, but the immune serum contains invertase, and is capable of converting dextrose into lævulose, and the latter into a disaccharide. The results indicate that the production of amylase depends on different factors to that of invertase, for the former is increased in the serum after injection of dextrose, lævulose, and *d*-galactose, and all the polysaccharides which yield these sugars on hydrolysis, whereas the latter is produced only after injection of lævulose, galactose, and the disaccharides from which they can be produced. It is probable that the immunisation takes place in stages, the polysaccharide being first hydrolysed, yielding lævulose or galactose, both of which are then converted into a new sugar (both yielding the same product), which is the immediately acting antigen.

S. B. S.

**Antagonism of the Properties of Guanine and Adrenaline.**

DESGREZ and DORÉANS (*Compt. rend.*, 1913, 157, 946—947).—Subcutaneous injection of guanine previous to similar injection of adrenaline diminished the toxicity of the latter to a certain extent, in that the injected rabbit or guinea-pig survived the control animal receiving no guanine, often by several hours. Similarly, guanine very noticeably reduced the glycosuria ordinarily produced by adrenaline. W. G.

**Lipoid Anaphylaxis.** FREDERICK P. WILSON (*J. Path. Bact.*, 1913, 17, 163—168).—The attempts to sensitise guinea pigs to various lipoids gave negative results. The possible presence of minute amounts of protein with the lipoids may be the cause of apparently positive results. W. D. H.

**The [Physiological Action of] Aromatic Mercury Compounds. III. FERDINAND BLUMENTHAL and KURT OPPENHEIM**

(*Biochem. Zeitsch.*, 1913, 57, 261—296. *Compare A.*, 1911, ii, 517, 1017).—The toxicity of the various salicylmercury compounds in which the mercury is directly attached to a carbon atom, was investigated. Asarol, the double salt of sodium hydroxymercurisalicylate,  $\text{OH}\cdot\text{Hg}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Na}$ , with sodium monohydroxybutyrate, is the most poisonous to rabbits and rats. Then follows mercurysalicyl,  $\text{OH}\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{Hg} \\ \text{CO} \end{smallmatrix}\rangle\text{O}$ , dissolved in diethylene-

diamine; then follow embarin, and then enésol, a combination of mercurysalicyl with arsenic. The percentage of mercury in the two latter compounds is less than in the others. The toxicity of the following compounds was also ascertained—sodium hydroxymercurinitrobenzoate, sodium hydroxymercuriacetylaminobenzoate (toxynone),  $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{Hg}\cdot\text{OH})\cdot\text{CO}_2\text{Na}$ , mercuric chloride, mercuric *p*-aminobenzoate, mercuric chloride, mercurous chloride, mercuric *o*-aminobenzoate, mercuric paranucleate, mercuric potassium nitrite, and mercuric potassium thiocyanate. Various methods of administration were employed. The results are chiefly of therapeutic interest. It was found that the chief organs concerned in the excretion of mercury were the kidneys and intestine, and these show the chief anatomical changes in animals poisoned by mercury. S. B. S.

**The Effect of Asymmetric Nitrogen Atoms on Physiological Activity.** P. P. LAIDLAW (*J. Pharmacol. exp. Ther.*, 1913 4, 461—469).—An asymmetric nitrogen atom may exercise a profound influence on physiological activity. In the case of the *l*-canadine methochlorides, the  $\beta$ -salt is twelve times as active as the  $\alpha$ -salt. In the *d*-isomerides the  $\beta$ -variety is only three times as active as the  $\alpha$ -salt. In both cases the levorotatory salt is weaker than the dextrorotatory salt, but not in equal degree. The differences may possibly be connected with differences in solubility. W. D. H.

**The Influence of the Subsidiary Alkaloids of Opium on the Action of Morphine.** WALTHER STRAUB (*Biochem. Zeitsch.*, 1913, 57, 156—160).—A reply to certain criticisms of Meissner (*A.*, 1913, i, 1279). S. B. S.



**The Action of Codeine and Thebaine on the Intestine.** J. PAL and E. POPPER (*Biochem. Zeitsch.*, 1913, **57**, 492—494).—The authors have shown that the opium alkaloids can be divided into two classes in respect to their action on the intestine. The chief effect of the one class (the phenanthrene group), which includes codeine and thebaine, is to excite the wall of the intestine, increasing its tonus and peristaltic action. This action is illustrated by four tracings. The results are not in accordance with those obtained by Meissner (*A.*, 1913, **i**, 1279). In the case of thebaine, it is suggested that the alkaloid used by Meissner was contaminated with papaverine, which belongs to the second group of opium alkaloids, and exerts an antagonising action to thebaine. No explanation can be offered to explain the discrepancy of the results obtained with codeine.

S. B. S.

**The Influence of 2-Phenyleinchonic Acid (Atophan) on Uric Acid Elimination.** OTTO FOLIN and HENRY LYMAN (*J. Pharmacol. expt. Ther.*, 1913, **4**, 539—546).—The statement made by recent clinical observers that atophan increases the excretion of uric acid is confirmed. This is supplemented by estimations of the uric acid in the blood by the Folin-Denis method. Four cases of gout and one of albuminuria were utilised; the uric acid of the urine rose, and that of the blood sank. The increased output is due to elimination of accumulated uric acid in the blood, due to kidney inefficiency. A rise in other nitrogenous excreta occurred in some cases but not in all. In a sixth case (severe gout) there was not a high amount of uric acid in the blood during the greater part of the course of the disease; but later on it rose, and then atophan produced the usual result. The drug acts on the kidneys, and does not "mobilise" deposited urates. In a healthy man the drug caused an increase in the urine, and a drop in the blood uric acid.

W. D. H.

**The Constituents and Effects of Strophanthus Drugs.** EWALD HESSEL (*Chem. Zentr.*, 1913, **ii**, 869—870; from *Sitzungsber. Abhandl. naturf. Ges. Rostock.* 1913. **5**. pp. 43. Compare Sieburg, *A.*, 1913, **i**, 640).—The hæmolytic action and toxicity of sodium *g*-strophantate and allied products is described. The crude sodium salt contains what is probably a cholesteride, which nullifies the activity of the substance. On purification through the medium of the lead or barium salt, the hæmolytic action becomes evident.

J. C. W.

**Action of Protoveratrine and Aconitine on the Neuro-muscular Apparatus of the Frog.** (MRS) MARJORY MACNAUGHTON (*Quart. J. expt. Physiol.*, 1913. **7**, 131—144).—The action of protoveratrine on nerve closely resembles that of yohimbine, so that it exhibits fatigue after action, and recovery on rest. Protoveratrine fatigue is, however, most lasting, and there is no "snap reflex," and no "Wedensky effect." The action of aconitine on nerve resembles that of protoveratrine.

If the protoveratrine is applied to the muscle, the myoneural

junction is affected, and stimulation through the nerve produces rapid and permanent fatigue; aconitine is without this action.

W. D. H.

**The Toxic Action of Products obtained from the Animals of the same Species.** FRIEDRICH SIMON (*Biochem Zeitsch.*, 1913, 57, 337—374).—Livers of rabbits were allowed to autolyse, or were treated with pepsin or trypsin, the products of digestion were treated with alcohol, and the precipitated powder was then dried. The effects of the administration to rabbits of the various preparations thus obtained was investigated. The temperature changes and the onset of albuminuria were regarded as symptoms of toxic effect. The toxic effects were, however, in no case very marked, nor could they be considered as constant. The products were also injected into rats. Relatively large doses of digestion products produced short-lasting convulsions, or increase in rapidity of respiration lasting for some hours.

S. B. S.

**The Tolerance Shown by Elasmobranch Fish towards Certain Nephrotoxic Agents.** W. DENIS (*J. Biol. Chem.*, 1913, 16, 395—398).—In the dog fish, large doses of uranium nitrate and potassium chromate cause little or no accumulation of waste nitrogenous products. The elimination of these substances by the kidneys is normally small, and the animals are apparently able to utilise the liver or perhaps the intestine as an excretory organ.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Oxidation of Manganous Carbonate by Microbes.** M. W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 397—401).

—When two pieces of filter paper, with a little manganous carbonate between them, and moistened with a dilute solution of ammonium chloride and potassium phosphate, are infected with garden soil and kept at about 25°, dark brown or black spots of a manganic compound will appear on them after some days. The characteristic reactions of the manganic compound thus produced are the sudden decomposition of hydrogen peroxide and the oxidation of hydriodic acid. An examination of the related microbes shows that bacteria and various species of mould are the cause of the oxidation.

Pure cultures of the bacteria were obtained on agar plates containing 0·05—0·1% of manganous lactate. Small, capsulated colonies appear, which, after being crushed, prove to consist of delicate, quickly-moving rodlets, whilst the brown wall of the capsula again gives the usual manganic reactions.

The mould species are readily grown on agar plates containing nothing but manganous carbonate and some mineral salts; on pure agar, without manganous carbonate, they also develop, but less

quickly, so that the carbonate evidently serves as a food, and not only as a catalyst. These moulds belong to very different groups of the fungi, and consist of species of the genera *Botrytes*, *Sporocybe*, *Trichocladium*, and in particular of *Mycogone*, two of which, *Papulospora manganica* and *Sporocybe chartoikoon*, are fully described.

Oxidation appears to occur as well within as without the mycelium. It could not be brought about by oxydase or peroxydase of different origin.

The statement found in many textbooks, that manganous carbonate is readily oxidised on exposure to air, appears to require some modification, since the author has been able to preserve an aqueous suspension of this substance for years without taking any special precautions, whilst the manganous carbonate agar plates continue unchanged for months with free access of air. H. W.

**The Behaviour of Certain Bacteria towards *d*-Glucosamine.** KURT MEYER (*Biochem. Zeitsch.*, 1913, 57, 297—299).—The behaviour of various species of bacteria grown in Barsievsky's medium with addition of glucosamine was investigated. It was ascertained whether acid was formed, or gas evolved. The results obtained were similar to those when dextrose was employed instead of glucosamine. The differences of behaviour towards the two substances are not sufficient to be of diagnostic value. S. B. S.

**A So-called Biochemical Variation of the Bulgarian Lactic Ferment.** F. DUCHÁČEK (*Compt. rend.*, 1913, 157, 1095—1097).—An explanation of the differences observed by Bertrand and Effront in the biochemical behaviour of the lactic ferment. The author shows that the two workers were dealing with quite different material. Bertrand's pure lactic ferment decomposes only lactose and some of the hexoses, causing coagulation of the milk by the acidity produced, whilst Effront's commercial sample contained a proteolytic ferment, and but a very feeble form of the Bulgarian ferment proper. He has studied both these forms, and gives an account of the variations in their properties, and as a result does not agree with Effront that there is a biochemical variation of the Bulgarian ferment. W. G.

**Bacterial and Enzymic Changes in Milk and Cream at 0°.** M. E. PENNINGTON, J. S. HEPBURN, E. Q. ST. JOHN, E. WITMER, M. O. STAFFORD, and J. I. BURRELL (*J. Biol. Chem.*, 1913, 16, 331—368).—Milk and cream kept at freezing point undergo changes, such as proteolysis, lactic acid fermentation, and liberation of fatty acids. The enzymes responsible for these and other changes are mainly secreted by bacteria, which accommodate themselves to the low temperature and proliferate. *Micrococcus aurantiacus* (Cohn) and *M. ovalis* (Escherich), which belong to the group of acid-formers, were the predominant organisms found. W. D. H.

**The Rate and Magnitude of the Increase of Yeast in Wort.** TOR CARLSON (*Biochem. Zeitsch.*, 1913, 57, 313—334).—The yeast formed in the wort was measured by centrifugalising in tubes

terminating in graduated capillaries, until the amount of sediment formed is constant. The relationship between the time of sedimentation and the speed of the centrifuge was determined experimentally. The rate of growth of yeast was plotted on a curve. At the commencement, the rate of increase is an exponential function of the time. Afterwards, however, the foodstuff in the wort commences appreciably to diminish, and this is accompanied by a diminution of the rate of increase in the yeast, until finally the curve (representing this rate) runs nearly parallel with the abscissa (representing the time). The rate of growth may be fairly well expressed by the equation:

$$K = 1/\Delta t \cdot \log(y_{\infty} - y_1)y_2/(y_{\infty} - y_2)y,$$

where  $y_{\infty}$  represents the maximum amount of yeast which can be formed in a given wort, and  $y_2$  and  $y_1$  the amounts formed at the end and beginning of the time  $t$ . In a current of air the rate is increased by about 12%, and in a current of nitrogen by 25%, whereas in a current of oxygen it is diminished by about 15%. Alcohol also diminishes the rate, and in the presence of 12% the growth practically ceases. The relationship between the amount of yeast formed and the dilution of the wort was also investigated, as the maximum of amount formed is not in the most concentrated yeast. The relationship between the dilution ( $u$ ) and the amount may be represented by the equation:

$$q = 1/u Y_{\infty} / y_{\infty} (Y_{\infty} - y_{\infty}),$$

where  $Y$  represents the limiting value. The concentration of the alcohol formed determines in this case the magnitude of the crop.

S. B. S.

**Fermentations with Yeast in Absence of Sugar. XIII. The Rôle of the Aldehyde Formation in the Fermentation of Sugars and the So-called Auto-fermentation.** C. NEUBERG and JOH. KERB (*Biochem. Zeitsch.*, 1913, 58, 158–170).—Aldehyde has been found as a fermentation product, and it is theoretically possible that it is an essential intermediary product (the equations being given in the text). The authors draw the conclusion, however, that this is not the case. The chief reason for this is, that the quantities formed are extremely small, even when their amount is increased by the addition of zinc chloride, and there is no evidence that even these minimal quantities are formed from the sugars. Furthermore, they do not regard the experimental evidence as satisfactory, which tends to show that acetaldehyde can be reduced to alcohol by the yeast.

S. B. S.

**Influence of Mercury on Alcoholic Fermentation.** P. NOTTIN (*Compt. rend.*, 1913, 157, 1005–1008).—The phenomenon observed by Lindet and Ammann (compare A., 1913, i, 144) with respect to the action of mercury on alcoholic fermentation is due essentially to mechanical action. The retardation of the fermentation is due to the formation of mercury salts by the more or less prolonged contact of the metal with the naturally acid must. The increase in production of yeast is due to the action of the mercury in destroying

the supersaturation with respect to carbonic acid, thus allowing the yeast to breathe and vegetate better. Apart from these effects, the metal and its salts seem to be without marked action on the zymase or on its selective power.

W. G.

**Influence of Metals on the Development of *Aspergillus niger* Cultivated on Raulin's Liquid.** M. BORNAND (*Centr. Bakt. Par.*, 1913, [ii], 39, 488—496).—*Aspergillus niger* has been grown on Raulin's liquid contained in capsules of the metals, silver, aluminium, copper, iron, tin, lead, zinc, nickel, and in a glass capsule with a layer of mercury. Control cultures were carried on in glass capsules. In the case of silver, contrary to the results obtained by Cadur and Thiry (compare *Compt. rend. Soc. Biol.*, 1913, 487) and Clément (*ibid.*, 1913, 749), the author finds that this metal produces a retardation in the development, but does not prevent sporulation, which is, however, much weaker than in the control. It is not possible to accustom *Aspergillus niger* to develop in a normal manner on Raulin's liquid in a silver capsule. With the other metals the development of the mould was checked, except in the case of aluminium and platinum, mercury entirely inhibiting development even after ten days. In no case was sporulation complete. The metals which were most active in checking development were found to be most readily attacked and dissolved by Raulin's liquid, the exception being mercury, which, however, vaporises slowly. In the case of copper the mycelium is green and vermiculated (compare Sauton, *Ann. Inst. Pasteur*, 1911, 27, 923), but when re-sown on Raulin's liquid in a glass vessel, it develops normally and sporulates completely. It is not possible to obtain a normal development of *Aspergillus niger* by replacing the salts of iron and zinc in Raulin's liquid by the metals themselves in the form of containing vessels.

W. G.

**The Substitution of Zinc by Various Chemical Elements in the Culture of *Aspergillus niger* [*Sterigmatocystis nigra*]. The Case of Cadmium and Glucinum.** M. JAVILLIER (*Chem. Zentr.*, 1913, ii, 603; from *Bull. Sci. Pharmacol.*, 1913, 20, 321—337. Compare A., 1913, i, 236, 326; Lepierre, A., 1913, i, 326, 327).—The author reaffirms his statement that cadmium and glucinum, unlike zinc, do not further the growth of *Aspergillus*. After four days the mycelium is by no means so heavy with cadmium salts as with zinc salts of the same concentration. In time, however, the same weight may be reached, but it is due to the formation of spores at the expense of the mycelium in the case of zinc, cadmium having an adverse effect on sporulation. During four days glucinum salts give no greater growth than a culture without zinc, and even after some time the weight of mycelium is never so great as with zinc.

J. C. W.

**Comparative Influence of Zinc, Cadmium, and Glucinum on the Growth of Some Hyphomycetes.** M. JAVILLIER and (Mme.) H. TSCHERNORUTZKY (*Compt. rend.*, 1913, 157, 1173—1176).—Three

different types of *Hyphomycetes* have been grown on Raulin's liquid containing no zinc, cadmium, or glucinum, and on similar liquid to which one of these metals has been added in the form of salts at dilutions varying from 1 in 100,000,000 to 1 in 5000. The results show that, in all three cases examined, zinc has a marked superiority as a biological catalyst even in minute quantities. Cadmium is similar in its action to zinc, but has greater toxicity. Glucinum is almost completely inactive. W. G.

**Influence of Radioactive Emanations on Vegetation.** J. STOKLASA and V. ZDOBNICKY (*Compt. rend.*, 1913, 157, 1082—1084. Compare A., 1913, i, 1421).—Plants have been grown under the following conditions, and thus submitted to the influence of radium emanation: (1) Culture in Knopp's nutritive solution, made either with artificially radioactive water or with naturally radioactive water; (2) in pots filled with earth and watered with artificially radioactive water; (3) culture in large vessels (85 litres capacity), the air being rendered radioactive by emanation. In all cases radioactive emanation in small quantities exerted a favourable influence on the development of the plant, the mechanism of gaseous exchanges, flowering, fertilisation, and markedly on the crop weight. Large quantities of emanation, on the other hand, arrest growth. The chlorophyll is altered, and plasmolysis occurs. The experiments were conducted with various species of plants, giving in some cases an increase in the dry weight of the crop amounting to 164%. W. G.

**The Genesis of Carbohydrates.** J. PARNAS (*Chem. Zentr.*, 1913, ii, 1314; from *Naturwiss.*, 1913, 1, 819—820).—An adverse criticism of Baur's view that oxalic acid is the primary product in the assimilation of carbon dioxide by plants (compare A., 1908, ii, 780; A., 1913, i, 443). J. C. W.

**Photochemical Processes in the Diurnal Disappearance of Acids in Succulents.** H. A. SPOEHR (*Biochem. Zeitsch.*, 1913, 57, 95—111).—Attention is called to the well-known fact that juices of plants are more acid in the morning, and that the acidity, for the most part, disappears on exposure to light. Experimental evidence is brought forward to show that this disappearance is not due to the action of ferments, as it also takes place in the heated juices after their exposure to light. It is shown, furthermore, that certain plant acids, especially dibasic acids, readily undergo decomposition (but only in the presence of air) when exposed to ultra-violet light in quartz vessels. Malic and tartaric acids lose two molecules of carbon dioxide under these conditions, and the alcohols thus formed are oxidised further to acetaldehyde and acetic acid. The latter acid also undergoes decomposition, yielding formaldehyde and formic acid. The last-named acid yields carbon dioxide as final oxidation product. Acetaldehyde, under conditions of light-oxidation, can give rise to oxalic acid. Under the conditions of light-oxidation, therefore, the ordinary plant acids can give rise to

volatile oxidation products. The discovery of formaldehyde as product of light-oxidation of acids throws some doubt on the significance of Baeyer's hypothesis, according to which the aldehyde is a direct photochemical product of carbon dioxide, as it can be produced from plant acids. S. B. S.

**Distribution of Organic Bases, Particularly Adenine and Choline, in the Vegetable Kingdom.** K. YOSHIMURA (*Zeitsch. physiol. Chem.*, 1913, 88, 334—345).—The flowers of *Chrysanthemum sinense* contain adenine, choline, and a little stachydrine; the leaves contain adenine, a little choline, and some stachydrine. The latter are remarkable in containing nearly 3% of calcium oxide calculated on the dried material.

Young material of *Chrysanthemum coronarium* contains adenine and a little choline, but no betaine. *Artemisia vulgaris* and rice gluten contain both adenine and choline, but no betaine. *Morus alba* contains adenine, choline, and trigonelline. E. F. A.

**New Tannin Reaction and its Relation to Anthocyanin.** KUNO PECHE (*Ber. deut. botan. Ges.*, 1913, 31, 462—471).—When sections of the leaf or rind of *Prunus laurocerasus* are quickly heated in a mixture of equal parts of potassium hydroxide (20%) and formaldehyde, a bluish-green coloration is produced in the cells with tannins which give a green coloration with ferric chloride. The colour is changed to red by acids. The colours resemble the anthocyanins except as regards solubility. A soluble pigment was obtained from the sap of *Mespilus germanica*.

The formaldehyde only acts in preserving the phenolic hydroxyl from oxidation.

In the Rosaceæ, the pigments produced in this manner are only formed from tannins which give a green coloration with ferric chloride. It was also shown that in the Rosaceæ the anthocyanins are formed from the same group of tannoids. N. H. J. M.

**Experimental Production of an Anthocyanin Identical with that which is Formed in Red Leaves in the Autumn, Starting with a Compound Extracted from Green Leaves.** RAOUL COMBES (*Compt. rend.*, 1913, 157, 1002—1005. Compare A., 1909, ii, 426; 1911, ii, 1125).—The author has isolated from the green leaves of *Ampelopsis hederacea* a substance crystallising in rosettes of brownish-yellow needles (*loc. cit.*), which, when dissolved in alcohol, acidified with hydrochloric acid, is reduced by nascent hydrogen, generated by sodium amalgam, giving a compound crystallising in purple needles, and identical in its behaviour and properties with the natural anthocyanin extracted from red leaves. This supports the view that the anthocyan pigments in leaves are formed as a result of the modification of a continuous phenomenon which takes place in the leaf organs during the whole of their existence. W. G.

**Constituents of Aloes.** F. TUTIN and W. J. S. NAUNTON (*Pharm. Journ.*, 1913, [iv], 37, 836).—The primary object of this



investigation was to ascertain whether aloes contain any anthraquinone derivatives other than aloe-emodin, but no such compounds were found.

In addition to aloe-emodin the following substances were identified in Curaçao aloes: salicylic acid (?); a fatty acid, m. p. 75—78°; cinnamic and *p*-coumaric acids.

According to Tschirch and Hoffbauer (A., 1905, i, 913) Curaçao aloes contains cinnamic acid, but no *p*-coumaric acid.

A small amount of glucosidic material is also present, which after hydrolysis yielded *d*-phenylglucosazone; no pentose could be detected. F. B.

**The Araliaceæ Family, with Special Reference to the Glucosides and Oxydases of the Leaves of *Polyscias nodosa*, Forst. and *Hedera Helix*, L. A. W. VAN DER HAAR** (*Pharm. Weekblad*, 1913, 50, 1350—1359, 1381—1393, 1413—1427).—An investigation of the substances present in the leaves of the East Indian *Polyscias nodosa*, Forst. and the European *Hedera Helix*.

The leaves of *Polyscias nodosa* were extracted with light petroleum, ether, 95% alcohol, 50% alcohol, and finally with water. The light petroleum extracted a vegetable wax (a myricyl ester) and chlorophyll; the ether, chlorophyll and a trace of tannin; the 95% alcohol, a trace of saponin and of tannin, much chlorophyll, but no alkaloids; the 50% alcohol, much saponin, reducing carbohydrates, a trace of tannin and of acids, but no alkaloids; the water, peroxydases and other enzymes.

The saponins were extracted with 95% alcohol, precipitated by ether, dialysed in aqueous solution, extracted with methyl alcohol after evaporation, and purified by means of magnesium oxide. Two individuals were isolated from the product: *Polyscias α*-saponin,  $C_{22}H_{36}O_{10}$ , and *Polyscias Δ*-saponin,  $C_{25}H_{42}O_{10}$ , homologous compounds belonging to Kobert's series,  $C_nH_{2n-8}O_{10}$ . Intermediate homologues may have been present, but were not isolated.

The saponins thus obtained are white, amorphous products, which begin to decompose at 200°, and carbonise at 225°. With concentrated sulphuric acid they give the usual violet coloration, addition of water to the mixture precipitating a crystalline substance, m. p. 230—234° (uncorr.). On fusion with potassium hydroxide the products were a crystalline substance, m. p. 150—152°, which gives a faint red coloration with ferric chloride; and acetic, formic, and butyric acids. Concentrated nitric acid converted the saponins into picric acid and benzoic acid. They can be salted out by means of ammonium sulphate. They yield a *hepta-acetyl* derivative, m. p. 155—160°, so that the formulæ of the homologues are  $C_{22}H_{28}O_3(OH)_7$  and  $C_{25}H_{35}O_3(OH)_7$ .

Inversion of these saponins with dilute mineral acids yields equimolecular proportions of a sapogenin, arabinose, and dextrose, along with traces of methylpentoses. *Polyscias sapogenin*,  $C_{26}H_{44}O_4$ , forms rhombic prisms, m. p. 324°,  $[\alpha]_D^{18} + 75.58^\circ$  in pyridine. It gives the characteristic violet coloration with sulphuric acid, and its properties indicate the presence of a lactone ring, but the absence

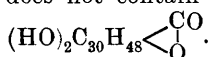
of hydroxyl, methoxyl, and ethoxyl groups, and also of double linkings. It exhibits great stability towards oxidisers. Its formula may be written  $C_{25}H_{44}O_2 < \begin{smallmatrix} CO \\ | \\ O \end{smallmatrix}$ . At  $300^\circ/60$  mm. it yields two sublimates, one light in colour, and the other darker. The second has m. p.  $327^\circ$ .

A detailed account of the physiological action of the various products is given.

The leaves of *Hedera Helix*, L., contain two kinds of glucosides, soluble or insoluble in water. The soluble are denoted by  $\Delta$ , and the insoluble comprise the amorphous or  $\gamma$ , the crystalline or  $\beta$ , and  $\alpha$ -hederin, m. p.  $256-257^\circ$ . On inversion the  $\Delta$ -glucosides yield an insoluble fission-product.

The formula of  $\alpha$ -hederin is possibly  $C_{31}H_{50}O_4$ . It forms small, colourless needles,  $[\alpha]_D^{10} + 9.68^\circ$  in alcohol. The substance has an acidic character. It dissolves in concentrated sulphuric acid to an orange solution, which becomes bright cherry-red, and finally colourless as a violet precipitate is deposited. After inversion it reduces Fehling's solution, but not before. It is inverted with difficulty, the products being an insoluble product and a soluble sugar. It forms a *penta-acetyl* derivative, m. p. ca.  $155^\circ$ , and contains one methoxyl group, so that its formula may be written  $C_{41}H_{58}O_5(OH)_5(OCH_3)$ .

The insoluble product of the inversion of  $\alpha$ -hederin by 5% sulphuric acid is  $\alpha$ -hederagenin,  $C_{31}H_{50}O_4$ , m. p.  $325-326^\circ$ ,  $[\alpha]_D^9 + 81.2^\circ$  in pyridine. In concentrated sulphuric acid it dissolves to a colourless solution, which changes through yellow and orange to violet, indicating it to be the reacting substance in the sulphuric acid test for  $\alpha$ -hederin. It has one lactone ring, forms a *diacetyl* derivative, m. p.  $110^\circ$ , and a *dibenzoyl* derivative, but does not contain a methoxyl group. Its formula may be written



On distillation with zinc dust in a current of hydrogen,  $\alpha$ -hederagenin yields water and a greenish-yellow, fluorescent oil, which contains a *sesquiterpene*,  $C_{15}H_{24}$ , which is optically inactive and volatile with steam. The non-volatile residue is a semi-solid, yellow, fluorescent substance.

The insoluble inversion product of  $\alpha$ -hederin contains arabinose and rhamnose. These sugars are also present along with  $\alpha$ -hederagenin in the inversion product obtained from the mother liquor of the extraction of  $\alpha$ -hederin.

A. J. W.

**Existence of Maltase in Cereals.** ZENON WIERZCHOWSKI (*Biochem. Zeitsch.* 1913, 57, 125-131).—All the cereals examined were repeatedly extracted with water until the diastase content was removed, and the action of the solid residue on starch and maltose solution was investigated. All kinds were found to contain a maltase, especially millet, maize, and buckwheat. In all the grains it was not found possible to extract quantitatively the diastase. In those kinds in which the diastase could be quantitatively

removed, it was found that starch was present during the whole fermentative process. The ferment acts, therefore, like the one already described by the author in maize (A., 1913, i, 1255), in directly degrading the starch into dextrose without the intermediate stages of dextrin formation. From certain of the grains small quantities of the maltase can be extracted by water. The dry powder has, however, more powerful enzymatic properties than aqueous extracts. S. B. S.

**The Digestibility of the Nitrogenous Substances in Cocoa Beans and Pods.** S. GOY (*Biochem. Zeitsch.*, 1913, 58, 137—147).—The digestibility of the proteins of the beans by pepsin varies greatly according to their origin and method of roasting. The percentage of digestible protein varied between 25 and 63. The percentage of digestible proteins of the pod varied between 3.6 and 29. S. B. S.

**Arsenic and Manganese in Some Sea-water Plants.** HENRI MARCELET (*Chem. Zentr.*, 1913, ii, 1412—1413; from *Bull. Sci. Pharmacol.*, 1913, 20, 480—482).—Colorimetric estimations of manganese by means of silver nitrate and potassium persulphate show that marine plants contain unevenly distributed quantities of that metal (1.5 to 36.3 mg. per 100 grams of dry material). The quantity of manganese bears no relation to the amount of arsenic present. Marine grasses contain more of these elements in the chlorophyll-bearing parts than in the roots. J. C. W.

**Composition of Oil-seeds of Two *Symphonia* spp. from Eastern Madagascar.** ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1913, [iv], 13, 1039—1042).—The seeds of *S. laevis* yield 35.2%, and those of *S. Louveli* 40.0%, of a semi-solid, yellow fat having the following constants (where two figures are given the first is for the fat of *S. laevis* and the second for that of *S. Louveli*):  $D_4^{20}$  0.872, 0.879; m. p. 15—16°; acid number 8.4; saponification number 189; Reichert value 1.65; Hehner value 94.3, 94.1; iodine value 66.7, 67.6; m. p. of fatty acids 42.5°, 43°; saturated fatty acids 40%, 35%; unsaturated fatty acids 60%, 65%. The saturated fatty acids in both cases appear to consist of a mixture of margaric, arachidic, lauric, and decolic acids. T. A. H.

**Production of Alcohol by Wheat Germs.** S. KOSTYTSCHEV and A. SCHELOUMOV (*Ber. deut. bot. Ges.*, 1913, 31, 422—431).—No alcohol is produced by living wheat germs when aerated; even in presence of toluene very little alcohol is formed ( $\text{CO}_2$ : EtOH = 100:3). When aeration is deficient, considerable amounts of alcohol may be formed ( $\text{CO}_2$ : EtOH = 100:50).

Further experiments with wheat germs, incapable of germination, showed that alcohol is produced in considerable amounts even when thoroughly aerated. N. H. J. M.

**Nuclear Degeneration Caused by Uranium in Vegetable Cells.** C. ACQUA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 390—392).—When plants are grown in solutions containing traces of uranyl

nitrate, root growth is rapidly arrested owing to the penetration of uranium into the nuclei of the meristem. It can be seen there in the form of a yellow substance, probably the yellow oxide. The chromatin of these nuclei is found to have disappeared, so that karyokinetic division is no longer possible. R. V. S.

**The Influence of Iron in the Development of Barley, and the Specificity of its Action.** J. WOLFF (*Compt. rend.*, 1913, 157, 1022—1024. Compare Mazé, Ruot, and Lemoigne, A., 1912, ii, 1088).—Working with aseptic solutions and carefully purified barley seeds free from all moulds and bacteria, the author has shown that ferrous sulphate to the extent of 0.4 gram per litre has a very favourable influence on the growth of the barley plant. In one case the dry weight ratios of iron-free to iron-containing media were as 45:160. Neither chromium nor nickel can replace the iron. Nickel, even in small amounts, checks all development of the plant, whilst chromium, at the rate of 0.01 gram in 500 c.c. of culture liquid, first caused extraordinary root development, and then the plants became chlorotic and died. W. G.

**The Influence of Salts Common in Alkali Soils on the Growth of the Rice Plant.** K. MIYAKE (*J. Biol. Chem.*, 1913, 16, 235—264).—Alkali salts may have both toxic and stimulant effects on the growth of rice seedlings, according to their concentrations; the toxic concentrations of magnesium sulphate and chloride, calcium chloride, and carbonate are greater than  $N/100$ , while sodium sulphate and sodium hydrogen carbonate are greater than  $N/50$ . The greatest stimulation was observed with the salts in the following concentrations: magnesium sulphate,  $N/500$ ; magnesium chloride and calcium chloride,  $N/1000$  to  $N/5000$ ; sodium chloride,  $N/10$  to  $N/100$ ; sodium carbonate and sodium hydrogen carbonate,  $N/100$  to  $N/500$ . Two salts, however, in toxic concentrations lead to loss of poisonous effects; this is due to the ions formed on dissociation. Bivalent cations are markedly antagonised by univalent cations, although the reverse does not hold; the antagonism of anions is less marked. The curve of antagonism between sodium and potassium shows two maxima. The antagonistic action of calcium on other metallic ions is most important; barium and strontium can replace it. W. D. H.

**Decomposition of Proteins in the Seedlings of Kentucky Tobacco.** F. TRAETTA-MOSCA (*Gazzetta*, 1913, 43, ii, 445—452).—The seedlings of the tobacco plant contain proteolytic ferments, and among the products of their action the author has identified lysine, histidine, arginine, glutamine, leucine, and aspartic acid. Choline was also found. R. V. S.

**Presence of Barium and Arsenic in Italian Manufactured Tobaccos.** R. SPALLINO (*Gazzetta*, 1913, 43, ii, 475—481).—These tobaccos all contain barium, the quantity varying from 0.019 to 0.036%, calculated as sulphate obtainable from the dried

material. A proportion amounting to 0·003—0·009% is in a state soluble in water. Seven tobaccos examined contained 0·08—1·02 mg. of arsenic per 100 grams of dry material. R. V. S.

**Humic Acids. III. Composition of *Sphagna* and their Power of Absorbing Bases. Influence of Locality and Importance of the Single Nutrients.** EUGEN GULLY (*Bied. Zentr.*, 1913, **42**, 652—655; from *Mitt. K. Bayr. Moorkulturanst.*, 1913, Heft. 5).—Numerous analyses of *Sphagna* of different origin showed that more food is taken up than is required for growth, the amounts varying with the different varieties. The composition of the living and the dead portions of *Sphagna* differ considerably, the dead portions containing less potassium, phosphoric acid, and nitrogen than the living portions; the amount of calcium remains the same in some varieties. The predominance of *Sphagna* is caused partly by deficient nutritive matter, especially potassium.

As a rule, the absorptive power for bases is somewhat higher in dead than in living peat moss. N. H. J. M.

**Soil Solution and the Mineral Constituents of the Soil.** ALFRED DANIEL HALL, WINIFRED ELSIE BRENCHLEY, and LILIAN MARINO UNDERWOOD (*Phil. Trans.*, 1913, [B], **204**, 179—200).—Water culture experiments are described, in which wheat and barley were grown in extracts of soil from differently manured plots of the permanent wheat and barley experimental fields at Rothamsted; nitrogen was supplied in the form of sodium nitrate. The results showed that the growth varied with the different extracts, and that the yields corresponded with the average yields of the plots themselves. The relative composition of the extracts was found to be similar to that of the soils as judged either by the total or citric acid soluble plant food they contain. Further experiments, in which the soil extracts were compared with artificial nutrient solutions, showed that the former gave better results than the latter, owing perhaps to the presence of nitrogen compounds of special value in the earlier stages of growth. Notwithstanding the sixty years' growth of wheat and barley on the respective fields, no evidence of any soluble toxin was obtained. The weights of wheat and barley were almost exactly the same, whether grown in extracts from wheat or barley soil; and boiling the extracts had no effect.

Further experiments are described, in which barley was grown in solutions containing dihydrogen potassium phosphate, magnesium and calcium sulphates, and sodium chloride (each 0·5 gram), potassium nitrate (1 gram), and ferric chloride (0·04 gram per litre), and in the same solutions diluted to 1/5, 1/10, and 1/20 respectively. From the commencement the growth proceeded in the order of the concentration and the final yield in the strongest solution was about twice that of the next, and six times that of the lowest. The results were confirmed by sand culture experiments, in which the solutions of different strengths were allowed to percolate through the sand.

Finally, experiments were made, in which water cultures were compared with cultures in coarse sand, fine sand, silt, and kaolin; and on the effect of aeration in water cultures. In sand cultures containing 20% of nutritive solution it was found that there was no retardation of growth due to slow diffusion, although with that amount of water the sand could readily be crumbled. The yield was better than in water cultures supplying the same amounts of nutrients. Similar results were obtained when the nutritive solutions were placed in porous cylinders in the sand in which the plants were growing, so that the solutions had to pass through the porous cell before reaching the roots. In all these experiments the results depended on the concentration of the solutions.

Comparing coarse and fine sand with salt and kaolin, the coarse sand gave much the best results; water cultures next; then kaolin, silt, and fine sand.

Very striking results were obtained in water cultures with barley and lupines. The solutions were (1) not aerated; (2) aerated daily; and (3) aerated continuously. Continuous aeration nearly doubled the yield as compared with no aeration, and the conclusion is drawn that the superiority of sand cultures over ordinary water cultures is due to the better aeration.

N. H. J. M.

**Displacement of the Potash Contained in Certain Felspathic Rocks by Some Substances Used as Fertilisers.** G. ANDRÉ (*Compt. rend.*, 1913, 157, 856—858).—An examination of the effect of such salts as sodium nitrate, calcium phosphate, etc., commonly used as fertilisers, on a felspar steadily ground in a mortar with aqueous solutions of these salts for 130 hours. The amounts of potassium oxide thus rendered soluble vary with the salts used. Ammonium sulphate (1% solution) gives the highest figure, rendering 7.38% of the total  $K_2O$  in the felspar soluble. Sodium chloride and sodium nitrate have the same effect, rendering 3.25% soluble. Sparingly soluble calcium carbonate and phosphate only have a slight effect, while the more soluble superphosphate is much more active.

W. G.

**Contribution to the Study of Clays.** A. MÜNTZ and H. GAUDECHON (*Compt. rend.*, 1913, 157, 968—974).—A study of the sedimentation of clays. Clay suspensions of definite concentrations were left for the clay to settle over varying periods of time in jars 30 cm. high, holding one litre of liquid. The liquid was siphoned off in four equal fractions, and the amount of clay left in each and in the deposit determined. The top fraction loses its fine particles most readily, having at the end of six days lost 84% of its total clay in suspension. If in addition to the gravitational effect an electrical effect is introduced, it is found that the fine particles, which are most stable under the action of gravity, are the most rapidly deposited under the influence of the electrical fields, produced by the insertion of two electrodes of a circuit.

Clays of different origin show different rates of disappearance

of the clay from the top 250 c.c. of liquid, and the author suggests that this might form a method of identifying and classifying clays.

W. G.

**Occurrence of Arsenic in Soils.** JOSEPH E. GREAVES (*Biochem. Bull.*, 1913, 2, 519—523).—Some virgin soils contain arsenic from the decay of rocks. Many cultivated soils contain a larger quantity, but there is no uniform relationship of the total arsenic to that which is soluble in water. The same is true when arsenic is added to the soil. Lead arsenate is regarded as the safest of the arsenical insecticides.

W. D. H.

**Presence of Arsenic as a Normal Constituent of Soil.** GINO ZUCCARI (*Gazzetta*, 1913, 43, ii, 398—403).—Samples of unmanured soil from twenty different localities all contained arsenic, the quantities found in 100 grams of soil varying from 0.187 to 6.000 mg.

R. V. S.

**Composition of Rain-water Collected in the Hebrides and in Iceland.** NORMAN H. J. MILLER (*J. Scot. Met. Soc.*, 1913, 16, 141—158).—Estimations of ammonia, nitrates, and chlorides in monthly samples of rain-water, collected at the Butt of Lewis from December, 1908, to November, 1912, and at Víflsstadir, Iceland, from November, 1911, to September, 1912 (the October sample being lost). Also for several months at other places in the Hebrides and west coast of Scotland. The average amounts of nitrogen per acre per annum at the Butt of Lewis (1) and the amounts at Víflsstadir (2), calculated from the eleven months, are as follows:

	Rainfall. Inches.	N. per million.		N. per acre (lb.).		
		As ammonia.	As nitrates.	As ammonia.	As nitrates.	Total.
1.	39.70	0.034	0.032	0.311	0.289	0.600
2.	38.34	0.091	0.030	0.802	0.263	1.065

The amounts of ammonia, per acre, at the Butt of Lewis are the lowest hitherto recorded, and the Iceland results are the next lowest, with exception of New Zealand and Madras. The nitrates are also very much lower than the great majority of results previously obtained.

Rain-water collected at Shillay (Monach Islands) and at Barrahead contained considerably more ammonia and nitrates than was found at the Butt of Lewis. The results so far obtained indicate that the total nitrogen at the two places is about 1.8 and 2.2 lb. respectively per acre per annum, or about half the amount found at Rothamsted.

N. H. J. M.

## Organic Chemistry.

**Preparation of Isoprene.** BADISCHE ANILIN- & SODA-FABRIK (D. R.-P. 268100, 268101).—Isoprene is obtained by applying the process described in the chief patent (255519, A, 1913, i, 438), which consists in heating the substances there mentioned to a high temperature under diminished pressure in the presence of catalysts, to methylbutenyl acetate (1st patent) or methylbutenyl ether (2nd patent).

J. C. C.

**Preparation of Isoprene.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 268102).—Instead of *as*-dimethylallene, as described in the chief patent (A., 1913, i, 1), *isopropylacetylene* is dropped on to strongly heated aluminium oxide under a pressure of 40–50 mm.

J. C. C.

**Preparation of Erythrene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 262553, 262884).—Erythrene can be obtained by submitting *cyclopentane* or 1-methyl*cyclopentane*-3-ol or other homologues and derivatives of *cyclopentane* to pyrogenic decomposition.

The second patent states that *cyclohexanol* can also be used.

J. C. C.

**Preparation of Erythrene and Other Unsaturated Compounds.** ALBERT GERLACH and RUDOLF KOETSCHAU (D.R.-P. 267079, 267080).—The pyrogenic decomposition of oleic acid or oils, fats, and waxes derived from the acids of the oleic series is advantageously carried out by means of an electrically heated metallic spiral placed inside the reaction vessel, the latter being externally heated to the boiling point of the contents.

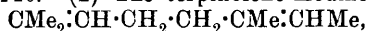
The second patent mentions that such substances as wool fat, cholesterol, etc., may be used in this process for obtaining erythrene and the other unsaturated hydrocarbons which are also produced.

J. C. C.

**Catalytic Decomposition of Alkylidenehydrazines.** Investigation of the Hydrocarbons from Citral and Citronellal. N. KISHNER (*J. Russ. Phys. Chem., Soc.*, 1913, 45, 1779–1787. Compare A., 1913, i, 1161).—The hydrocarbon, b. p. 164–165°/755 mm., obtained from citralhydrazone (A., 1911, i, 1027), has been prepared in larger quantity from unpurified citral and subjected to further investigation. It is found to be a mixture of two isomerides, the one present in larger quantity (119 grams) being (1) the limonene modification,  $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe:CHMe}$ , b. p. 162–163°/760 mm.,  $D_4^{20}$  0.7677,  $n_D$  1.4422. When this hydrocarbon is converted by means of fuming hydrobromic acid into the dibromo-derivative,  $\text{C}_{10}\text{H}_{20}\text{Br}_2$ , and the latter either distilled with aniline or boiled in a reflux apparatus with alcoholic potassium hydroxide, the linaloolene obtained by Semmler by the action of sodium on linalool (“Die



Aetherischen Ole," I, 527) is formed; when alkali is used for decomposing the dibromo-compound, the unsaturated alcohol,  $C_{10}H_{19}\cdot OH$ , b. p. 190—195°, is also obtained. Reduction of the limonene modification by Sabatier and Senderens' method yields inactive  $\beta\zeta$ -dimethyloctane,  $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMeEt$ , b. p. 158—159.5°/776 mm. (157.4—158°/748 mm.),  $D_0^{20}$  0.7287 (0.7281),  $n_D$  1.4100 (1.4097). Similar reduction of the linaloolene obtained above does not yield this same dimethyloctane, but an isomeride, b. p. 161—162°/772 mm.,  $D_0^{20}$  0.7399,  $n_D$  1.4146. (2) The terpinolene modification,



obtained in smaller quantity (25 grams), has b. p. 163—165°/760 mm.,  $D_0^{20}$  0.7699,  $n_D$  1.4439, and yields acetone and other products on oxidation with permanganate.

An optically active  $\beta\zeta$ -dimethyloctane was previously obtained (A., 1911, i, 1027) by reducing with hydriodic acid in a sealed tube the hydrocarbon,  $C_{10}H_{20}$ , formed when citronellaldehydehydrazone is distilled with fused potassium hydroxide. As this method of reduction often leads to partial racemisation, Sabatier and Senderens' method was employed, the resulting hydrocarbon having the properties, b. p. 159.5°/753 mm.,  $D_0^{20}$  0.7308,  $n_D$  1.4106,  $[\alpha]_D + 6.43^\circ$ , which are changed, after purification with fuming nitric acid, to b. p. 160—161°/772 mm.,  $D_0^{20}$  0.7301,  $n_D$  1.4109,  $[\alpha]_D + 6.27^\circ$ . Combination of the hydrocarbon,  $C_{10}H_{20}$ , with hydrogen bromide and distillation of the bromo-derivative,  $C_{10}H_{21}Br$ , with quinoline yields a hydrocarbon,  $C_{10}H_{20}$ , which has slightly different physical constants, and on reduction by Sabatier and Senderens' method gives the hydrocarbon,  $C_{10}H_{22}$ , b. p. 159.5—160°/760 mm.,  $D_0^{20}$  0.7293,  $n_D$  1.4115,  $[\alpha]_D + 6.97^\circ$ .

For the dihydromyrcene obtained by Semmler (A., 1901, i, 732), the author suggests the formula  $CH_2\cdot CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot Cet\cdot CH_2$ .

T. H. P.

**Simultaneous Oxidation of Saturated and Unsaturated Hydrocarbons by means of Potassium Permanganate.** N. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1788—1792).—The results of the author's previous experiments on the purification of saturated hydrocarbons by treatment with potassium permanganate raise the question: Does admixture of an unsaturated hydrocarbon influence the stability of a saturated hydrocarbon as regards its oxidisability? In other words, is the oxidation of a mixture of a saturated and an unsaturated hydrocarbon to be regarded as a coupled or induced reaction?

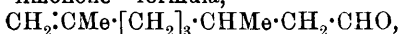
Various experiments have been made with  $\beta\zeta$ -dimethyloctane, the unsaturated hydrocarbon,  $C_{10}H_{22}$ , b. p. 161—162°/772 mm. (preceding abstract), the hydrocarbon,  $C_{10}H_{20}$  (*loc. cit.*), and *d*- $\beta\zeta$ -dimethyloctane, (*loc. cit.*), in order to ascertain whether they are oxidised more readily in presence of menthene than alone. The results show that the unsaturated hydrocarbon does not occasion considerable increase in the rapidity with which the saturated hydrocarbon oxidises. This reaction shows complete analogy to the coupled or induced oxidations investigated by Schilov (A., 1903, ii, 276).

The oxidation of different saturated hydrocarbons is influenced in

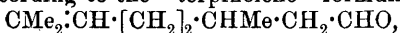
the above manner to different extents.  $\beta\zeta$ -Dimethyloctane contains two tertiary hydrogen atoms, and these undergo oxidation far more readily than those of other hydrocarbon radicles, such as the methyl or methylene group; this circumstance explains the results obtained by Nametkin (A., 1913, i, 1285) with mixtures of propane or cyclopropane with an unsaturated hydrocarbon, and it is probable that a mixture of isobutane with propylene would exhibit different behaviour. When the products of oxidation of a mixture of  $\beta\zeta$ -dimethyloctane with menthene are distilled, a distinct odour of tertiary alcohols is perceptible, indicating that the initial stage of the oxidation of the dimethyloctane consists in hydroxylation of the tertiary hydrogen.

T. H. P.

**Influence of Constitution on the Rotatory Power of Optically Active Substances. VII. Optically Active Hydrocarbons from Citronellal.** H. RUPE and ALPHONS JÄGER (*Annalen*, 1914, 402, 149—186. Compare A., 1913, i, 884).—Continuing the investigation of the influence of certain radicles on the rotatory power of optically active substances, the authors have selected citronellaldehyde as a very suitable material for their purpose because it contains only one centre of optical activity and, by the introduction of alkyl and aryl groups by the Grignard reaction, is readily converted into secondary alcohols from which unsaturated hydrocarbons are obtained by the loss of water. Semmler's hypothesis that citronellal reacts sometimes according to the "limonene" formula,



at other times according to the "terpinolene" formula,

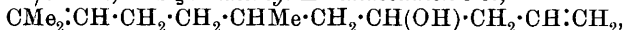


is, even if true, without weight in so far as the authors' purpose is concerned because the double linking in both formulæ is so widely removed from the centre of optical activity as to be without appreciable influence on the rotatory power. Quite different is the case of the double linking produced in the unsaturated hydrocarbons when these are obtained from the secondary alcohols by the (indirect) elimination of water. This double linking can occupy different positions (in suitable substances), and since it is within the sphere of influence of the asymmetric carbon, the determination of its exact position is a matter of prime importance.

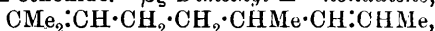
$\beta\zeta$ -Dimethyl- $\Delta^{\alpha}$ -nonen- $\theta$ -ol (Rupe and Splittgerber, A., 1907, i, 711),  $\beta\zeta$ -dimethyl- $\Delta^{\beta}$ -decen- $\theta$ -ol (Austerwell and Cochlin, A., 1910, i, 572),  $\beta\zeta$ -dimethyl- $\Delta^{\beta}$ -undecen- $\theta$ -ol,



b. p. 124°/9 mm., and  $\zeta\kappa$ -dimethyl- $\Delta^{\alpha}$ -undecadien- $\delta$ -ol,

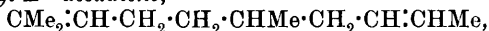


b. p. 123—124°/10 mm., are obtained in the usual manner from citronellal and magnesium methyl, ethyl, propyl, and allyl bromides respectively. These carbinols are converted by phosphorus tribromide at 100—105° into the corresponding bromides, from which hydrogen bromide is then eliminated by boiling with pyridine or, better, alcoholic sodium ethoxide.  $\beta\zeta$ -Dimethyl- $\Delta^{\beta}$ -nonadiene,



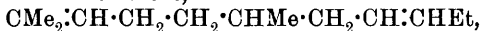
has b. p. 61—62°/9 mm.,  $D_4^{20}$  0.7730,  $[\alpha]_D^{20}$  -8.12°,  $[\alpha]_D^{20}$  -10.37°,  $[\alpha]_E^{20}$  -12.29°, and  $[\alpha]_F^{20}$  -16.17°. By treatment in glacial acetic acid with 6—8% unpurified ozone and subsequent decomposition by water on the water-bath, the dimethylnonadiene yields  $\delta$ -acetyl- $\alpha$ -methylvaleric acid,  $\text{CH}_3\text{Ac}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  (isolated as the semicarbazone,  $\text{C}_9\text{H}_{17}\text{O}_3\text{N}_3$ , m. p. 129—130°, colourless needles), and  $\alpha$ -methylglutaric acid (and possibly also a little  $\beta$ -methyladipic acid). The formation of these two acids not only proves that the new double linking in the dimethylnonadiene is as near as possible to the asymmetric carbon atom, but also is evidence in favour of Semmler's hypothesis that citronellaldehyde reacts in two forms (*v. supra*).

$\beta\zeta$ -Dimethyl- $\Delta^{8,9}$ -decadiene,



has b. p. 81—82°/9 mm.,  $D_4^{20}$  0.7813, and  $[\alpha]_D^{20}$  -6.64°. The position of the new double linking is proved by the decomposition of the ozonide by hot water, whereby  $\epsilon$ -acetyl- $\beta$ -methylhexoic acid (isolated as the semicarbazone,  $\text{C}_{10}\text{H}_{19}\text{O}_3\text{N}_3$ , m. p. 135—136°) and  $\beta$ -methyladipic acid are obtained (again evidence of Semmler's hypothesis).

$\beta\zeta$ -Dimethyl- $\Delta^{8,9}$ -undecadiene,



has b. p. 90—91°/8 mm.,  $D_4^{20}$  0.7873,  $[\alpha]_D^{20}$  -5.22°,  $[\alpha]_D^{20}$  -6.68°,  $[\alpha]_E^{20}$  -7.98°,  $[\alpha]_F^{20}$  -10.55°, and  $n_D$  1.44614,  $n_D$  1.44903,  $n_\beta$  1.45602,  $n_\gamma$  1.46215. The position of the new double linking is determined by the value of  $[\alpha]_D^{20}$ , which is practically identical with that of the dimethyldecadiene. The abnormally high value of  $[\alpha]_D^{20}$  of the dimethylnonadiene must be due to the presence of the double linking in the immediate neighbourhood of the asymmetric carbon atom. The molecular refractions of the three hydrocarbons are very nearly normal.

$\zeta\kappa$ -Dimethyl- $\Delta^{8,9}$ -undecatriene,



has b. p. 94—95°/8 mm.,  $D_4^{20}$  0.8005,  $[\alpha]_D^{20}$  -7.87°, -10.12°, -12.34°, -16.92° for the C, D, E, and F lines, and  $n_D$  1.46887, 1.47261, 1.48216, 1.49040 for the  $\alpha$ , D,  $\beta$ , and  $\gamma$  lines. The presence of the conjugated double linking is indicated by the pronounced exaltations of the specific and the molecular refractions. The molecular rotation is considerably greater than that of the dimethylundecadiene; also it is noteworthy that a comparison of the specific rotatory powers of the dimethylnonadiene and the dimethylundecatriene shows that the double linking in the immediate neighbourhood of the asymmetric carbon atom has the same effect on the rotatory power as the conjugated double linking at a greater distance.

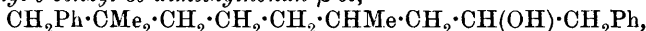
The interaction of citronellaldehyde and an excess of magnesium cyclohexyl bromide in ether leads to the formation of  $\theta$ -cyclohexyl- $\beta\zeta$ -dimethyl- $\Delta^8$ -octen- $\theta$ -ol,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_{11}$ , b. p. 166—167°/10 mm.; by-products are isopulegol and probably cyclohexane and decahydrodiphenyl (isopulegol is also obtained as a by-product in the preparation of  $\zeta\kappa$ -dimethyl- $\Delta^8$ -undecadien- $\delta$ -ol unless a large excess of allyl bromide is employed). The bromide obtained from the carbinol is converted by boiling pyridine into  $\gamma\gamma$ -dimethyl- $\Delta^8$ -octadienylcyclohexane,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_{11}$

(or  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}:\text{C}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\text{CH}_2$ ), b. p. 142—143°/9 mm.,  $D_4^{20}$  0.8468,  $[\alpha]_D^{20} - 5.03^\circ$ ,  $[\alpha]_D^{20} - 6.40^\circ$ , and  $[\alpha]_E^{20} - 7.65^\circ$ . The alternative formula is necessary because the decomposition of the ozonide by water yields adipic and cyclohexanecarboxylic acids. The adipic acid is produced from the intermediately formed cyclohexanone; the authors show that by treatment with ozone in carbon tetrachloride and subsequent decomposition by water, cyclohexanone is converted into adipic acid. The specific rotatory power of the dimethyloctadienylcyclohexane, despite the position of the double linking in the immediate neighbourhood of the asymmetric carbon atom, is almost the same as those of the dimethyldecadiene and dimethylundecadiene. Apparently, therefore, the influence of a saturated hydroaromatic group on the rotatory power is smaller than that of an alkyl group.

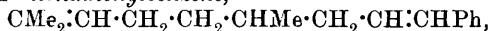
In comparison with the preceding dimethyloctadienylcyclohexane,  $\gamma\gamma$ -dimethyl- $\Delta^{2,5}$ -octadienylbenzene (Klages and Sautter, A., 1906, i, 489) has a very high rotatory power,  $[\alpha]_D^{20} - 63.24^\circ$ . This is evidently due to the conjugated double linking in the immediate neighbourhood of the asymmetric carbon atom, because its product of reduction,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , has  $[\alpha]_D - 7.26^\circ$ , and, moreover, when the conjugated double linking is situated further away from the centre of optical activity, the rotatory power is quite small. Thus  $\iota$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta^8$ -nonen- $\theta$ -ol,



b. p. 178—179°/9 mm., obtained in 20% yield from citronellaldehyde and magnesium benzyl chloride (the main product, 80% yield, is  $\alpha$ -phenyl- $\theta$ -benzyl- $\delta\theta$ -dimethylnonan- $\beta$ -ol,

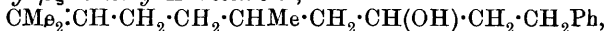


b. p. 243—244°/9 mm), is converted through the bromide into  $\delta\theta$ -dimethyl- $\Delta^{2,7}$ -nonadienylbenzene,



b. p. 159—160°/9 mm.,  $D_4^{20}$  0.8894,  $[\alpha]_D^{20} - 3.33^\circ$ , and  $n_a$  1.51360,  $n_D$  1.51770,  $n_\beta$  1.52960, and  $n_\gamma$  1.53964.

$\kappa$ -Phenyl- $\beta\zeta$ -dimethyl- $\Delta^8$ -decen- $\theta$ -ol,



b. p. 188—189°/9 mm., obtained from citronellaldehyde and magnesium  $\beta$ -phenylethyl bromide, is converted through the bromide into  $\epsilon$ -dimethyl- $\Delta^{2,9}$ -decadienylbenzene,



b. p. 163—164°/9 mm.,  $D_4^{20}$  0.8852,  $[\alpha]^{20} - 4.54^\circ$ ,  $-5.76^\circ$ ,  $-6.84^\circ$ ,  $-8.90^\circ$  for the C, D, E, and F lines, and  $n_a$  1.50375,  $n_D$  1.50766,  $n_\beta$  1.51768, and  $n_\gamma$  1.52629. C. S.

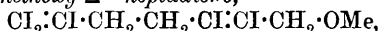
**Preparation of Allyl Alcohol.** A. KOEHLER (*Bull. Soc. chim.*, 1913, [iv], 13, 1103—1105. Compare Chattaway, T., 1913, 105, 151).—The author has increased the yield of allyl alcohol from 20% to 32% by replacing the oxalic acid with formic acid in its preparation. One hundred grams of glycerol are heated with 80 grams of formic acid for one hour on a water-bath, and the product fractionally distilled and collected in three fractions: (1) up to 200°, (2) 200—260°, (3) residue. The saponification index of fraction (2) is determined,

and it is then carefully poured on to twice the calculated quantity of solid potassium hydroxide. The whole is boiled for one hour, allowed to cool, and the top layer decanted and dried over anhydrous potassium carbonate. The intermediate product is monoformin. W. G.

**Preparation of Chlorohydrins.** HENRY V. WALKER (D.R.-P. 267205).—Chlorohydrins are obtained by treating gas-naphtha (which contains about 40% of olefines and 60% of paraffins) with a mixture of alkali hydrogen carbonate and hypochlorite solutions. J. C. C.

**Preparation of Monochlorobutylene Glycol Ether.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 262832).—*Chlorobutylene glycol ether* [ $\gamma$ -chlorobutyl  $\gamma$ -hydroxybutyl ether],  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , a colourless liquid, b. p. 82—86°/18 mm., is prepared by treating butylene  $\alpha$ -glycol with concentrated hydrochloric acid. It may be used for the preparation of erythrene. J. C. C.

**Preparation of True Acetylenic Derivatives starting with Dipropargyl.** LESPIEAU (*Compt. rend.*, 1913, 157, 1439—1440).—In the preparation of the dimethyl ether of the glycol ( $\Delta^{\beta\zeta}$ -octadi-inene- $\alpha\theta$ -diol),  $\text{OH}\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OH}$ , from the dimagnesium derivative of dipropargyl (compare A., 1910, i, 535), there is always produced at the same time an appreciable quantity of  $\eta$ -methoxy- $\Delta^{\alpha\epsilon}$ -heptadi-inene,  $\text{CH}_3\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OMe}$ , b. p. 67·5°/11 mm.,  $D^{15}_{20}$  0·9156,  $n^{15}_{\text{D}}$  1·50125. The fact that this is a true acetylenic derivative is shown by the following properties. With aqueous silver nitrate solution, it gives a precipitate soluble in warm water, crystallising out in slender needles on cooling. With cuprous chloride it gives a yellow precipitate, which with iodine yields  $\alpha\alpha\beta\epsilon\zeta$ -pentaiodo- $\eta$ -methoxy- $\Delta^{\alpha\epsilon}$ -heptadiene,



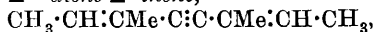
m. p. 95°. Finally, the ether reacts with magnesium ethyl bromide, giving a magnesium derivative, which with chloromethyl ether yields the dimethyl ether of  $\Delta^{\beta\zeta}$ -octadi-inene- $\alpha\theta$ -diol. This magnesium derivative also reacts with carbon dioxide, giving  $\eta$ -methoxy- $\Delta^{\alpha\epsilon}$ -heptadi-inene- $\alpha$ -carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OMe}$ , m. p. 46—47°. W. G.

**$\Delta\gamma$ -Acetylenic Glycols and the Ketohydrofurans Derived from them.** GEORGES DUPONT (*Ann. Chim. Phys.*, 1913, [viii], 30, 485—587).—A résumé of work already published (compare A., 1909, i, 545; 1910, i, 85, 379, 456; 1911, i, 173, 554, 804; 1912, i, 290, 483; 1913, i, 696, and Iotsitch, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 239, 242; 1903, 35, 430, 1269; 1906, 38, 252, 656).

The following new compounds are described:

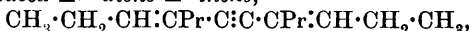
$\delta\eta$ -Dipropyl- $\Delta^{\epsilon}$ -decinene- $\delta\eta$ -diol,  $\text{OH}\cdot\text{CPr}_2\cdot\text{C}\equiv\text{C}\cdot\text{CPr}_2\cdot\text{OH}$ , m. p. 120°, which on hydrogenation yields  $\delta\eta$ -dipropyldodecan- $\delta\eta$ -diol, m. p. 82—84°, and  $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\beta}$ -butinene- $\alpha\delta$ -diol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{C}\equiv\text{C}\cdot\text{CPh}_2\cdot\text{OH}$ , m. p. 193°.

$\gamma\zeta$ -Dimethylocta- $\Delta^{\beta\zeta}$ -diene- $\Delta^{\delta}$ -inene,



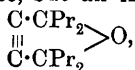
a liquid with an agreeable odour, b. p.  $170^{\circ}$ , m. p.  $-45^{\circ}$ ,  $n_D$  1.4977,  $D^{22}$  0.8071.

$\delta\eta$ -Dipropyldeca- $\Delta^7$ -diene- $\Delta^6$ -inene,



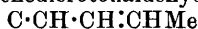
a yellow liquid, b. p.  $125-127^{\circ}/18$  mm.,  $n_D$  1.4890,  $D^{19}$  0.81313, on hydrogenation yielding  $\delta\eta$ -dipropyldecane, b. p.  $125-127^{\circ}/18$  mm.,  $n_D$  1.4450,  $D$  1.7887.

Dipropyl  $\Delta^6$ -decinene- $\delta\eta$ -diol does not give the corresponding hydrofuran with mercuric sulphate, but an internal anhydride,



b. p.  $137^{\circ}/18$  mm.,  $n_D$  1.4747,  $D^{23}$  0.8404. On hydrogenation it yields 3-keto-2:2:5:5-tetrapropyldihydrofuran, b. p.  $132^{\circ}/18$  mm.,  $n_D$  1.4498,  $D$  0.8203.

Similarly, acetylenedicrotonaldehyde (compare A., 1911, i, 804



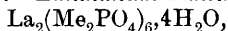
gives the compound  $\begin{array}{c} ||| \\ > \text{O} \end{array}$ , b. p.  $105^{\circ}/20$  mm.,  $n_D$  1.5802,  $D^{20}$  0.9548.

W. G.

Products Obtained by the Action of Bromine on Ether, by Schutzenberger, McIntosh, and the Author. V. V. TSHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1845—1860).—Criticism of Arbuzov's results and conclusions (compare A., 1913, i, 815). T. H. P.

Dimethyl Phosphates of the Rare Earths. J. C. MORGAN and C. JAMES (*J. Amer. Chem. Soc.*, 1914, 36, 10—16; *Chem. News*, 1914, 109, 13—15).—In order to determine the value of dimethylphosphoric acid for the separation of the rare earths, a study has been made of the following salts. The solubilities are expressed as parts of the anhydrous salt per 100 parts of water.

Yttrium dimethyl phosphate, long, white needles, solubility 2.80 at  $25^{\circ}$  and about 0.55 at  $95^{\circ}$ . Lanthanum dimethyl phosphate,



white, hexagonal crystals, solubility 103.7 at  $25^{\circ}$ . Cerous dimethyl phosphate,  $\text{Ce}_2(\text{Me}_2\text{PO}_4)_6, \text{H}_2\text{O}$ , white, hexagonal plates, solubility 79.6 at  $25^{\circ}$  and about 65 at  $95^{\circ}$ . Praseodymium dimethyl phosphate, green, hexagonal crystals, solubility 64.1 at  $25^{\circ}$ . Neodymium dimethyl phosphate,  $\text{Nd}_2(\text{Me}_2\text{PO}_4)_6$ , lilac-coloured, hexagonal plates, solubility 56.1 at  $25^{\circ}$  and 22.3 at  $95^{\circ}$ . Samarium dimethyl phosphate, cream-coloured, hexagonal prisms, solubility 35.2 at  $25^{\circ}$  and about 10.8 at  $95^{\circ}$ . Gadolinium dimethyl phosphate, long, white needles, solubility 23.0 at  $25^{\circ}$  and 6.7 at  $95^{\circ}$ . Erbium dimethyl phosphate, long needles, solubility 1.78 at  $25^{\circ}$ . Ytterbium dimethyl phosphate, long, white needles, solubility 1.2 at  $25^{\circ}$  and 0.25 at  $95^{\circ}$ .

Fractionation experiments were made by preparing a solution of the rare earths in dimethylphosphoric acid, gradually raising the temperature, and collecting the precipitates; additional fractions were obtained by evaporation of the mother liquor. In the case of a material

containing gadolinium with just sufficient terbium to colour the oxide orange-brown, the gadolinium collected in the most soluble fraction, and the terbium in the least soluble. Similar experiments with other mixtures of rare earths showed that the rate of separation by this method is much greater than by other methods. Lanthanum, cerium, praseodymium, and neodymium are left in the mother liquor. Samarium, europium, and gadolinium are much less soluble than these, but more soluble than terbium, dysprosium, and holmium. Erbium, thulium, yttrium, and ytterbium collect in the least soluble fractions.

Some difficulty is encountered in the application of this method owing to the fact that the dimethyl phosphates gradually decompose with formation of a gelatinous precipitate which renders filtration troublesome. E. G.

**Preparation of Methylbutenyl Esters.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 267553).—When  $\beta\gamma$ - or  $\beta\delta$ -dibromo- $\beta$ -methylbutane is boiled with acetic acid and sodium acetate, mixtures of the corresponding *methylbutenyl acetates* are obtained. J. C. C.

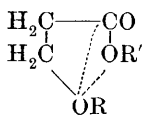
**Decomposition of Hydroxy-acids by Soda-Lime.** LEONARD CARPENTER (*Chem. News*, 1914, 109, 5).—When sodium lactate intimately mixed with soda-lime is destructively distilled in an iron tube under reduced pressure at a temperature just below redness, a product is obtained which consists of an aqueous solution of acetone and a brown, oily layer composed mainly of mesityl oxide. It appears that ethyl alcohol, if formed, is immediately oxidised probably to acetic acid, which then loses water and carbon dioxide, giving acetone.

The same product was also obtained by the action of soda-lime on citric acid. It is to be noted, also, that very little charring occurs during heating. H. W.

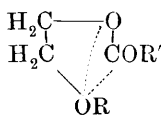
**Influence of the Position of the Oxygen Atom in the Chain on the Velocity of Hydrolysis of Esters.** M. H. PALOMAA (*Chem. Zentr.*, 1913, ii, 1956—1960; from *Ann. Acad. Sci. Fennicae*, 1913, [A], 4, No. 2, 1—104. Compare A., 1913, i, 6).—The rate of hydrolysis of esters of hydroxy- and alkoxy-acids, of monoesters and ether-esters of glycols, of esters of ketonic acids and keto-alcohols by 0.1*N*- and 0.2*N*-hydrochloric acid at 25°, has been determined in comparison with the rates of hydrolysis of esters of fatty acids. The constants are calculated from the formula for a reaction of the first order:  $k = 1/0.4343t \cdot \log a/(a-x)$ .

The results show that a reaction minimum occurs at a definite median position of the oxygen atom in the chain, which, since it occurs when the oxygen atom is in the  $\beta$ -position to the ester group, suggests the possibility of intramolecular ring formation, substances being thereby produced which have a more saturated character than open chain compounds, and thus yield with greater difficulty the additive products which are initially formed in the hydrolysis of esters by

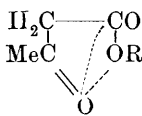
acids. The following formulæ are suggested, partial valencies being indicated by the dotted lines :



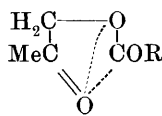
Esters of  
alkoxy-acids.



Ether esters of  
ethylene glycol.

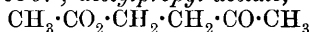


Esters of  
acetoacetic acid.



Ester of  
acetone alcohol.

The following substances are described: Ethyl glycollate, b. p.  $158^\circ$ ,  $D_4^{15}$  1.0869; methyl methoxyacetate, b. p.  $131$ — $131.4^\circ$ ,  $D_4^{15}$  1.0578; methyl ethoxyacetate, b. p.  $144.5$ — $145^\circ$ ,  $D_4^{15}$  1.0112; ethyl ethoxyacetate, b. p.  $158/752$  mm.,  $D_4^{15}$  0.9754; methyl *n*-propoxyacetate, b. p.  $161.5$ — $162^\circ$ ,  $D_4^{15}$  0.9867; ethyl *n*-propoxyacetate, b. p.  $174$ — $174.5^\circ/764$  mm.,  $D_4^{15}$  0.9551; methyl *n*-butoxyacetate, b. p.  $180$ — $180.5^\circ/765$  mm.,  $D_4^{15}$  0.9675; methyl isobutoxyacetate, b. p.  $171.5$ — $172.5^\circ/767$  mm.,  $D_4^{15}$  0.9605; methyl  $\alpha$ -methoxypropionate, b. p.  $129.5^\circ/752$  mm.,  $D_4^{15}$  1.0108; methyl  $\gamma$ -methoxybutyrate (from  $\gamma$ -methoxybutyric acid and methyl alcohol in the presence of phosphoric acid), b. p.  $162.5$ — $163.5^\circ/767$  mm.,  $D_4^{15}$  0.9879; methyl  $\gamma$ -ethoxybutyrate, b. p.  $175.5^\circ/760$  mm.,  $D_4^{15}$  0.9622; methyl  $\delta$ -methoxyvalerate, b. p.  $184.5$ — $185.5^\circ/767$  mm.,  $D_4^{15}$  0.9747; *n*-propoxymethyl acetate,  $\text{CH}_3\cdot\text{CO}_2\cdot\text{CH}_2\text{OPr}$  (from chloromethylpropyl ether and potassium acetate), b. p.  $150$ — $151.5^\circ/759$  mm.,  $D_4^{15}$  0.9521; methoxymethyl propionate,  $\text{C}_2\text{H}_5\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{OMe}$ , b. p.  $134.7$ — $135.5^\circ/752$  mm.,  $D_4^{15}$  1.0024; ethoxymethyl propionate, b. p.  $149.5$ — $150.5^\circ/75.5$  mm.,  $D_4^{15}$  0.9709; *n*-propoxymethyl propionate, b. p.  $166$ — $168^\circ$ ,  $D_4^{15}$  0.9484;  $\beta$ -hydroxyethyl formate,  $\text{H}\cdot\text{CO}_2(\text{CH}_2)_2\cdot\text{OH}$  (from ethylene glycol and 95% formic acid), b. p.  $179$ — $180.5^\circ/766$  mm.,  $D_4^{15}$  1.1989;  $\beta$ -methoxyethyl formate (from methoxyethylene glycol and formic acid), b. p.  $131$ — $131.5^\circ/767$  mm.,  $D_4^{15}$  1.0484;  $\beta$ -ethoxyethyl formate, b. p.  $141.0$ — $141.7^\circ/748$  mm.,  $D_4^{15}$  1.0013;  $\gamma$ -ethoxypropyl formate, b. p.  $157$ — $159^\circ/766$  mm.,  $D_4^{15}$  0.9762;  $\beta$ -ethoxyethyl acetate (from ethylene glycol monomethyl ether and acetyl chloride in the presence of pyridine), b. p.  $156$ — $156.5^\circ/761$  mm.,  $D_4^{15}$  0.9810;  $\beta$ -ethoxyethyl *n*-butyrate, b. p.  $188^\circ$ ,  $D_4^{15}$  0.9438;  $\gamma$ -hydroxypropyl formate (trimethylene glycol formate) (from trimethylene glycol and formic acid), b. p.  $195$ — $197^\circ/757$  mm.,  $D_4^{15}$  1.1405;  $\gamma$ -methoxypropyl formate, b. p.  $146$ — $147^\circ/767$  mm.,  $D_4^{15}$  1.0057;  $\gamma$ -ethoxypropyl formate, b. p.  $157.5$ — $159^\circ/742$  mm.,  $D_4^{15}$  0.9731; trimethylene glycol mono-*n*-propyl ether, b. p.  $170$ — $172^\circ$ ,  $D_4^{15}$  0.9076;  $\gamma$ -propoxypropyl formate (from previous compound and formic acid), b. p.  $174.5$ — $176^\circ$ ;  $\gamma$ -hydroxypropyl acetate (from trimethylene glycol and glacial acetic acid), b. p.  $202.5$ — $204^\circ$ ;  $\gamma$ -methoxypropyl acetate (from trimethylene glycol monomethyl ether and acetyl chloride in the presence of pyridine), b. p.  $162$ — $163.5^\circ/762$  mm.,  $D_4^{15}$  0.9803;  $\gamma$ -ethoxypropyl acetate, b. p.  $174.5$ — $175.5^\circ$ ,  $D_4^{15}$  0.9567; acetylpropyl acetate,



(from acetylpropyl alcohol and acetic anhydride), b. p.  $211$ — $213^\circ$ ,  $D_4^{15}$  1.0217.

H. W.

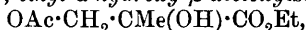


**Action of Dimethylamine on the Two Chlorohydroxyisobutyric Acids and their Derivatives.** E. FOURNEAU and M. TIFFENEAU (*Bull. Soc. chim.*, 1914, [iv], 15, 19—26).—It is known that the two isomeric iodohydrins derived from styrene, namely,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\text{I}$  and  $\text{CHPh}\cdot\text{CH}_2\cdot\text{OH}$  (Tiffeneau and Fournéau, A., 1913, i, 1337), as also the two chlorolactic acids react with dimethylamine, yielding the same product; for example, in the former case,

$$\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NMe}_2.$$

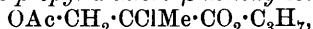
In the present investigation it is shown that even where one of the positions affected is a tertiary one, a similar behaviour is observed.

When ethyl  $\beta$ -chloro- $\alpha$ -hydroxyisobutyrate is heated with fused sodium acetate at 190—200°, *ethyl  $\alpha$ -hydroxy- $\beta$ -acetoxyisobutyrate*,



$D_4^a$  1.135, b. p. 226—229°, is obtained. The following compounds can be prepared in a similar manner: *Propyl  $\alpha$ -hydroxy- $\beta$ -acetoxyisobutyrate*,  $D_4^a$  1.001, b. p. 244—245°/770 mm. *Propyl  $\alpha$ -hydroxy- $\beta$ -valeroxyisobutyrate*, b. p. 272°. *Ethyl  $\alpha$ -hydroxy- $\beta$ -benzoyloxyisobutyrate*, m. p. 38°, b. p. 175—176°/18 mm. *Propyl  $\alpha$ -hydroxy- $\beta$ -benzoyloxyisobutyrate*,  $D_4^a$  1.1457, b. p. 205—208°/29 mm. *Ethyl  $\alpha$ -hydroxy- $\beta$ -salicyloxyisobutyrate*, rectangular prisms, m. p. 52°, b. p. 197°/16 mm. *Propyl  $\alpha$ -hydroxy- $\beta$ -salicyloxyisobutyrate*, b. p. 200°/17 mm.

By the gradual addition of thionyl chloride to a mixture of the substance with pyridine at 0°, propyl  $\alpha$ -hydroxy- $\beta$ -acetoxyisobutyrate can be converted into *propyl  $\alpha$ -chloro- $\beta$ -acetoxyisobutyrate*,



b. p. 147—150°/50 mm. *Ethyl  $\alpha$ -chloro- $\beta$ -acetoxyisobutyrate*,  $D_4^a$  1.1686, b. p. 216—217°/760 mm., and *propyl  $\alpha$ -chloro- $\beta$ -benzoyloxyisobutyrate*, b. p. 198—200° are obtainable in a similar manner.

These immediately preceding esters are hydrolysable by boiling with five times their weight of 10% hydrochloric acid with formation of  *$\alpha$ -chloro- $\beta$ -hydroxyisobutyric acid*, hygroscopic, rectangular prisms, m. p. 77°, soluble in most solvents; its *ethyl* ester, obtained by the action of alcohol containing a little sulphuric acid, has b. p. 201—202°.

When heated at 100° for ten hours with dimethylamine in benzene solution, ethyl  $\alpha$ -chloro- $\beta$ -hydroxyisobutyrate is converted into the *ethyl* ester, b. p. 192—194°, of  $\beta$ -dimethylamino- $\alpha$ -hydroxyisobutyric acid, which is produced by hydrolysis of the ester with water; this acid, m. p. 173—174°, is identical with that previously described (Fournéau, A., 1909, i, 210); the ester gives a benzoyl derivative, m. p. 140° (compare Fournéau, *loc. cit.*), of which the *hydrochloride* and *picrate* form hygroscopic, prismatic needles, m. p. 140—141°, and elongated lamellæ, m. p. 127°, respectively.

Ethyl  $\alpha$ -chloro- $\beta$ -acetoxyisobutyrate and propyl  $\alpha$ -chloro- $\beta$ -benzoyloxyisobutyrate also slowly react with dimethylamine in benzene solution, the former at 100°, and the latter at 125—130°. The product is again the dimethylamino-ester just described, but in the experiment with the former of the two esters the main product was accompanied by a small quantity of an acid substance, m. p. 130°, and possibly  $\beta$ -dimethylamino- $\alpha$ -acetoxyisobutyric acid.

Thus  $\alpha$ -chloro- $\beta$ -hydroxy- and  $\beta$ -chloro- $\alpha$ -hydroxy-*isobutyric* acid derivatives yield the same product with dimethylamine. D. F. T.

**Double Aluminium Oxalates.** W. STORTENBEKER (*Rec. trav. Chim.*, 1913, 32, 226—243. Compare Wyruboff and Rosenheim, *Zeitsch. anorg. Chem.*, 1909, 63, 121).—The author has examined and described a number of double aluminio-oxalates of sodium ammonium and rubidium together with mixed crystals of these substances. It is shown that mixed crystals and compounds of the same substances can be obtained, and also that chemical compounds may be accompanied by mixed crystals which have the same crystalline form. The most probable interpretation of the last fact is that mixtures are formed of the compound and the simple salt which crystallise with the same amount of water of crystallisation and in the same form.

J. F. S.

**Stereochemistry of the Halogenosuccinic Acids. II.** BROR HOLMBERG (*J. pr. Chem.*, 1913, [ii], 88, 553—603).—In the previous paper (A., 1913, i, 824) the author has shown that measurements of the rate of formation of bromine ions from *l*-bromosuccinic acid in neutral solution did not give concordant values for a unimolecular reaction, and pointed out that this was probably due to the reconversion of the  $\beta$ -propiolactonecarboxylic acid, under the influence of the bromide formed in the reaction, into the bromo-acid. This view has been confirmed in the case of the decomposition of sodium *l*-bromosuccinate, by removing the bromide almost as fast as it is formed by the gradual addition of silver nitrate, when concordant values for a reaction of the first order were obtained.

According to Senter (T., 1910, 97, 346; 1911, 99, 95, 1049) the presence of silver bromide exerts an accelerating influence on the hydrolysis of the bromo-derivatives of fatty acids. The behaviour of *l*-bromosuccinic acid in the presence of silver salts has been investigated by the author, but no accelerating influence could be observed. Further, the presence of silver salts during the decomposition of sodium *l*-bromosuccinate has no influence on the configuration of the resulting malic acid, the sign of rotation of the latter being determined by the reaction of the solution in which the hydrolysis of the immediately-formed  $\beta$ -propiolactonecarboxylic acid takes place; in acid solution the lactone is hydrolysed to *l*-malic acid, and in alkaline solution to the *d*-acid.

Attempts have also been made to isolate the lactonic acid formed by the decomposition of sodium *l*-bromosuccinate in neutral solution, but hitherto the compound has been obtained only as a syrup. An aqueous solution of the sodium salt of the lactonic acid is readily obtained by removing the malate and unchanged bromosuccinate from the solution resulting from the decomposition of the sodium salt of *l*-bromo-acid, by precipitation with silver nitrate.

The sodium salt reacts with sodium chloride, bromide, and iodide in aqueous solution to form the salts of the corresponding *l*-halogeno-

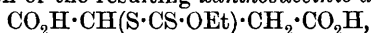
succinic acids; with ammonia it yields almost pure *d*- $\beta$ -malamic acid, which is hydrolysed by hydrochloric acid to *d*-malic acid. In neutral solution the lactonic acid is moderately stable, but is readily hydrolysed in acid or alkaline solution to *l*- and *d*-malic acids respectively; the salts with the common metals are soluble in water.

The transformation of *l*-bromosuccinic acid into propiolactone-carboxylic acid and reconversion of the latter into the *l*-bromo-acid is accompanied by very little racemisation, and the author therefore assumes that these reactions take place without change of configuration; *l*-bromosuccinic acid must therefore have the same configuration as the *d*-lactonic acid to which it gives rise. Further, since change of configuration is unlikely to occur when substitution is not effected at the asymmetric atom, the conclusion is drawn that *d*- $\beta$ -malamic acid obtained from the *d*-lactone has the same configuration as the *l*-bromo-acid. The author considers that *d*-malic acid corresponds with the *d*-lactone, and that the hydrolysis of the latter is accompanied by configurative change only in acid solution.

The racemisation of *l*-bromosuccinic acid by sodium bromide and hydrobromic acid has also been studied. It is found that racemisation takes place readily in acid solution, but not in neutral solution. From the results so far obtained the conclusion is drawn that the racemisation is almost entirely restricted to the non-ionised acid and is determined by the presence of the bromine ion.

The halogen in the *l*-bromo-acid is readily replaced by iodine, by the action of potassium iodide in neutral solution; the iodosuccinic acid thus formed is levorotatory, but could not be isolated in a pure condition. The pure *l*-acid can, however, be obtained by the action of potassium iodide on a solution of sodium salt of *d*-propiolactonecarboxylic acid, prepared in the manner described above. It has m. p. 150—152° (decomp.),  $[\alpha]_D - 74.1^\circ$  in ethyl acetate solution.

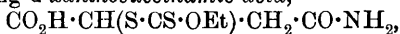
The interaction of sodium and potassium xanthate with the sodium, potassium, barium, strontium, and calcium salts of *l*-bromosuccinic acid under various conditions has also been investigated, and it is found that the sign of rotation of the resulting *xanthosuccinic acids*,



depends, not only on the particular salt of the bromo acid, but also on the concentration of the solution and the amount of xanthate employed.

The purest specimen of *l*-xanthosuccinic acid hitherto obtained has m. p. 131—132°,  $[\alpha]_D - 92.6^\circ$  in ethyl acetate solution.

*l*-Bromosuccinic acid reacts with the potassium and sodium xanthates, yielding *d*-xanthosuccinamic acid,



which forms flat, obliquely-cut, colourless prisms, m. p. 137—138° (decomp.),  $[\alpha]_D + 64^\circ$  in ethyl acetate, and is hydrolysed to *d*-xanthosuccinic acid.  
F. B.

### Crystallography of Symmetric Dibasic Aliphatic Acids.

JULIEN DRUGMAN (*Zeitsch. Kryst. Min.*, 1913, 53, 240—259).—Malonic acid ( $D^{15}$  1.6305; triclinic,  $a:b:c = 0.7440:1:0.4573$ ;  $\alpha = 102^\circ 42'$ ,  $\beta = 100^\circ 44'$ ,  $\gamma = 63^\circ 48'$ ).

Dimethylmalonic acid ( $D^{171}$  1.357; tetragonal-trapezohedral,  $a:c = 1:1.2830$ ).

Potassium hydrogen dimethylmalonate,  $+2H_2O$  ( $D^{141}$  1.540; triclinic,  $a:b:c = 0.6299:1:1.2682$ ;  $a = 89^\circ 14'$ ,  $\beta = 100^\circ 14\frac{1}{2}'$ ,  $\gamma = 94^\circ 39'$ ).

Calcium dimethylmalonate (rhombic,  $a:b:c = 0.617:1:0.937$ ).

Diethylmalonic acid (triclinic,  $a:b:c = 0.6928:1:0.5334$ ;  $a = 89^\circ 35'$ ,  $\beta = 93^\circ 37'$ ,  $\gamma = 88^\circ 29'$ ).

Potassium hydrogen diethylmalonate,  $+H_2O?$  (tetragonal, pseudocubic,  $a:c = 1:1.000$ ; optically uniaxial and positive).

Glutaric acid ( $D^{145}$  1.429; monoclinic,  $a:b:c = 2.0448:1:2.6734$ ;  $\beta = 97^\circ 2'$ ).

$\beta\beta$ -Dimethylglutaric acid (T., 1911, 99, 434; monoclinic,  $a:b:c = 0.4909:1:1.1171$ ;  $\beta = 91^\circ 55'$ ).

$\alpha\gamma$ -Dihydroxy- $\alpha\gamma$ -dimethylglutaric acid (triclinic,  $a:b:c = 1.6589:1:0.9910$ ;  $a = 91^\circ 54'$ ,  $\beta = 98^\circ 19\frac{1}{2}'$ ,  $\gamma = 95^\circ 46'$ ).

$\alpha\gamma$ -Dihydroxy- $\alpha\gamma$ -dimethylglutaric acid-monolactone (rhombic,  $a:b:c = 0.6186:1:1.4939$ , Prendel, 1891).

$n$ -Pimelic acid,  $\alpha$ -modification (m.p. (?) 101—102°,  $D^{145}$  1.329; monoclinic,  $a:b:c = 3.697:1:1.2058$ ;  $\beta = 105^\circ 40'$ , von Lang, 1893);  $\beta$ -modification (m. p. 101—102°,  $D^{15}$  1.282; monoclinic,  $a:b:c = 2.15:1:1$ ;  $\beta = 136^\circ$ ).

$\gamma$ -Methylpimelic acid ( $D^{15}$  1.641; monoclinic,  $a:b:c = 1.696:1:1.648$ ,  $\beta = 103^\circ 22'$ ). L. J. S.

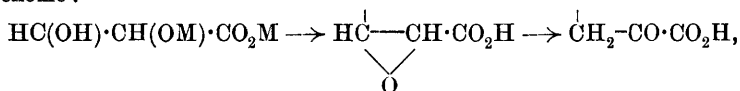
**Crystallography of the Isomeric Citraconic and Mesaconic Acids ( $C_5H_6O_4$ ).** JULIEN DRUGMAN (*Zeitsch. Kryst. Min.*, 1913, 53, 260—262).—Citraconic acid (triclinic,  $a:b:c = 1.1525:1:0.7550$ ;  $a = 98^\circ 22'$ ,  $\beta = 108^\circ 48\frac{1}{2}'$ ,  $\gamma = 88^\circ 31'$ ).

Mesaconic acid (rhombic,  $a:b:c = 0.8536:1:0.8421$ ). L. J. S.

**Syntheses by means of Organometallic Derivatives of Zinc.** Preparation of  $\alpha$ -Ketonic Acids. E. E. BLAISE (*Compt. rend.*, 1913, 157, 1440—1443. Compare A., 1912, i, 236, 410).— $\alpha$ -Ketonic acids can be prepared indirectly by aid of zinc alkyl iodide through the formation of the corresponding mixed *cycloacetals*. Ethyl chloroglyoxylate condenses with  $\alpha$ -hydroxyisobutyric acid, giving the acid,  $OEt \cdot CO \cdot CO_2 \cdot CMe_2 \cdot CO_2H$ , m. p.  $83^\circ$ , which on warming with thionyl chloride gives the *chloride*, b. p.  $120.5^\circ/12$  mm., and yields an *anilide*, m. p.  $95^\circ$ . The acid chloride reacts with zinc propyl iodide to give the *cycloacetal*,  $\begin{matrix} CMe_2 \cdot O \\ | \\ CO-O \end{matrix} > CPr \cdot CO_2Et$ , b. p.  $123—124^\circ/11$  mm., which on heating on a water-bath with alcoholic hydrochloric acid yields *ethyl butyrylformate*, b. p.  $70.5^\circ/11$  mm., and ethyl hydroxyisobutyrate. At the same time a small amount of the corresponding *diethylacetal*, b. p.  $96^\circ/11$  mm., is formed, this compound being also obtained by the action of ethyl orthoformate on the  $\alpha$ -ketonic ester in the presence of one drop of sulphuric acid. Ethyl butyrylformate is readily hydrolysed by boiling with 5% aqueous oxalic acid, giving the corresponding *acid*, b. p.  $79^\circ/12$  mm., which furnishes a *p*-nitrophenylhydrazone, m. p.  $205^\circ$ , and a *semicarbazone*, m. p.  $220^\circ$ .

W. G.

**Action of Lime on Reducing Sugars and the Products formed thereby.** A. SCHWEIZER (*Chem. Zentr.*, 1913, ii, 1791; from *Arch. Suikerind. Ned.-Indie*, 27, reprint 12 pp.).—The action of alkali on dextrose solutions leads to the formation of products which are more or less deeply coloured according to the temperature of reaction, etc. The dextrose is thereby decomposed with formation of salts of lactic and saccharic acids, etc. Addition of acids renders the solutions colourless. The author is led to the conclusion that this phenomenon is to be attributed to the alcoholic function of the decomposition products, and that the metallic atoms of these compounds are displaced by acids in accordance with the following scheme:



where M represents the atom of a univalent metal. This supposition receives support from the deep colorations imparted by the addition of ferric salts. From carbonation experiments made at 28° with an excess of lime, the conclusion is drawn that the colourless salts of lactic acid and the coloured salts of saccharic, glyceric acids, etc., are simultaneously formed at all temperatures, in contrast to the assumption that the former are alone produced by the action of alkali on dextrose below 55°, whilst the latter are formed above this temperature.

For the investigation of the properties of the product of decomposition, solutions of dextrose decomposition product (prepared by the action of lime on invert sugar) were treated with lime, and then carbonated. The following results were obtained: On boiling, the colour of the solution deepens and an additional quantity of calcium salts is formed. When carbonated, a portion of the coloured salt is removed (it is shown that the primary products of the action of alkali on dextrose are here involved), whilst the portion of the salts which remains undergoes further decomposition, whereby fresh quantities of lime are dissolved. The removal of coloured products occurs not only in alkaline, but also in neutral solution, but whether, in the latter case, additive products are formed from calcium carbonate and the salts of organic acids has not been determined. The alteration in colour of the calcium salts of these compounds with increasing alkalinity or acidity has also been investigated. The colour is lightest in acid media, and increases in intensity until the neutral point is reached; a sudden, marked darkening then occurs which diminishes with increasing alkalinity. H. W.

**Action of Cyanides of the Alkali and of the Alkaline Earth Metals on Dextrose.** E. RUPP and A. HÖLZLE (*Arch. Pharm.*, 1913, 251, 553—556).—Equal molecular quantities of dextrose and potassium cyanide in aqueous solution react according to the equation

$$\text{OH} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{CHO} + \text{KCN} + 2\text{H}_2\text{O} \\ = \text{OH} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_5 \cdot \text{CO}_2\text{K} + \text{NH}_3.$$

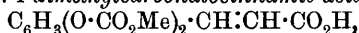
The quantity of ammonia evolved and of potassium carbonate obtained

by the incineration of the dried residue correspond very closely with the theoretical amounts. The acid has been isolated in the form of its anhydride, which exhibits all the properties of  $\alpha$ -glucoheptoic anhydride. The reaction between dextrose and barium cyanide follows a similar course. C. S.

**Some Acyl Derivatives of Dextrose and Mannose.** EMIL FISCHER and RUDOLF OETKER (*Ber.*, 1913, 46, 4029—4040).—Following the discovery of the galloyldextroses and of pentabenzoyldextrose (A., 1912, i, 888), the authors found that cinnamoyl chloride condensed even more readily than did benzoyl chloride when shaken with dextrose and quinoline in chloroform solution. The study of this reaction has been extended to substituted cinnamoyl chlorides and to mannose and mannitol. The derivatives of mannose so obtained were all *laevo*-rotatory, and, consequently, the configuration of the sugar may be retained in them.

*Hexacinnamoylmannitol*,  $C_6H_8O_6(C_9H_7O)_6$ , from very finely powdered dry mannitol and cinnamoyl chloride, forms tufted prisms or needles from ethyl acetate, m. p. 99—100°,  $[\alpha]_D^{20} + 12.96^\circ$ ,  $[\alpha]_D^{20} + 13.15^\circ$  (in chloroform).  $\alpha$ -Pentacinnamoyldextrose and  $\beta$ -pentacinnamoyldextrose have already been described (*ibid.*). *Pentacinnamoylmannose* crystallises with 1 mol. benzene in mycelium-like masses, m. p. 108—112°,  $[\alpha]_D^{20} - 91.3^\circ$ ,  $-91.66^\circ$  (benzene),  $[\alpha]_D^{20}$ , calculated for the benzene-free compound,  $-99.9^\circ$ ,  $-100.3^\circ$ . *Pentabenzoylmannose*,  $C_6H_7O_6Bz_5$ , forms long, radiating needles from alcohol, m. p. 161—161.5° (corr.),  $[\alpha]_D^{20} - 80.44^\circ$ ,  $-80.7^\circ$  (chloroform). *Penta-acetylmannose*,  $C_6H_7O_6Ac_5$ , was obtained by shaking together mannose, pyridine and acetic anhydride at 0°; it has m. p. 117.5° (corr.),  $[\alpha]_D^{18} - 24.8^\circ$ ,  $[\alpha]_D^{20} - 24.9^\circ$  (chloroform), and a very bitter taste.

Similar derivatives were prepared from caffeic acid, which was applied in the form of the dimethylcarbonato-derivative. Methyl chlorocarbonate was gradually added to a dilute solution of the sodium salt, at  $-5^\circ$ , in a hydrogen atmosphere, when the solution was acidified and the 3 : 4-dimethylcarbonatocinnamic acid,



precipitated. It formed curved needles from aqueous acetone, m. p. 145—146° (corr.). The *chloride*,  $C_{13}H_{11}O_7Cl$ , was obtained by the action of phosphorus pentachloride, in glistening needles, m. p. 108.5—109.5° (corr.). From it, the esters were prepared; the *ethyl* ester forms flat needles or prisms, m. p. 98° (corr.), and the *methyl* ester crystallises in tufted spikes, m. p. 95—96.5° (corr.). The chloride was condensed with  $\alpha$ -dextrose, forming *penta-3 : 4-dimethylcarbonatocinnamoyldextrose*,  $C_6H_7O_6(C_{13}H_{11}O_7)_5$ , as a colourless, amorphous mass with indefinite constants. The easily hydrolysed carbonato-groups were removed by the action of dilute sodium hydroxide below 20°, in an atmosphere of hydrogen. On acidifying, a resinous mass was formed, which was fractionally precipitated by chloroform from a solution in ethyl acetate. The pale yellow, amorphous mass so obtained was probably the expected *penta-3 : 4-dihydroxycinnamoyldextrose*, but the constants and analytical data were inconclusive. It is very sparingly soluble in hot water, and gives a deep green

coloration with alcoholic ferric chloride, and a pale yellow precipitate with alcoholic potassium acetate.

J. C. W.

**Influence of Alcoholic Content on the Biochemical Synthesis of  $\alpha$ -Methylglucoside by  $\alpha$ -Glucosidase.** A. AUBRY (*J. Pharm. Chim.*, 1914, [vii], 9, 19—23).—The biochemical synthesis of a number of alkylglucosides has been effected by Bourquelot, Hérissé and Bridel (A., 1913, i, 323, 428, 747) by the action of  $\alpha$ -glucosidase on solutions of dextrose in water containing the respective alcohols. In every case, excessive concentration of alcohol destroys the ferment. The present investigation was undertaken to determine the concentration of alcohol most favourable to the synthesis and also the point at which the ferment is immediately destroyed.

Experiments were performed by adding a constant amount of a maceration of bottom yeast to solutions of dextrose in water made progressively richer in methyl alcohol. The course of the reaction was followed polarimetrically, and, finally, the dextrose determined by the method of Mohr-Bertrand. Small amounts of toluene (which appears to have a slightly toxic effect on the ferment) were also added.

The synthesising action of the ferment is very obvious even in the most dilute alcoholic solutions, and increases until the solution contains 16 grams of methyl alcohol in 100 c.c. At greater concentrations of alcohol, the toxic effect becomes more marked, occurring immediately in solutions containing 34—36 grams of methyl alcohol in 100 c.c. at the ordinary temperature. At higher temperatures, the toxic action becomes more pronounced; thus, at 40°, immediate destruction of the ferment takes place in a solution containing 16 grams of methyl alcohol in 100 c.c.

H. W.

**Influence of the Strength of the Alcohol on the Biochemical Synthesis of  $\alpha$ -Ethylglucoside and  $\alpha$ -Propylglucoside.** ÉM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1914, 158, 70—72; *J. Pharm. Chim.*, 1914, [vii], 9, 62—66. Compare preceding abstract).—The optimum concentration of alcohol for the synthesis of  $\alpha$ -glucosides by  $\alpha$ -glucosidase is for ethyl and propyl alcohols respectively 20% and 16%. Above these concentrations the synthesis is masked by the more rapid decomposition of the glucoside by the same ferment.

W. G.

**Optimum Experimental Conditions for the Preparation of  $\beta$ -Ethylglucoside.** J. COIRRE (*J. Pharm. Chim.*, 1913, [vii], 8, 553—559).—The conditions under which the maximum amount of  $\beta$ -ethylglucoside is formed by the interaction of emulsin, dextrose, and alcohol are discussed theoretically, and a process for the preparation and purification of this compound under these conditions is described.

T. A. H.

**Characterisation of the Organ Pentose as *d*-Ribose.** J. VON BRAUN (*Ber.*, 1913, 46, 3949—3951).—4:4'-Bismethylhydrazinodiphenylmethane (von Braun, A., 1908, i, 700, 737; 1910, i, 524) proves a very convenient reagent for distinguishing between the

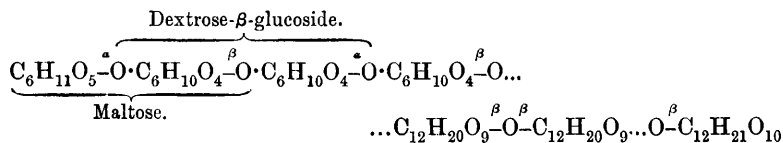
various pentoses. It is already known that, whereas xylose fails to react with this substance, active arabinose readily gives an amorphous, sparingly soluble hydrazone, m. p. 180°.

*d*-Ribose is now found to yield a microcrystalline *dihydrazone*,  $(C_5H_{10}O_4 \cdot N \cdot NMe \cdot C_6H_4)_2CH_2$ , m. p. 141—142°, whilst *d*-lyxose gives an analogous but much more sparingly soluble *dihydrazone*, m. p. 156°.

The behaviour of a specimen of the pentose obtainable from inosic acid towards this reagent proved the identity of the pentose with *d*-ribose.

D. F. T.

**Starch and its Hydrolytic Degradation Products.** OSCAR VON FRIEDRICHS (*Arkiv. Kem. Min. Geol.*, 1913, 5, No. 2, 1—40).—It has been shown already that starch can be converted completely into maltose. Since maltose is a dextrose- $\alpha$ -glucoside, it follows that the amylase which converts starch into maltose, but cannot hydrolyse it further to dextrose, is a  $\beta$ -enzyme, and, consequently, every other linking between the glucoside-forming dextrose residues in starch corresponds with the  $\beta$ -configuration in  $\beta$ -dextrose. Starch may be represented, therefore, thus:



The dicarbonyl binding represented as  $\overset{\beta}{\text{O}}\text{-}\overset{\beta}{\text{O}}$  may occupy any other possible position to that just given, but both linkings must have the  $\beta$ -configuration, otherwise dextrose would be liberated during the hydrolysis of starch by diastase.

That starch is not hydrolysed by emulsin is not remarkable, for it is known that gentianose, which contains a  $\beta$ -glucoside linking, is not hydrolysed by emulsin.

If the amylase which hydrolyses starch is a  $\beta$ -enzyme, it might be expected to hydrolyse  $\beta$ -methylglucoside; this, however, was not found to be the case; on the other hand, neither does it hydrolyse  $\alpha$ -methylglucoside.

Assuming the above formula for starch to be correct, then starch when hydrolysed by acids should yield dextrose, maltose, and a dextrose- $\beta$ -glucoside. It has been found possible to isolate a  $\beta$ -glucosidodextrose from the products of the hydrolysis of starch by acids which appears to be identical with Fischer's *isomaltose*, but this point could not be established definitely. The disaccharide isolated had  $[\alpha]_D + 59.1^\circ$ , was readily hydrolysed by emulsin, and yielded an osazone, m. p. 146°.

The products formed by heating starch with an aqueous solution of oxalic acid under pressure have been isolated as far as possible by means of repeated fractional extraction with aqueous alcohol. The properties of many of these compounds are given below, also the molecular weights determined by the diffusion method of Öholm (A., 1905, ii, 147; 1910, ii, 273).



Amylodextrin, probably a mixture,  $[\alpha]_D^{18} + 196^\circ$ ; mol. wt., 13630; reducing power 0.6—0.9% of that maltose.

Erythrodextrin I,  $[\alpha]_D^{18} + 196^\circ$ ; mol. wt., 3290; reducing power 3.6% of that of maltose.

Erythrodextrin II,  $[\alpha]_D^{18} + 193.1^\circ$ ; mol. wt., 2080; reducing power 10% of that of maltose.

Achroodextrin,  $[\alpha]_D^{18} + 179^\circ$ , probably identical with the maltodextrin  $\alpha$  of Ling and Baker; mol. wt., 1060; reducing power 30% of that of maltose.

Achroodextrin,  $[\alpha]_D^{18} + 172.8^\circ$ , probably identical with the maltodextrin  $\beta$  of Ling and Baker, and the achroodextrin III of Prior; mol. wt., 1020; reducing power 42% of that of maltose.

Achroodextrin,  $[\alpha]_D^{18} + 162.6^\circ$ ; mol. wt., 680; reducing power 58% of that of maltose.

The molecular weight values obtained indicate that the last described achroodextrin is formed by the condensation of four dextrose molecules, whilst the molecule of amylo-dextrin is built up of four molecules of erythrodextrin I, which is probably formed by the condensation of twenty molecules of dextrose.

An investigation of the rate of formation of fermentable sugar from erythrodextrin I and erythrodextrin II by the action of oxalic acid shows that at first very little, if any, is formed, although a decided diminution in optical rotatory power takes place from the very commencement of the interaction of the reagents; fermentable sugar is formed in rapidly increasing quantity only after the lapse of a relatively long period, which under the conditions of the experiment extended to about 280 minutes in the case of erythrodextrin I and about 120 minutes in the case of erythrodextrin II. The conclusion is drawn from this that maltose and dextrose are not formed in the early stages of the hydrolysis of starch or the higher dextrans by acids, but only after these have been broken down into simpler compounds.

W. H. G.

**Behaviour of Starch Dextrans towards Certain Yeasts.** OSCAR VON FRIEDRICHS (*Arkiv. Kem. Min. Geol.*, 1913, 5, No. 3, 1—14).—The behaviour of the dextrans formed by the action of acids on starch (compare preceding abstract) towards certain yeasts has been studied, and the rate at which they are fermented by some of them measured.

The achroodextrans  $[\alpha]_D + 162.6^\circ$ ,  $+172.8^\circ$  and  $+179^\circ$ , and the erythrodextrans  $[\alpha]_D + 193.1^\circ$  and  $196^\circ$ , are not fermented by *Saccharomyces fragilis*, *S. Marxianus*, *S. ellipsoideus* II, *S. exiguus* or *S. Pastorianus* I, although the two last mentioned are possibly able to ferment slowly the achroodextrans  $[\alpha]_D + 162.6^\circ$  and  $+172.8^\circ$ .

The three achroodextrans are slowly fermented by *Saccharomyces thermantiton*, but the two erythrodextrans are not attacked by it.

The yeast Sinner II appears to be unable to ferment the two erythrodextrans or the achroodextrin  $[\alpha]_D + 179^\circ$ , although the achroodextrans  $[\alpha]_D + 172.8^\circ$  and  $+162.6^\circ$  are destroyed by it, the latter more readily than the former.

*Schizosaccharomyces Pombe* attacks energetically all the dextrans investigated, the erythrodextrin  $[\alpha]_D + 196^\circ$  least readily and the achroodextrins most readily.

The achroodextrins are also fermented very readily by *Saccharia suaveolens* and *Mucor Rouxii*; the erythrodextrins are also attacked with ease by the latter.

Generally speaking, the dextrans with the higher molecular weights are not so readily attacked as those with the lower molecular weights, whilst *Schizosaccharomyces Pombe* alone is capable of fermenting the achroodextrins as rapidly as it does dextrose.

The yeasts which are found to split up  $\alpha$ -methylglucoside are capable of fermenting the dextrans only to a very limited extent, whilst *Saccharia suaveolens*, which is known to be capable of fermenting  $\beta$ -methylglucoside, is found to ferment the achroodextrins very energetically.

The results support the view that  $\beta$ -glucoside linkings are present in the starch and dextrin molecules.

W. H. G.

**Synthetic isoMaltose.** OSCAR VON FRIEDRICHS (*Arkiv. Kem. Min. Geol.*, 1913, 5, No. 4, 1—13).—The product obtained by the action of four parts of concentrated hydrochloric acid on one part of dextrose at  $10^\circ$  for twenty-four hours is composed approximately of 68% dextrose, 18% isomaltose, 8% maltose, and 6% unknown polysaccharides.

The assumption has been made that isomaltose is a  $\beta$ -dextroseglycoside, since it is hydrolysed by emulsin and not by maltase (compare E. F. Armstrong, A., 1906, i, 127); but several trials have shown definitely that the optical rotatory power of a solution of isomaltose which has been partly hydrolysed by emulsin is lowered on the addition of alkali, a behaviour which it is difficult to explain except on the assumption that isomaltose is an  $\alpha$ -dextroseglycoside. It was also observed that the optical rotatory power of the solution, instead of decreasing as the isomaltose was hydrolysed into dextrose, increased as the interaction of the isomaltose and emulsin proceeded, the measurements being made in each case after the addition of alkali; it has not been found possible to account for this.

isoMaltose is hydrolysed by an extract of *Aspergillus niger*, but not by an extract of Kephir. It undergoes fermentation when treated with *Aspergillus niger*, *Saccharomyces fragilis*, *S. exiguus* and *Saccharia suaveolens*, but is not affected by *Saccharomyces Kefir*, *S. Marxianus*, *S. cerevisiae* Saaz or *S. cerevisiae* Froberg.

W. H. G.

**Theory of the Dry Distillation of Wood.** PETER KLASON (*Arkiv. Kem. Min. Geol.*, 1913, 5, No. 7, 1—42. Compare A., 1908, i, 717, 955).—The author has distilled dry beech wood under the following conditions: in a cathode-light vacuum, under 5 mm. pressure, and at ordinary pressure with various velocities in which the distillations between the temperatures  $250^\circ$  and  $400^\circ$  lasted respectively three, eight, and sixteen hours and fourteen days. The percentages of charcoal, pitch, acetic acid, formic acid, wood spirit, methyl alcohol, acetone, and formaldehyde were determined in each case, and

also the percentage composition of the charcoal and pitch. The gases obtained were also analysed and their calorific values determined.

The conclusion is arrived at that the dry distillation takes place in two stages. The first stage, which is practically the only one when a cathode-light vacuum is used, takes place essentially according to the equation:  $2C_{42}H_{80}O_{28}(\text{wood}) = 3C_{10}H_5O(\text{primary charcoal}) + 19H_2O + 3CO_2 + 3CO + 2.5CH_3 \cdot CO_2H + H \cdot CO_2H + CH_3 \cdot OH + C_{36}H_{43}O_{16}(\text{pitch}) + C_5H_8O(\text{primary tar oils})$ . The second stage, which takes place completely when the heating is very slow, since no pitch is then obtained, is represented by the equation:  $C_{36}H_{43}O_{16}(\text{pitch}) = C_{30}H_{20}O_3(\text{secondary charcoal}) + 9H_2O + 2CO_2 + C_4H_9(\text{secondary tar oils})$ . The slower the rise in temperature, the more the yield of pitch diminishes, and the yields of charcoal, water, carbon dioxide, and tar oils increase.

The yield of acetic acid is about 6.5% under ordinary pressures and is independent of the rate of heating; under diminished pressure the yield is increased only about 0.5%. The yield of formic acid (2.4%) is greatest under diminished pressure; at ordinary pressures it varies from 0.71 to 0.33% as the time of distillation is increased.

Contrary to what has been stated previously by Norlin, the yield (1.5%) of methyl alcohol is independent of the rate of heating, whilst the quantity of water and carbon dioxide formed increases with the time of distillation.

Acetone is essentially a secondary product produced from the acetic acid, and consequently its yield decreases as the time of distillation increases. The formaldehyde in the wood spirit forms about 1% of the dry wood taken.

The heat of reaction, calculated at  $0^\circ$ , during the dry distillation, which is taken as the difference between the heats of combustion of the wood and its products of distillation, is positive, both for the primary and secondary reactions. The heat developed during the actual dry distillation between  $250^\circ$  and  $400^\circ$  is negative for vacuum distillations, and positive for distillations at ordinary pressure.

The ratio between the acetic acid and formic acid percentages is a measure of the rate of carbonisation, of the quantities of pitch and charcoal, and of the character of the charcoal. The ratio is about 32 for vacuum distillations, and 11 and 5 respectively for quick and slow distillations at ordinary pressures. If it sinks below 5, it denotes that the reaction products have been strongly overheated. T. S. P.

**Action of Chlorine on Pinewood.** EMIL HEUSER and RUDOLF SIEBER (*Zeitsch. angew. Chem.*, 1913, 26, 801—806).—The action of chlorine on pinewood is very energetic at first and quickly reaches a point when very little change occurs; thus, treatment of the wood, for thirty minutes, one hour, and two hours leads to the production of hydrogen chloride to the extent of 20%, 27%, and 32% respectively of the weight of dry wood taken, and the treated wood loses about 20%, 36%, and 42% respectively of its original weight when extracted with an aqueous solution of sodium sulphite; the interaction proceeds very slowly after two hours, for only about 35% of hydrogen chloride is formed in twenty-two hours and only about 45% of the wood is removed by a solution of sodium sulphite. During the first two hours,

that is, so long as lignin is present, the chlorine acts to only a very slight extent on the cellulose, but when all the lignin has been converted into chlorinated derivatives, the cellulose slowly undergoes oxidation, being converted entirely into oxycellulose in twenty-two hours.

As stated already, about 32% of hydrogen chloride is formed in two hours, but only about 9.5% of chlorine is found combined with the wood at the end of this period; similarly, only about 7% of a chlorinated lignin compound can be extracted from the treated wood by means of ethyl alcohol; it is probable, therefore, that the greater part of the hydrogen chloride formed during the reaction owes its origin to the oxidation of the "wood-lignin" by the chlorine.

It was not found possible to obtain a derivative of pyrogallol from the chlorinated "wood-lignin" compound, and not a trace of furfuraldehyde was obtained by treating it with 12% hydrochloric acid.

W. H. G.

**Ethylamine Compounds of Mercuric Chloride.** RAGNAR WIDMAN (*Arkiv. Kem. Min. Geol.*, 1913, 5, No. 1, 1—36).—The author has investigated the various equilibria which exist between the components: mercuric chloride, ethylamine, and hydrochloric acid in aqueous solutions at ordinary temperatures (compare Strömholm, A., 1906, i, 935), and finds that the following compounds, each of which is white in colour, are capable of existing as solid phases:  $\text{HgCl}_2 \cdot \text{NH}_2\text{Et}$ ,  $\text{NH}_2\text{Et} \cdot \text{Hg}_2\text{Cl}_3$ ,  $\text{HgCl}_2 \cdot 2\text{NH}_2\text{Et}$ ,  $(\text{NEt})_2\text{Hg}_3\text{Cl}_2$ ,  $(\text{NEt})_2\text{Hg}_5\text{Cl}_6$ .

The two first are obtained from solutions containing an excess of mercuric chloride, and can be transformed one into the other according to the following scheme:



The third and fourth compounds are prepared from solutions containing an excess of ethylamine, and are connected by the equation:  $3(\text{HgCl}_2 \cdot 2\text{NH}_2\text{Et}) \rightleftharpoons (\text{NEt})_2\text{Hg}_3\text{Cl}_2 + 4\text{NH}_3\text{EtCl}$ .

The compound  $(\text{NEt})_2\text{Hg}_5\text{Cl}_6$  is obtained, among other ways, by shaking or boiling the compound  $\text{NH}_2\text{Et} \cdot \text{Hg}_2\text{Cl}_3$  with a strong solution of mercuric chloride. The compound  $(\text{NEt})_2\text{Hg}_6\text{Cl}_8$ , described by Strömholm, does not exist.

T. S. P.

**Decomposition of Betaine by Alkali.** FR. ALBERS (*Chem. Zeit.*, 1913, 37, 1533—1534, 1545—1547).—On heating betaine with potassium hydroxide at 200—220°, about one-third of the nitrogen is eliminated as trimethylamine, the only other volatile compound formed being carbon dioxide. A compound stable in alkaline solution at 220° is formed, giving a *hydrochloride*,  $\text{C}_4\text{H}_9\text{O}_2\text{N} \cdot \text{HCl}$ , m. p. 187—189°. The *platinichloride* forms a yellow, matted, crystalline mass, m. p. 120—121°.

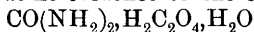
When the decomposition is effected at 500—540°, rather less trimethylamine is found as well as methylamine and ammonia, the last being formed by secondary decomposition from the amines. About 15% less than the theoretical quantity of amines is formed. Methane and hydrogen are liberated, as well as a little carbon monoxide and perhaps nitrogen; no hydrogen cyanide is formed.

The treatment thus fails to liberate more than 85% at most of the betaine nitrogen as ammonia or amines. E. F. A.

**Preparation of Dimethylaminomethyl Alcohol.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 268012. Compare this vol., i, 20).—Dimethylaminomethyl alcohol can be prepared by treating trimethylamine or its salts with a halogen (such as chlorine) or hypochlorous or hypobromous acid in the presence of water, thus avoiding the preparation of the halogen additive compounds of trimethylamine as described in the chief patent (*loc. cit.*). J. C. C.

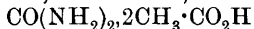
**Combinations of Carbamide with Acids.** D. F. DU TOIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 555—556).—The author has investigated the nature of the solid phases which occur in contact with solution in the system carbamide-acid-water for a number of different acids.

In the case of oxalic acid, the compound  $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$  was found at 20° and 30°, but no evidence of the compound



was obtained at these temperatures.

With acetic acid at 16.5°, 30° and 32°, the compound



was obtained. It melts at about 35°, is very soluble in, but not dissociated by, water.

In the case of hydrochloric acid, the compounds  $2\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$  and  $\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$  were found at 20°, whilst with nitric acid,  $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$  was the only salt formed at this temperature. The solubility of the nitrate decreases as the concentration of nitric acid in the solution increases, attaining a minimum at about 70%.

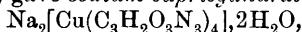
At 20°, sulphuric acid was found to give rise to the compounds  $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$  and  $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ , but no evidence was obtained of the existence of  $\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{SO}_4$ , which has been described by Hantzsch. H. M. D.

**Internally Complex Salts. X. Salt and Complex Salt Formation with Imido-compounds.** H. LEY and F. WERNER (*Ber.*, 1913, 46, 4040—4050).—The formation of complex salts of compounds in which the alkyl or aryl radicles and the oxygen atoms of the acid-imides have been successively replaced by imino- or amino-groups has already been studied in a number of cases (A., 1907, i, 301, 730). The remaining possible imido-compounds, namely, the acid-imides, acylcarbamides, biuret, and the imino-acid-imides are now reviewed.

**I. Acid-imides.**—The copper and magnesium salts are very readily hydrolysed. The dialysis of the copper oxide sol obtained by hydrolysing a 1—2% solution of copper succinimide has been quantitatively followed, succinimide being estimated by distilling with concentrated alkali and titrating the ammonia evolved. Even after twenty-one days the solution still contained about 1% of succinimide, and was with difficulty prevented from coagulating. Magnesium succinimide was obtained in the form of an alkaline solution by the addition of magnesium filings to mercury succinimide or by the action of mag-

nesium powder on aqueous succinimide. From such a solution, silver nitrate deposited *silver succinimide*,  $C_4H_4O_2NaAg, \frac{1}{2}H_2O$ , in slender columns. On evaporating the solution of magnesium succinimide, *magnesium succinamate*,  $Mg(C_4H_6O_3N)_2, 6H_2O$ , crystallised in large, hexagonal tablets, m. p. 86—88°. The salt is extremely soluble and is considerably dissociated in solution. Certain indications were obtained of the existence, in concentrated solutions, of complex salts of the type  $[(RN)_4Mg]Na_2$ , interesting from their connexion with the grouping,  $N_2Mg \cdots N_2$ , in chlorophyll. Ferric salts of succinimide could not be obtained.

Compounds containing the above complex anion were obtained in the case of cyanuric acid. Copper acetate and the sodium salt, in concentrated solution, gave *sodium cupricyanurate*,

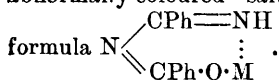


as a heavy, violet, crystalline precipitate.

Copper cyanurate combines with two molecules of ammonia. Claus and Putensen (A., 1889, 30) assigned the formula  $Cu[NH_4(C_3HO_3N_3)]_2$  to this compound, from which the conclusion might be drawn that copper dimethyl cyanurate would not combine with ammonia. An ammoniacal solution of dimethyl hydrogen cyanurate gives with copper sulphate, however, a deep blue coloration, followed by precipitation of the reddish-violet *diammine*,  $Cu(C_5H_6O_3N_3)_2, 2NH_3$ , which becomes dark blue in an atmosphere of ammonia, probably forming a tetrammine. Claus and Putensen's compound is therefore a diammine.

II and III. *Acylcarbamides and Biuret*.—No metallic derivatives of acylcarbamides (benzoylcarbamide and benzoylphenylcarbamide) could be obtained. Owing to the similarity in colour between the alkali-copper acid-imides of the type  $(CuA_4)M_2$  and the alkali-copper biurets (compare Tschugaev, A., 1907, i, 595), attempts were made to prepare similarly constituted compounds of biuret. Only the known derivative,  $K_2Cu(C_2H_2O_2N_3)_2$ , and a *basic salt*,  $KCu(C_2H_2O_2N_3)_2, 3H_2O$ , well-defined, reddish-violet columns, could be obtained. They are internally complex salts, akin to those prepared from amino- and hydroxyacethydroxamic acids (A., 1913, i, 346).

IV. *Imino-acid-imides*.—Sodium dibenzamide and copper acetate gave the normal, bluish-green, easily hydrolysed *copper dibenzamide*. Iminodibenzamide, however, gave a lustrous, pale greyish-brown *copper salt*,  $Cu(C_{14}H_{11}ON_2)_2$ . It dissolves in pyridine with deep blue colour. Similarly, nickel forms a pale yellow, very stable *salt*. These abnormally-coloured salts are most probably represented by the



J. C. W.

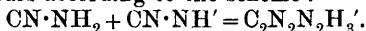
**Some Double and Complex Cyanates.** PAUL PASCAL (*Bull. Soc. chim.*, 1914, [iv], 15, 11—19).—When a fresh solution of potassium cyanate in 70% alcohol is added to a neutral solution of uranyl nitrate, a voluminous, yellow precipitate, possessing a greenish fluorescence, of *potassium uranylcyanate*,  $[UO_2(CNO)_4]K_2$ , is produced. This compound is very soluble in water, and, owing to hydrolysis, the solution gives all the tests for uranium. After a few minutes the

aqueous solution deposits a yellowish-orange, insoluble compound, having the composition  $[(\text{UO}_2)_2(\text{CNO})_5]\text{K}$ .

If to a 25% solution of uranyl nitrate a tenth of its weight of potassium uranylecyanate is added, and then sufficient alcohol to produce a turbidity, *uranyl cyanate*,  $\text{UO}_2(\text{CNO})_2$ , is obtained as a golden-yellow precipitate. On the other hand, a solution of potassium uranylecyanate containing 30–50% of potassium cyanate deposits spontaneously the yellow compound,  $[\text{UO}_2(\text{CNO})_3]\text{K}$ .

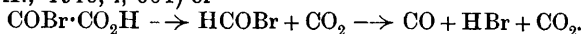
The cryoscopic behaviour of solutions of uranyl cyanate containing various proportions of potassium cyanate indicates that the compound  $[\text{UO}_2(\text{CNO})_4]\text{K}_2$  is present in solutions containing an excess of potassium cyanate. Solutions containing cobaltous cyanate and potassium cyanate behave similarly, indicating that potassium cobaltous cyanate is present; moreover, the molecular magnetic susceptibility is much less than that for ordinary cobaltous salts, and in migration experiments the cobalt wanders to the anode. T. S. P.

**Polymerisation of Cyanamide to Dicyanodiamide in Aqueous Solution.** G. GRUBE and J. KRÜGER (*Zeitsch. physikal. Chem.*, 1913, 86, 65–105).—The polymerisation of cyanamide in aqueous solution to dicyanodiamide,  $\text{CN}\cdot\text{NH}_2 \rightarrow (\text{CN}\cdot\text{NH}_2)_2$ , has been investigated by the usual kinetic method and by means of potential measurements. In the latter method the concentration of the hydrogen ion has been determined under different conditions. It is shown that the presence of alkali accelerates the reaction in a marked degree. Ammonia accelerates the velocity of polymerisation to an increasing amount as its concentration increases; in the case of sodium hydroxide and calcium hydroxide a maximum velocity is reached at a definite concentration, and at greater or smaller concentrations than this value, the velocity becomes smaller. The dissociation constant of cyanamide is of the order of magnitude  $10^{-11}$ , and that of dicyanodiamide  $10^{-13}$ . From these figures it follows that a molecular solution of monosodium cyanamide is dissociated to the extent of 3%, and one of mono-ammonium cyanamide to the extent of 79–89%. It is shown that the polymerisation occurs according to the scheme:



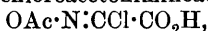
This is proved by the fact that the reaction has a maximum velocity when the condition  $(\text{CNNH}') = (\text{CNNH}_2)$  is fulfilled. The method of preparation of dicyanodiamide from calcium nitride is discussed, and a method proposed for its preparation without the addition of any further alkali. J. F. S.

**Chloro- and Bromo-oximinoacetic Acids.** J. HOUBEN and H. KAUFFMANN (*Ber.*, 1913, 46, 4001–4010).—It was hoped from an examination of the behaviour of chloro- and bromo-oximinoacetic acids to decide whether the easy decomposition of oxalic acid bromide (and chloride) [bromo- and chloro-glyoxylic acids] occurs in the stages:  $\text{COBr}\cdot\text{CO}_2\text{H} \rightarrow (\text{CO})_2\text{O} + \text{HBr} \rightarrow \text{CO} + \text{CO}_2 + \text{HBr}$  (Staudinger and Anthes, *A.*, 1913, i, 604) or



The present results, however, fail to give a decisive answer to this question.

Chloro-oximinoacetic acid (compare Houben and Kauffmann, A., 1913, i, 1159) when neutralised with sodium hydroxide in aqueous solution gives a green precipitate with copper acetate, a deep red coloration with ferrous sulphate, a yellow precipitate with silver nitrate, and a yellow turbidity with lead acetate; *ammonium* salt, colourless precipitate from ether. The molecular weight of the acid in acetic acid solution by cryoscopic measurement agrees with that of an acetyl derivative. When heated with acetyl chloride for half an hour, the acid is converted into chloroacetoximinoacetic acid,



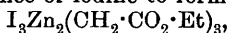
stellar aggregates of needles, m. p. 73—74° (decomp.), which is converted by phosphorus pentachloride under light petroleum into chloroacetoximinoacetyl chloride,  $\text{OAc}\cdot\text{N}:\text{CCl}\cdot\text{COCl}$ , a colourless oil, b. p. 95°/13 mm.

Ethyl bromo-oximinoacetate (compare Jovitschitsch, A., 1906, i, 1161) is obtained conveniently by shaking a mixture of the nitrolic acid of ethyl acetate,  $\text{NO}_2\cdot\text{C}(\text{:NOH})\cdot\text{CO}_2\text{Et}$ , with aqueous hydrobromic acid and ether for two hours, when the nitro-group becomes replaced by bromine; the product, m. p. 93°, was hydrolysed by heating under reflux condenser with ether and hydrobromic acid, the resulting *bromo-oximinoacetic acid*,  $\text{OH}\cdot\text{N}:\text{CBr}\cdot\text{CO}_2\text{H}$ , being found in the ethereal solution. Bromo-oximinoacetic acid is a very hygroscopic, crystalline substance, decomp. at 110°, which, unlike the chloro-oximinoacetic acid, is decomposed by water with great readiness, the products of decomposition being fulminic acid, hydrobromic acid, and carbon dioxide. If the acid is heated carefully in a vacuum (15 mm.), decomposition occurs and pale yellow crystals form in the ice-cooled receiver, but these could not be further examined, as they decompose rapidly with formation of gaseous products. These crystals may have been of the formula  $\begin{array}{c} \text{CO} \\ | \\ \text{O} \end{array} > \text{C}:\text{N}\cdot\text{OH}$  or  $\text{CHBr}\cdot\text{N}\cdot\text{OH}$ ,

which would be expected respectively if the decomposition had occurred analogously to either of the two suggested modes of decomposition of bromoglyoxylic acid.

D. F. T.

**Organo-metallic Ester Compounds. II. Iodo-zinc-ester Compounds.** BRUNO EMMERT and WILHELM ELLER (*Ber.*, 1913, 46, 1508—1511. Compare A., 1911, i, 846).—Zinc reacts with ethyl iodoacetate in the presence of iodine to form the compound



which, when rapidly heated, decomposes at 133—140°. In the presence of ethyl ether, reaction takes place more readily, and, after removal of the solvent, a syrupy mass remains, which evolves the remainder of the ether when placed in a vacuum for a protracted period. The crystalline compound described above is thereby obtained, which is only partly dissolved on protracted contact with ether. When cautiously decomposed by water, it yields ethyl acetoacetate, which is recognised by its odour and by the ferric chloride reaction, whilst with



dilute sulphuric acid it gives ethyl acetoacetate and ethyl iodoacetate. On distillation it yields a few drops of an iodine-free organometallic liquid, which commences to boil at about  $180^{\circ}$ , thereby becoming black and exploding. With anhydrous ethyl alcohol it yields the crystalline additive product,  $I_2Zn_2(CH_2 \cdot CO_2Et)_3 \cdot 2EtOH$ , needles.

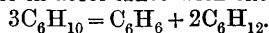
Compounds of zinc with ethyl  $\beta$ -iodopropionate and ethyl *o*-iodobenzoate were also obtained by heating the requisite components; on account of their extreme sensitiveness to moisture, they were not further investigated. H. W.

**Hydration and Certain Other Transformations of 1:1:2-Trimethylcyclopropane.** N. KISHNER and G. CHONIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1770—1779).—Attempts to nitrate 1:1:2-trimethylcyclopropane by means of nitric acid (D 1.075), as suggested by Konovalov, gave unsatisfactory results, the hydrocarbon being either unattacked or, at higher temperatures, converted into oxidation products. The action of nitric acid in presence of glacial acetic acid causes rupture of the trimethylene ring and formation of products of hydration of the trimethylcyclopropane. These products consist principally of dimethylisopropylcarbinol, but the other possible alcohol, methyltert.-butylcarbinol, could not be detected.

The action of hydrobromic acid on 1:1:2-trimethylcyclopropane has already been referred to briefly (compare Kishner, A., 1912, i, 245), but has now been more thoroughly investigated. The bromo-products obtained, on distillation with aniline to convert them into the corresponding unsaturated hydrocarbons, yield  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butene and  $\beta\gamma$ -dimethyl- $\Delta^{\alpha}$ -butene; the parent bromo-compound of the former of these is  $\beta$ -bromo- $\beta\gamma$ -dimethylbutane, whilst the latter may be derived also from  $\beta$ -bromo- $\beta\gamma$ -dimethylbutane or from  $\alpha$ -bromo- $\beta\gamma$ -dimethylbutane.

The action of fuming hydrochloric acid on 1:1:2-trimethylcyclopropane in a sealed tube at  $100^{\circ}$  gives a theoretical yield of  $\beta$ -chloro- $\beta\gamma$ -dimethylbutane,  $CM_{e_2}Cl \cdot CHMe_2(?)$ , b. p.  $112-112.5^{\circ}/759$  mm.,  $D_4^{20}$  0.8724,  $n_D$  1.4178. T. H. P.

**Stability of Cyclic Hydrocarbons in Connexion with their Configuration.** The Transformation of *cycloHexene* into *Benzene* and *cycloHexane*. J. BÖESEKEN and K. H. A. SILLEVIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 499—506).—When *cyclohexene* vapour, mixed with carbon dioxide, is passed in a slow current over finely-divided nickel, heated at  $180^{\circ}$ , it is converted into benzene and *cyclohexane* in accordance with the equation



The quantity of benzene actually obtained amounted to about 40%, the remainder consisting of *cyclohexane* and from 2—4% of unchanged *cyclohexene*. Since carbon monoxide was also found to have been produced, it is probable that the excess of benzene is due to a part of the hydrogen, which is formed as an intermediate product in accordance with  $C_6H_{10} = C_6H_6 + 2H_2$ , being used up in the reduction of the admixed carbon dioxide.

The experiments show that *cyclohexene* at  $180^{\circ}$  is metastable with

respect to a mixture of benzene and *cyclohexane*, and also with regard to a mixture of benzene and hydrogen.

Observations of other workers relative to the stability of the cyclic hydrocarbons are referred to in connexion with these experiments.

H. M. D.

**Thermal and Cryoscopic Investigation of Mixtures of Benzene and Ethyl Alcohol.** F. VIALA (*Bull. Soc. chim.*, 1914, [iv], 15, 5—11).—The freezing point curve of mixtures of alcohol and benzene has a eutectic point at a molecular concentration of 97·5% of alcohol; no compound is formed. The freezing point of alcohol is found to be  $-113\cdot9^{\circ}$ .

The specific heat of a mixture of benzene and alcohol is greater than corresponds with the law of mixtures. From the results of the specific heat measurements the author has calculated the heat of dilution of various solutions and then applied Baud's equation (A., 1913, ii, 233) in order to determine the molecular weight of alcohol in benzene solution. It was found that in dilute solutions the alcohol consists of simple molecules, but association takes place with increasing concentration, until in concentrated solutions (50% and over) the association into double molecules is complete. The association does not vary with the concentration in the latter solutions, and consequently the conclusion is drawn that pure alcohol consists of double molecules, at all events between the temperatures  $231^{\circ}$  and  $275\cdot5^{\circ}$  abs.

T. S. P.

**The Supposed Benzene-potassium of H. Abeljanz.** W. SCHLENK and HEINRICH MEYER (*Ber.*, 1913, 46, 4060—4061).—Abeljanz (A., 1876, i, 703) described a bluish-black, crystalline mass which he obtained by heating benzene with potassium at  $240$ — $250^{\circ}$  and assumed to be a mixture of the compounds  $C_6H_5K$  and  $C_6H_4K_2$ . The authors find that the substance is merely potassium coated with a film of carbon. A considerable quantity of diphenyl was present in the solvent. The evolution of hydrogen under the influence of moisture and the formation of diphenyl and diphenylbenzene, which Abeljanz observed, are thus accounted for.

J. C. W.

**Vacuum Coal-tar.** AMÉ PICTET and MAURICE BOUVIER (*Compt. rend.*, 1913, 157, 1436—1439. Compare A., 1913, i, 1315).—A study of the tar obtained by distilling coal under reduced pressure (15—18 mm.) at  $450^{\circ}$ . The tar contains neither phenols nor aromatic hydrocarbons, but yields both on decomposition at a red heat. The tar, after washing with dilute sodium hydroxide and dilute sulphuric acid, was fractionated under reduced pressure. The fractions were found to contain alcohols and unsaturated hydrocarbons, which were not obtainable in sufficient quantity for identification. These fractions freed from the alcohols by treatment with sodium, and from the unsaturated hydrocarbons by treatment with sulphuric acid, were then further fractionated and two of the principal fractions studied.

Fraction I, b. p.  $172$ — $174^{\circ}$ ,  $D_{20}^{23}$  0·7765,  $n_D^{23}$  1·4196, had by analysis and molecular weight determination, the composition  $C_{10}H_{20}$ .

Fraction II, b. p. 189—191°,  $D_{20}^{22}$  0.7838,  $n_D^{22}$  1.4234, had the composition  $C_{11}H_{22}$ .

These two fractions had all the properties of naphthenes, and were identical in physical properties with two hydrocarbons isolated by Mabery from Canadian petroleum (compare *J. Amer. Chem. Soc.*, 1911, 33, 251). A chemical study of the hydrocarbon  $C_{10}H_{20}$  shows it to be 1:2:4:5-tetramethylcyclohexane, and from it the authors have prepared a dibromo-derivative, m. p. 202°, and a dinitro-derivative, m. p. 205°.

They suggest that the other hydrocarbon,  $C_{11}H_{22}$ , is the analogue of the first, being pentamethylcyclohexane. W. G.

**A Method of Synthesis of Benzyl Chloride and its Homologues.** MARCEL SOMMELET (*Compt. rend.*, 1913, 157, 1443—1445).—Methyl chloromethyl ether reacts readily with benzene and its homologues in carbon disulphide or carbon tetrachloride in the presence of stannic chloride to give benzyl chloride and its homologues. The chloro-ether and the hydrocarbon in solution are cooled to  $-10^\circ$ , and the stannic chloride run in drop by drop. By this method the author has prepared benzyl chloride, *p*-tolyl chloride, and the three dimethylbenzyl chlorides.

3:4-Dimethylbenzyl chloride is a liquid, b. p. 116—117°/24 mm., which on heating with potassium acetate in acetic acid yields 3:4-dimethylbenzyl acetate,  $C_6H_3Me_2 \cdot OAc$ , b. p. 146—148°/28 mm., furnishing on hydrolysis 3:4-dimethylbenzyl alcohol, m. p. 62.5—63.5°.

2:4-Dimethylbenzyl chloride, b. p. 110°, gives the acetate, b. p. 157°/50 mm., and the alcohol, b. p. 151—152°/44 mm., yielding a phenylurethane, m. p. 78—79°. These two alcohols on oxidation give the corresponding dimethylbenzoic acids.

2:5-Dimethylbenzyl chloride, b. p. 120—121°/28 mm., yields an acetate, b. p. 138—141°/28 mm., and an alcohol, b. p. 142—143°/37 mm., which gives a phenylurethane, m. p. 86°.

All these chlorides are readily converted into the corresponding aldehydes by warming in aqueous alcoholic solution with hexamethylenetetramine (compare A., 1913, i, 1395). W. G.

**Friedel and Craft's Reaction. XIII. Action of Chlorides of Ethylene on Benzene.** J. BÖESEKEN and M. C. BASTET (*Rec. trav. chim.*, 1913, 32, 184—209. Compare A., 1911, i, 522, and earlier abstracts).—It has been previously shown that the Friedel and Crafts' reaction takes place when three molecules are present, the first of which is unsaturated, the second of which can be activated to such an extent that it is decomposed during the reaction into two parts, which then unite with the first molecule, and the third of which is a catalyst which can activate the two molecules (compare Böeseken and Prins, A., 1911, i, 173). In such condensations in the presence of benzene, it has been assumed that the molecule of the latter is always supersaturated, but from observations of Sieger (*Diss.*) the authors are led to the conclusion that this is not invariably the case. In the present paper, they describe a series of condensations of benzene with various chloro-derivatives of ethylene, in

which, in the first stage, the molecule of benzene is disrupted and forms a compound with the unsaturated molecule; this latter molecule becomes in its turn disrupted and combines with a second or third molecule of benzene which now behaves as if it were unsaturated.

Vinyl chloride, b. p.  $-18^{\circ}$ , is obtained by the decomposition of ethylene dichloride at  $600^{\circ}$ . A small quantity of carbon is simultaneously formed, and, in addition to hydrogen chloride, the gaseous product contains carbon dioxide, carbon monoxide, oxygen, and unsaturated hydrocarbons in small quantity. For purposes of experiment, the vinyl chloride was not condensed, but, after being freed from hydrogen chloride and dried, was passed directly into the reaction mixture. The latter is prepared by warming a mixture of mercuric chloride and aluminium powder with benzene. A vigorous reaction occurs with the formation of a complex product containing mercurous chloride, aluminium chloride, and benzene, which remains for some time at  $0^{\circ}$  in supersaturated solution. In these circumstances, vinyl chloride is readily and completely absorbed with the formation of *aa*-diphenylethane and small amounts of 9:10-dimethyldihydroanthracene, m. p.  $178-179^{\circ}$ . Benzophenone is obtained by oxidation of the former, the absence of benzoic acid showing that the original product does not contain dibenzyl.

A possible explanation of the course of the reaction consists in the assumption of an initial formation of styrene and subsequent combination of the latter with benzene. To test this point, styrene (obtained by the rapid distillation of cinnamic acid with the help of a long fractionating column) has been condensed with benzene at  $0^{\circ}$  in the presence of aluminium-mercury couple. The product appears to be a polymeride of styrene, having a mean molecular weight of 250 in benzene solution; it does not contain *aa*-diphenylethane. When agitated with aluminium chloride in carbon disulphide solution (without benzene), styrene yields a substance of indefinite b. p. and mean molecular weight, 172, in benzene solution.

The possibility of the intermediate formation of ethylidene chloride has also been examined. Under conditions similar to those used in experiments with vinyl chloride, ethylidene chloride gives *aa*-diphenylethane, but the yields are considerably lower than in the original experiments, and, further, augmentation of the concentration of hydrogen chloride diminishes the quantity.

Finally, the interpretation is adopted that the first stage of the reaction consists in a disruption of the benzene molecule and combination with vinyl chloride to form  $\alpha$ -chlorophenylethane,  $\text{Ph}\cdot\text{CHCl}\cdot\text{CH}_3$ , which, in its turn, is disrupted and combines with a further molecule of benzene to yield *aa*-diphenylethane (compare Schramm, A., 1893, i, 563). The formation of 9:10-dimethyldihydroanthracene is explained by the assumption of the condensation of two molecules of  $\alpha$ -chlorophenylethane.

*aa*-Diphenylethane, when prepared by Friedel and Craft's reaction and freshly distilled, shows a marked fluorescence. This appears to be due to an impurity formed during the condensation. The fluorescence gradually disappears when the substance is preserved, but re-appears on

repeated distillation, especially in an oxidising atmosphere. It can be removed by boiling under ordinary pressure or by treatment with sodium in alcoholic solution.

The condensation of the two symmetrical acetylene dichlorides (compare Chavanne, A., 1912, i, 330) with benzene in the presence of aluminium-mercury couple at 20° has also been investigated. The products obtained in each case are identical, consisting of dibenzyl, triphenylethane, and tetraphenylethane. At 0°, reaction is extremely slow. At 80°, reaction is more complete than at 20°, but also more complicated, a larger quantity of residue being formed, whilst, also, the amounts of dibenzyl and tetraphenylethane (which are certainly the products of an abnormal reaction) are increased relatively to the amount of triphenylethane.

Trichloroethylene,  $\text{CCl}_2\cdot\text{CHCl}$ , scarcely reacts with benzene in the presence of the aluminium-mercury couple at the ordinary temperature. At higher temperatures, the main products are  $\alpha$ -diphenylethane and tetraphenylethane, and the course of the reaction is represented by the equations:  $\text{CHCl}\cdot\text{CCl}_2 + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CHCl}_2$  and  $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CHCl}_2 + 3\text{C}_6\text{H}_6 = \text{CH}(\text{C}_6\text{H}_5)_2\cdot\text{CH}(\text{C}_6\text{H}_5)_2 + 3\text{HCl}$ .

It has been previously shown that tetrachloroethylene does not react to a perceptible extent with benzene in the presence of powdered aluminium chloride at 80° (A., 1912, i, 65). The authors now show that very little action occurs between the pure substances at 80° in the presence of aluminium-mercury couple. The reaction observed with commercial tetrachloroethylene is attributed to impurities. The authors are led to the conclusions that the intensity of the action diminishes with an increase in the number of atoms of chlorine, and that reaction commences by an addition of benzene at the double bond. The chlorine atoms do not become active, even in tetrachloroethylene, but are activated in the additive products. With increase in the number of chlorine atoms, the second stage of the reaction becomes more complicated.

H. W.

**Quantitative Investigations on the Nitration of the Chlorotoluenes.** J. P. WIBAUT (*Rec. trav. chim.*, 1913, 32, 244—320).—The author has prepared the four nitro-*o*-chlorotoluenes in a state of purity and has studied the six curves of solidification of binary mixtures prepared from them. He has thus been enabled to investigate the products of nitration of *o*-chlorotoluene at 0°, and has shown by chemical means that all four possible isomerides are formed, whilst from thermal analyses, the relative proportions of the isomerides are deduced. A similar series of experiments has been effected with *m*-chlorotoluene. The results are in accord with the theoretical predictions of Holleman.

*o*-Chlorotoluene has b. p. 159.5°/759.5 mm. (corr.),  $n_D^{20}$  1.4977.

2-Chloro-4-nitrotoluene is prepared by the nitration of *o*-toluidine dissolved in concentrated sulphuric acid and successive treatment of the nitrotoluidine with nitrous acid and cuprous chloride. It has  $n_D^{20}$  1.5470, m. p. 62.3°, instead of 65° and 68° recorded in the literature. Reduction with iron powder in the presence of a small quantity of sulphuric acid converts it into *o*-chloro-*p*-toluidine,

m. p.  $23.1^{\circ}$ . The acetyl derivative, m. p.  $105^{\circ}$ , and the *benzoyl* derivative, needles, m. p.  $122^{\circ}$ , have been prepared.

2-Chloro-6-nitrotoluene,  $n_{D}^{69.4} 1.5377$ , m. p.  $35.3^{\circ}$  (Green and Lawson, T., 1891, 59, 1017, give  $37^{\circ}$ ) is prepared by reductions of 2:6-dinitrotoluene by hydrogen sulphide in ammoniacal solution and replacement of the amino-group by chlorine in the usual manner. 6-Chloro-*o*-toluidine has m. p.  $2.8^{\circ}$ , and rapidly darkens on exposure to air. The acetyl and benzoyl derivatives have m. p.  $156^{\circ}$  and  $170^{\circ}$  respectively.

For the preparation of 2-chloro-5-nitrotoluene, finely powdered aceto-*o*-toluide is added to a mixture of nitric acids (D 1.52 and 1.40 respectively) at  $30^{\circ}$ . The temperature must not rise above  $35-37^{\circ}$ . After remaining for twenty-four hours at the ordinary temperature, the product is poured on to ice. The mixture of acetyl compounds is hydrolysed with boiling hydrochloric acid, and 3-nitro-*o*-toluidine removed by passing steam through the mixture, accompanied by a smaller quantity of 5-nitro-*o*-toluidine. Crystallisation from alcohol enables the two isomerides to be obtained in the pure state, m. p.  $95^{\circ}$  and  $130^{\circ}$  respectively. The yields are unsatisfactory, but no improvement could be effected by nitrating in sulphuric acid or acetic acid solution. 2-Chloro-5-nitrotoluene has m. p.  $42.9^{\circ}$ ,  $n_{D}^{69.4} 1.5511$ . 6-Chloro-*m*-toluidine has m. p.  $83^{\circ}$  (acetyl derivative, m. p.  $92^{\circ}$ ; *benzoyl* derivative, needles, m. p.  $119.5^{\circ}$ ).

2-Chloro-3-nitrotoluene, prepared from 3-nitro-*o*-toluidine described above, has m. p.  $22.1^{\circ}$ ,  $n_{D}^{69.4} 1.5327$ ; the corresponding amino-compound (compare Wynne and Greeves, T., 1895, 67, 1548) solidifies at  $6.6^{\circ}$  (acetyl derivative, m. p.  $133^{\circ}$ ; *benzoyl* derivative, needles, m. p.  $125^{\circ}$ ).

*o*-Nitrotoluene is nitrated by gradually adding to it four times its weight of nitric acid (D 1.52) at  $-1$  to  $+1^{\circ}$ . After treatment with ice and extraction with benzene the product is distilled under diminished pressure. Measurement of the index of refraction of the various fractions proves the absence of unchanged *o*-chlorotoluene or dinitro-derivatives. Attempts to separate the isomerides by distillation under diminished pressure or by crystallisation at low temperatures were unsuccessful. Better results were obtained by reduction and acetylation of the mixture. Crystallisation from benzene then yields aceto-6-chloro-*o*-toluidide, whilst on concentrating the mother liquors, aceto-2-chloro-*m*-toluidide is obtained. 6-Chloro-*m*-toluidine is isolated during the distillation of the primary reduction product with steam. Neither 2-chloro-4-nitrotoluene nor any of its derivatives could be isolated, but the presence of the former is deduced from the fact that by precipitation of the acetylamino-derivatives (remaining after crystallisation of the greater bulk of the products) from benzene solution by addition of light petroleum, fractions are obtained which show a rise in m. p. on admixture with aceto-2-chloro-*p*-toluidide.

The solidification curves of the six binary mixtures of the *o*-chloro-nitrotoluenes have been determined. The curve has the ordinary form in the cases of the following pairs of isomerides (in which the methyl group and chlorine atom are in the positions 1 and 2 respectively), and the eutectic point is appended in brackets: 1:2:5 and 1:2:6 ( $7.2^{\circ}$ ); 1:2:5 and 1:2:3 ( $+1^{\circ}$ ); 1:2:6 and 1:2:4 ( $17.2^{\circ}$ ); 1:2:4 and 1:2:3 ( $8.2^{\circ}$ ); in the case of the isomerides, 1:2:5 and 1:2:4, the

curve rises to a maximum indicating the existence of a compound formed by a molecule of each component, whilst with isomerides, 1:2:6 and 1:2:3, a maximum is also found corresponding with the formation of a compound from two molecules of the latter and one of the former.

The application of Valetton's method (*Acad. Sci. Amsterdam*, 1910, 754) to synthetic mixtures of the four *o*-chloronitrotoluenes has shown that the proportions of the isomerides, 1:2:4-, 1:2:5-, and 1:2:6-, can be determined with sufficient accuracy; estimation of the 1:2:3-isomeride is not directly possible, since the formation of the compound, 1:2:3- and 1:2:6-, causes too great deviations. The mixture of isomerides, obtained by the action of nitric acid (D 1.52) on *o*-chlorotoluene at 0° during one and a-quarter hours, is thus shown to contain 43.4% of 1:2:5-, 17.0% of 1:2:4-, 20.7% of 1:2:6-, and (by difference) 18.8% of the 1:2:3-isomeride.

3-Chloro-6-nitrotoluene is obtained by the following method, which differs in several respects from that described by Cohen and Hodsman (T., 1907, 91, 974); aceto-*m*-toluidide is dissolved in cold concentrated sulphuric acid, and nitrated at -5° to -3° with a mixture of nitric acid (D 1.52) and concentrated sulphuric acid. After elimination of the acetyl group, 6-nitro-*m*-toluidine, m. p. 135° (instead of 138° recorded in the literature), is obtained, which is converted into 3-chloro-6-nitrotoluene in the usual manner. The latter has  $n_D^{20}$  1.5495, and appears to exist in a stable modification, m. p. 24.9°, and a metastable form, m. p. 24.2°.

3-Chloro-2-nitrotoluene is obtained by the method recommended by Brand and Zöller (A., 1907, i, 755). It has  $n_D^{20}$  1.5204, temperature of solidification, 23.4°. Certain observations lead the author to the conclusion that it may also exist in a metastable state.

For the preparation of 3-chloro-4-nitrotoluene,  $n_D^{20}$  1.5428, m. p. 24.2°, acet-*o*-toluidide has been converted into 5-chloro-4-nitro-*o*-toluidine, m. p. 124°, according to the method of Claus and Stapelberg (A., 1893, i, 580), who give 128° as m. p. Removal of the amino-group of this compound by the usual methods leads to the desired product, the structure of which is confirmed by transforming it into aceto-3-chloro-*m*-toluidide.

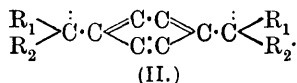
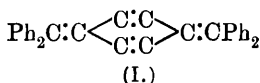
3-Chloro-5-nitrotoluene has  $n_D^{20}$  1.5404, m. p. 58.4°, whereas Hönig (A., 1887, 1034) gives 55°.

*m*-Chlorotoluene has been nitrated under the same conditions as the *o*-isomeride. Measurement of the index of refraction of the various fractions proves the absence of unchanged *m*-chlorotoluene or of its di-nitro-derivatives. The author has not attempted to isolate directly the various isomerides; but, since on theoretical grounds the formation of 3-chloro-5-nitrotoluene is considered improbable, he has applied Valetton's method to the determination of the proportions in which the three other isomerides are formed when *m*-chlorotoluene is nitrated at 0°; he thus finds 58.9% 3-chloro-6-nitrotoluene, 32.3% 3-chloro-4-nitrotoluene, and 8.8% 3-chloro-2-nitrotoluene. Investigation of the curves of solidification of binary mixtures of these three substances yields normal results in the cases of 3-chloro-4-nitrotoluene and 3-chloro-2-nitrotoluene (eutectic temperature about -4.5°) and of 3-chloro-

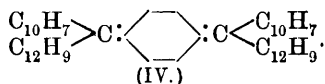
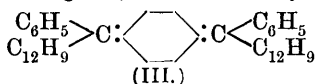
6-nitrotoluene and 3-chloro-2-nitrotoluene (eutectic temperature about  $-5^\circ$ ); in the case of 3-chloro-6-nitrotoluene and 3-chloro-4-nitrotoluene a compound appears to be formed from one molecule of each constituent, which, however, is mainly decomposed in the liquid state.

By somewhat modifying the theories of Holleman and Huisinga, a mathematical expression has been devised according to which the relative quantities of isomerides obtained by nitrating the chlorotoluenes can be sufficiently accurately calculated. H. W.

**Tri-arylmethyls. XI. Tetra-arylquinodimethanes** [Tetra-aryldimethylenecyclohexadienes]. W. SCHLENK and MAX BRAUNS (*Ber.*, 1913, **46**, 4061—4066).—It was previously found that the introduction of diphenyl or naphthyl groups in the hexaphenylethane molecule considerably enhanced the dissociation into free tri-arylmethyl radicals. The conclusion was therefore drawn that the above groups make larger demands on the affinity of the carbon atom than does the phenyl group. It was expected that the introduction of these groups into Thiele's tetraphenylquinodimethane [1:4-bisdiphenylmethylenep $\Delta^{2:5}$ -cyclohexadiene] (I) (A., 1904, i, 491) would similarly loosen the fourth valency of the methane-carbon atom and that compounds of the type (II) would be obtained.

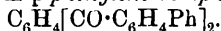


The diphenylbidiphenyl- and bidiphenyllydi- $\alpha$ -naphthylquinodimethanes (III and IV), however, proved to be indifferent towards additive agents, like Thiele's hydrocarbon.



The above conclusion was, however, justified, since it was found that the tetra-aryl-*p*-xylylene haloids which contained diphenyl or naphthyl groups, dissociated into the quinonoid hydrocarbons and the free halogen, even more readily than did the tetraphenyl compound.

Terephthaloyl chloride was condensed with diphenyl by means of aluminium chloride to form *p*-phenylene bitiphenyllyl diketone,



The not quite pure compound formed colourless leaflets, m. p.  $280-285^\circ$ . It was converted into *diphenylbidiphenyllylxylylene glycol*,  $\text{C}_6\text{H}_4[\text{CPh}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Ph}]_2$ , which formed a microcrystalline powder, m. p.  $105^\circ$ , by the action of magnesium phenyl bromide, and into *di- $\alpha$ -naphthylbidiphenyllylxylylene glycol*,  $\text{C}_{52}\text{H}_{38}\text{O}_2$ , by the action of magnesium  $\alpha$ -naphthyl bromide. Both compounds gave deep blue solutions in sulphuric acid. Hydrogen chloride converted them into the corresponding xylylene *dichlorides*,  $\text{C}_{44}\text{H}_{32}\text{Cl}_2$  and  $\text{C}_{52}\text{H}_{36}\text{Cl}_2$ . The former gave white crystals, m. p.  $254^\circ$  (decomp.), and the latter crystallised with  $2\text{C}_6\text{H}_6$ , and they both gave coloured solutions on boiling in benzene or xylene, owing to dissociation into the quinodimethanes. These compounds were prepared by boiling benzene solutions with copper powder in carbon dioxide atmospheres. *Diphenylbidiphenyllylquino-*



*dimethane* [1:4-bisphenyldiphenylmethylene- $\Delta^{2:5}$ -cyclohexadiene] (III) forms bright red, slender needles, decomp. about 200°, and *di- $\alpha$ -naphthylbidiphenylquinodimethane* [1:4-bis- $\alpha$ -naphthyl-diphenylmethylene- $\Delta^{2:5}$ -cyclohexadiene] (IV) forms orange needles, m. p. above 290°. Their solutions are strongly fluorescent, but soon become colourless in the light. They do not absorb iodine, and are scarcely affected in the air. J. C. W.

**Combinations of Aniline with Hydrochloric Acid.** J. C. THONUS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 553—555).—The equilibrium conditions characteristic of the system aniline–hydrochloric acid–water have been investigated. The following compounds occur as solid phases at 0°: 6NH<sub>2</sub>Ph, HCl; 5NH<sub>2</sub>Ph, 3HCl, H<sub>2</sub>O; NH<sub>2</sub>Ph, HCl; 10NH<sub>2</sub>Ph, 11HCl. Of the above four compounds, the first and second cease to exist at 25°, whilst experiments at 35° show that solid phases occur of the composition: 4NH<sub>2</sub>Ph, 5HCl;

10NH<sub>2</sub>Ph, 11HCl;  
NH<sub>2</sub>Ph, HCl; 2NH<sub>2</sub>Ph, HCl; 3NH<sub>2</sub>Ph, HCl.

A diagram is given showing the relationship between the various solid phases and solution at 0°. H. M. D.

**Preparation of *N*-Monoalkyl Derivatives of Homopiperonylamine.** HERMAN DECKER (D.R.-P. 267700).—*N*-Monoalkyl derivatives of homopiperonylamine are prepared by treating alkylidene derivatives of homopiperonylamine with alkylating agents in absence of water and decomposing the resulting quaternary ammonium compounds. Benzylidenehomopiperonylamine when treated with methyl iodide furnishes ultimately *N*-methylhomopiperonylamine, b p. 156—158°/24 mm. (corr.). This forms a *hydrochloride*, m. p. 178—180°, a *nitrate*, m. p. 166—167° (corr.), a *carbonate*, m. p. 72—75°, and a *hydriodide*, m. p. 135—136° (corr.). *N*-Ethylhomopiperonylamine, similarly prepared by means of ethyl iodide, has m. p. 126—128°. J. C. C.

**Preparation of 1:6-Dibromo-2-naphthylamine.** HARTWIG FRANZEN and ADOLF EIDIS (*J. pr. Chem.*, 1913, [ii], 88, 755—764).—The preparation of 1:6-dibromo-2-naphthylamine (compare Claus and Jäck, A., 1898, i, 324; also Claus and Philipson, A., 1891, 461) is best accomplished by the bromination of benzylidene- $\beta$ -naphthylamine in the manner indicated below; the isolation of the intermediate products is, however, unnecessary. Benzylidene- $\beta$ -naphthylamine combines with bromine in chloroform solution to form a *dibromide*, C<sub>10</sub>H<sub>7</sub>NBr·CHPhBr, which separates as a light yellow, crystalline powder and is converted by boiling in alcoholic solution into 1-bromo-2-naphthylamine. This crystallises in colourless needles, m. p. 63—64°, and condenses with benzaldehyde in alcoholic solution, yielding a *benzylidene* derivative (slender, yellow needles, m. p. 94°), which unites with bromine in chloroform solution to form a *dibromide*, C<sub>10</sub>H<sub>6</sub>Br·NBr·CHPhBr, m. p. 220°, with previous sintering and darkening at 210°. When boiled in alcoholic solution, the dibromide yields 1:6-dibromo-2-naphthylamine.

Bromination of aceto- $\beta$ -naphthylamide in glacial acetic acid gives rise to *aceto-1-bromo- $\beta$ -naphthylamide hydrobromide*,  $C_{12}H_{11}ONBr_2$ , a colourless, crystalline powder, m. p. 180—190° (compare Cosiner, A., 1881, 605). On treatment with ammonia or when crystallised from alcohol, the hydrobromide is converted into the free amide, which is hydrolysed by alcoholic hydrogen chloride to 1-bromo-2-naphthylamine, identical with that obtained by the method described above, but different from the compound, m. p. 75—79°, described under the same name by Morawski and Gläser (A., 1888, 1096). F. B.

**Acetylation of Organic Compounds.** E. KNOEVENAGEL (*Annalen*, 1913, 402, 111—148).—It has long been known that the presence of sodium acetate, sulphuric acid, or zinc chloride greatly facilitates the acetylation of organic compounds by acetic anhydride, but the manner in which the catalyst operates is still obscure. It does not act in virtue of its dehydrating power, because not only is a very small amount of the catalyst employed, but also other substances, such as strong acids or metallic salts of strong acids, which are devoid of desiccating properties, can also function as catalysts. Different catalysts produce different results, and at present generalisations cannot be stated, but this much is certain, that the action of a catalyst is not dependent simply on the concentration of the hydrogen ions or on its dehydrating power.

Acetylation by means of acetic anhydride is not limited to organic compounds containing hydroxyl groups; with a suitable catalyst, oxides, especially aldehydes, likewise certain unsaturated and ethereal compounds such as ethers, unsaturated ketones, open and cyclic anhydrides of polyhydric alcohols, amongst them polysaccharides, dextrin, starch, and cellulose, can unite with acetic anhydride in consequence of a more or less easy rupture of the linking between carbon and carbon or carbon and oxygen. When the acetate formation is accompanied by a degradation of the organic molecule, the phenomenon (which is quite analogous to ordinary hydrolysis) is termed acetolysis.

The acetylation of hydroxylic compounds, the acetate formation in the case of the compounds mentioned above, and the occurrence or non-occurrence of acetolysis are dependent, apart from the temperature and the quantity of the catalyst, so largely on the nature of the catalyst that it is possible, under selected experimental conditions, simultaneously to acetylate hydroxyl groups, to promote acetate formation at a carbon-oxygen linking, and, with suitable substances, to degrade the molecule or sometimes to leave it undegraded.

The preceding processes are being applied to elucidate the constitutions of the polysaccharides, dextrins, starch, and cellulose; the present paper, however, deals with their application to simpler classes of compounds.

The catalysts employed are ferric chloride, zinc chloride, hydrated stannous chloride, phosphorus trichloride, sulphuric acid, sulphoacetic acid, hydrated ferrous sulphate, hydrated copper sulphate, hydrated zinc sulphate, ammonium sulphate, and methylamine sulphate. The last two, although active in the acetylation of hydroxyl groups, are without effect in the conversion of aldehydes into diacetates. This

conversion is readily effected by all of the other catalysts, the *modus operandi* being to mix the aldehyde (1 mol.), acetic anhydride (1.1 mol.), and catalyst (1—5%) at the ordinary temperature, external cooling being employed to keep the temperature below 70°. Benzaldehyde gives an almost quantitative yield of benzylidene diacetate in the presence of copper sulphate or zinc chloride, and also with sulphuric acid or ferric chloride when the reaction is commenced in a freezing mixture. Similar experiments have been performed with furfuraldehyde (at 0—10°), cinnamaldehyde (ferric chloride acts too vigorously, but by dilution with glacial acetic acid a quantitative yield of cinnamylidene diacetate is obtained), vanillin (stannous chloride produces a nearly quantitative yield of the triacetate), anisaldehyde (successful results obtained only with stannous chloride, phosphorus trichloride, and copper sulphate; *anisylidene diacetate* has m.p. 67°), piperonal (quantitative or nearly quantitative yields with ferric chloride, stannous chloride, sulphoacetic acid, ferrous sulphate, and copper sulphate; *piperonylidene diacetate* has m. p. 80°), and protocatechualdehyde (the *tetra-acetate* has m. p. 131°; no success is obtained with copper sulphate). Salicylaldehyde yields the triacetate, m. p. 103°, or disalicylaldehyde, m. p. 129°, or a mixture of both; the triacetate is the main product in the presence of ferric chloride, zinc chloride, or sulphuric acid, whilst disalicylaldehyde is entirely or mainly produced when the catalyst is phosphorus trichloride, copper sulphate, or zinc sulphate; the remaining catalysts produce an approximately equal molecular mixture of both substances. In all cases disalicylaldehyde is the primary reaction product, and is subsequently converted into the triacetate in the presence of a suitable catalyst. The converse change of the triacetate into disalicylaldehyde cannot be accomplished. Salicylaldehyde and acetic anhydride yield the triacetate in the presence of 2% of sulphoacetic acid, but disalicylaldehyde when about 50% of the catalyst is employed; in the presence of acetylsulphuric acid, only the triacetate is formed.

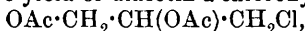
Paraformaldehyde and acetaldehyde are readily converted into the corresponding alkylidene diacetates by acetic anhydride and a little sulphuric acid or ferric chloride respectively.

Ketones, unlike aldehydes, do not react additively with acetic anhydride to form diacetates, even in the presence of the preceding catalysts. *p*-Benzoquinone and acetic anhydride, however, react in the presence of a little ferric chloride to give an almost quantitative yield of Thiele's hydroxyquinyl triacetate, m. p. 96°.

[With JUNG and RÜMSCHIN.]—Styryl methyl ketone and acetic anhydride react in the presence of a little sublimed ferric chloride to form after three to four days 5-acetoxy-2-acetyl-3:4-diphenyl-1-methyl- $\Delta^1$ -cyclopentene,  $\text{CMe} \begin{smallmatrix} \swarrow \text{CAc} & \text{---} & \text{CHPh} \\ \searrow \text{CH(OAc)} & \cdot & \text{CHPh} \end{smallmatrix}$ , m. p. 118°, by the hydrolysis of which

is obtained 5-hydroxy-2-acetyl-3:4-diphenyl-1-methyl- $\Delta^1$ -cyclopentene,  $\text{C}_{20}\text{H}_{20}\text{O}_2$ , m. p. 95° (*oxime*, m. p. 103° [decomp.]; *phenylhydrazone*, m. p. 94° [decomp.]; *tribromo-derivative*,  $\text{C}_{20}\text{H}_{19}\text{O}_2\text{Br}_3$ , m. p. 183° [decomp.]); the preceding acetate forms a *tribromo-derivative*,  $\text{C}_{22}\text{H}_{21}\text{O}_3\text{Br}_3$ , m. p. 194° (decomp.).

[With RÜMSCHIN.]—Ethyl ether is almost unattacked by acetic anhydride at 100° in the presence of sulphuric acid, potassium hydrogen sulphate, pyridine hydrogen sulphate, or ammonium persulphate. In the presence of a little ferric chloride, however, acetolysis occurs to a slight extent, ethyl acetate being formed. Epichlorohydrin and acetic anhydride react at the ordinary temperature in the presence of ferric chloride (but not of copper sulphate or sulphuric acid) to give an almost quantitative yield of diacetin- $\alpha$ -chlorohydrin,



b. p. 116—118°/11 mm. Epichlorohydrin, glacial acetic acid, and a little ferric chloride react at the ordinary temperature to form  $\alpha$ -acetin- $\gamma$ -chlorohydrin,  $\text{OAc} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$ , b. p. 120—121°/14 mm., in about 90% yield.

[With JAKOB TRANSIER.]—Cineol and acetic anhydride react to form, according to the temperature and the catalyst employed, a terpineol acetate, b. p. 104—106°/10 mm., and terpin diacetate, b. p. 145°/14 mm., in varying amounts; the most effective catalysts for the rupture of the cineol ring are sulphuric acid and ferric chloride. The terpineol thus formed is apparently identical with the compound synthesised by Perkin (T., 1904, 85, 654), since it has b. p. 102—103°/14 mm.,  $D_4^{20}$  0.9337, and  $n_D^{20}$  1.4783, and forms a phenylurethane, m. p. 109°, and nitrosochloride, m. p. 117°. Cineole and glacial acetic acid yield dicinene by warming with a little concentrated sulphuric acid on the water-bath.

The preceding experiments illustrate well the different results obtained by the action of acetic anhydride in the presence of various catalysts. The 6-ring in cineole is readily ruptured in the presence of many catalysts, the 3-ring in epichlorohydrin by only a few catalysts at the ordinary temperature, whilst the acetolysis of ethyl ether is only slight even with the strongest catalyst at 100°.

[With JUNG and RÜMSCHIN.]—Ethyl furylidenemalonate and acetic anhydride in the presence of a little sublimed ferric chloride react, ultimately on the water-bath, to form a *substance*,  $\text{C}_{16}\text{H}_{18}\text{O}_7$  or  $\text{C}_{14}\text{H}_{16}\text{O}_6$ , m. p. 70°, from which an *acid*,  $\text{C}_{15}\text{H}_{20}\text{O}_7$  or  $\text{C}_{13}\text{H}_{16}\text{O}_6$ , m. p. 144°, is obtained by boiling with water or hydrochloric acid, and an *acid*, m. p. 192—195° (*barium salt*,  $\text{C}_{11}\text{H}_{10}\text{O}_6\text{Ba} \cdot 4\text{H}_2\text{O}$ ), by boiling with an excess of aqueous barium hydroxide. The investigation of these substances is being continued. C. S.

Compounds of the Aminophenols with Zinc Chloride, Bromide and Iodide. A. KOPFIZ (*J. pr. Chem.*, 1913, [ii], 88, 744—754).—The three isomeric aminophenols combine with zinc haloids in aqueous solution, yielding additive compounds of the formula,  $2\text{C}_6\text{H}_7\text{ON} \cdot \text{ZnX}_2$ . On account of the tendency of the aminophenols to form basic zinc compounds, the preparation of the additive compounds is best accomplished by dissolving the aminophenols in a hot concentrated solution of the zinc haloid. The compounds are decomposed by water, but may be crystallised from strong solutions of the corresponding zinc haloid.

The compounds of zinc chloride with *o*- and *p*-aminophenols crystallise in reddish-violet needles, m. p. 184° and 247°

respectively; the corresponding compounds of zinc bromide in light brown or reddish-brown needles, m. p.  $170^{\circ}$  and  $234^{\circ}$ .

The compound of zinc iodide with *p*-aminophenol forms dark brown needles, m. p.  $208^{\circ}$ .

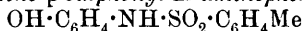
The compounds formed by *m*-aminophenol with zinc chloride (lustrous, white, silky needles, m. p.  $235^{\circ}$ ), zinc bromide (m. p.  $206^{\circ}$ ), and zinc iodide (white needles, m. p.  $190^{\circ}$ ) are also described.

All the above compounds melt with decomposition.

F. B.

**Nitration of Acyl Derivatives of *m*-Aminophenol and *m*-Anisidine.** FRÉDÉRIC REVERDIN and KARL WIDMER (*Ber.*, 1913, 46, 4066—4076).—The knowledge of mono- and dinitro-derivatives of these bases is extended by the preparation of some new compounds and by a re-examination of several of those already known.

I. *Acyl Derivatives of m-Aminophenol*.—*m*-Acetylaminophenyl acetate (Ikuta, A., 1893, i, 265) was prepared by heating *m*-aminophenol with acetic anhydride and sodium acetate at  $150$ — $160^{\circ}$ . It was accompanied by the unstable *triacetyl* derivative,  $C_6H_4(OAc) \cdot NAc_2$ , which is less soluble in water than the diacetyl compound, and has m. p.  $75$ — $77^{\circ}$ . *Toluene-p-sulphonyl-m-aminophenol*,

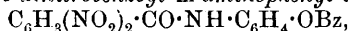


(Reverdin and de Luc), has m. p.  $158^{\circ}$ , and yields with acetic anhydride the *acetoxy*-derivative,  $C_{15}H_{15}O_4NS$ , in white needles, m. p.  $166^{\circ}$ . The *di-toluene-p-sulphonyl-m-aminophenol*,  $C_{20}H_{19}O_5NS_2$ , forms white needles, m. p.  $110^{\circ}$ .

II. *Nitration of the Diacyl Compounds*.—By the action of nitric acid on *m*-acetylaminophenyl acetate, Meldola obtained a mixture of 4- and 6-nitro-3-acetylaminophenols (T., 1906, 89, 925). This could not be confirmed.

The addition of the compound to fuming nitric acid, below  $4^{\circ}$ , resulted in the formation of 6-nitrodiacetyl-*m-aminophenol* [6-nitro-3-acetylaminophenyl acetate],  $C_{10}H_{10}O_5N_2$ , as white needles, m. p.  $113^{\circ}$ , which were hydrolysed by warm sodium carbonate to 6-nitro-3-acetylaminophenol (m. p.  $200^{\circ}$ ; Meldola,  $221^{\circ}$ ). The latter was completely hydrolysed by means of 5% hydrochloric acid to 6-nitro-3-aminophenol (Meldola), the constitution of which was confirmed by conversion into 3-chloro-6-nitrophenol and 6-nitroresorcinol. Other mononitro-derivatives could not be obtained.

By dissolving the diacetyl compound in a mixture of fuming nitric acid and acetic anhydride, 4:6-dinitro-3-acetylaminophenyl acetate was obtained in almost colourless needles, m. p.  $157^{\circ}$ . It was hydrolysed by sodium carbonate to the *N*-acetyl derivative and finally by concentrated sulphuric acid to 4:6-dinitro-*m-aminophenol* (both described by Meldola). Other acyl derivatives could, likewise, only be nitrated in the same positions. Thus *m*-benzoylaminophenyl benzoate (Ikuta, *loc. cit.*) yielded 4:6-dinitrobenzoyl-*m-aminophenyl benzoate*,



as a white, crystalline powder, m. p.  $70$ — $72^{\circ}$ . Similarly, the above toluenesulphonyl derivative formed 4:6-dinitrotoluene-*p-sulphonyl-m-aminophenyl toluene-p-sulphonate*,  $C_{20}H_{17}O_5N_3S_2$ , in white needles, m. p.  $120$ — $123^{\circ}$ .

III. *Nitration of m-Acetanisidide*.—By the addition of *m*-acetanisidide to nitric acid (D 1.4), 4-nitro- and 6-nitro-derivatives were obtained. The former was extracted by light petroleum. Meldola (*loc. cit.*) obtained it by other means. It was diazotised and coupled with  $\beta$ -naphthol, giving a red azo-compound,  $C_{17}H_{13}O_4N_3$ , m. p. 202°. The insoluble 6-nitro-*m*-acetanisidide crystallised from water in golden-yellow needles, m. p. 165°, which were further nitrated to the 4:6-dinitro-compound, of proved constitution (Meldola). It was hydrolysed to 6-nitro-*m*-anisidine,  $OMe \cdot C_6H_3(NH_2) \cdot NO_2$ , which formed dark yellow needles, m. p. 169°. By nitrating *m*-acetanisidide in glacial acetic acid solution, a 2-nitro-compound was also formed. It was the first to crystallise from a mixture with the 6-nitro-derivative, dissolved in hot water. 2-Nitro-*m*-acetanisidide is a brown powder, m. p. 265°, and 2-nitro-*m*-anisidine forms lemon-yellow needles, m. p. 143°. The only known dinitro-derivative was the 4:6-member (Meldola). Using fuming nitric acid in acetic acid solution, 2:4-dinitro-*m*-acetanisidide has also been obtained. It is less soluble in water than the 4:6-isomeride, and forms pale yellow needles, m. p. 202°. It was hydrolysed to 2:4-dinitro-*m*-anisidine (Blanksma, A., 1909, i, 150). Using acetic anhydride as the solvent, 2:6-dinitro-*m*-acetanisidide was also obtained. It crystallises from hot water as a middle fraction between the 2:4- and 4:6-isomerides. It forms white needles, m. p. 190°, and is converted by nitric acid into the 4:6-compound. 2:6-Dinitro-*m*-anisidine forms dark yellow needles, m. p. 146°. The constitution is assumed from the improbability of a substituent entering position 5, owing to the ortho-para orientating influence of the methoxy- and amino-groups.

Other dinitro- and also trinitro-compounds could not be obtained by nitration. J. C. W.

A New Synthesis of Higher Phenols. RIKO MAJIMA and IKUYA NAKAMURA (*Ber.*, 1913, 46, 4089—4095).—The preparation of tetra-, penta-, and hexa-decylveratroles and some allied products is described.

Myristyl chloride was condensed with veratrole by means of aluminium chloride, giving a 25% yield of *veratryl tridecyl ketone* (3:4-dimethoxybenzoyltridecane),  $C_6H_3(OMe)_2 \cdot CO \cdot C_{13}H_{27}$ , which formed long, slender, bulky needles, m. p. 74—75°, and was oxidised by nitric acid (D 1.12) to 3:4-dimethoxybenzoic acid. The *oxime* formed thick needles, m. p. 54—55°, which were reduced by aluminium amalgam to  $\alpha$ -*veratryltetradecylamine*, the *hydrochloride* of which formed prisms, m. p. 199°. The phosphate of the base was distilled under 0.8 mm., when *tetradecenylveratrole* ( $\alpha$ -*veratryl*- $\Delta^{\alpha}$ -*tetradecene*),

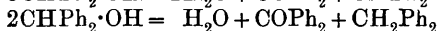
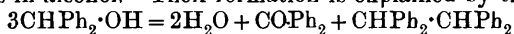
$C_6H_3(OMe)_2 \cdot CH:CH \cdot C_{13}H_{25}$ , was obtained in thin plates, m. p. 38—40°. This was reduced by platinum and hydrogen to *tetradecylveratrole* ( $\alpha$ -*veratryltetradecane*),  $C_6H_3(OMe)_2 \cdot C_{14}H_{29}$ , which formed long, flat crystals, m. p. 49—50°, b. p. 185—190°/0.5 mm. Subsequently the same compound was obtained by the direct reduction of the above ketone by means of zinc amalgam (Clemmensen, A., 1913, i, 733).

Pentadecyl chloride was also condensed with veratrole, yielding

*veratryl tetradecyl ketone*,  $C_{23}H_{38}O_2$ , b. p.  $220^\circ/0.3$  mm., m. p.  $64-65^\circ$ , which was reduced to *pentadecylveratrole* (*a-veratrylpentadecane*),  $C_6H_3(OMe)_2 \cdot C_{15}H_{31}$ , b. p.  $185-195^\circ/0.5-0.8$  mm., m. p.  $50-51^\circ$ . Similarly, palmityl chloride yielded *veratryl pentadecyl ketone*, b. p.  $230^\circ/0.5$  mm., m. p.  $79-80^\circ$ , which was reduced to *hexadecylveratrole* (*cetylveratrole*),  $C_6H_3(OMe)_2 \cdot C_{16}H_{33}$ , b. p.  $190-200^\circ/0.5$  mm., m. p.  $56-57^\circ$ .

For the preparation of pentadecic acid, methyl myristate was reduced by Bouveault's method to tetradecyl alcohol, which was converted into *tetradecyl iodide*, b. p.  $192-195^\circ/17.5$  mm., then into the *nitrile*, b. p.  $181-185^\circ/23$  mm.,  $D_4^{20} 0.8187$ , and this was hydrolysed. The method is alternative to that devised by Le Sueur (T., 1905, 87, 1898).  
J. C. W.

**Benzhydrol: Preparation of *s*-Tetraphenylethane.** PAUL SABATIER and M. MURAT (*Compt. rend.*, 1913, 157, 1496-1500).—A résumé, for the most part, of the chemistry of benzhydrol. Attempts to prepare this compound by the action of water on the Grignard compound  $CHPh_2 \cdot OMgBr$  gave only 3% of the desired alcohol, a little benzophenone, a large amount of diphenylmethane, and *s*-tetraphenylethane, the two hydrocarbons being separable by their solubilities in alcohol. Their formation is explained by the equations:



and is comparable to the action of ethyl alcohol and benzhydrol (compare Schmidlin and Banus, A., 1913, i, 34).  
W. G.

**Biochemical Studies on Cholesterol.** JOSEPH SAMUEL HEPBURN (*Chem. Zentr.*, 1913, ii, 2052-2053; from *J. Franklin Inst.*, 1913, 176, 405-452).—The brains of the sheep, after dehydration with alcohol, are extracted with three portions of ether at the ordinary temperature. Lipoids are removed from the concentrated ethereal solution by precipitation with acetone. The residue from the ether-acetone solution of each fraction is then saponified in two ways, either by hot alcoholic potassium hydroxide or by sodium ethoxide at the ordinary temperature. All six preparations of cholesterol so obtained melted between  $148.4^\circ$  and  $149.1^\circ$ . Two specimens of cholesterol obtained from gall stones had m. p.  $147.4^\circ$ , and mixtures of the different specimens had m. p.  $147.7-148^\circ$ .

Determination of the iodine number according to the methods of Hübl, Havas or Wys gives uniformly too high values for cholesterol, so that the usual iodine reagents cannot be employed for the volumetric determination of cholesterol in fat.

The author has also examined the various gravimetric methods which have been recommended for the estimation of cholesterol. Ritter's process (A., 1902, ii, 111), depending on the direct weighing of free cholesterol, gives unsatisfactory results. Concordant analyses could not be obtained, either by use of carbon dioxide or of hydrochloric acid, to neutralise the excess of sodium ethoxide employed for saponification; the yields obtained by use of hydrochloric acid were very bad. Excellent duplicates were obtained by Capenberg's method (*Chem. Zeit.*, 1909, 33, 985), but the yield was about 94%. The

estimation of cholesterol as benzoyl derivative (Dorée and Gardner, A., 1908, ii, 515) is not quantitative, giving as an average, 42·86% of the cholesterol actually present. The best and most trustworthy method is that recommended by Windaus (A., 1910, ii, 462), which consists in precipitation and weighing as digitonin-cholesteride. The average yield is 97·37%.

H. W.

*iso*Cholesterol, Coprosterol and the Classification of the Sterols. CHARLES DORÉE (*Biochem. J.*, 1913, 7, 616—621).—A useful summary of the properties of the chief sterols of animal origin (zoosterols) and of plant origin (phytosterols) is given. Animal cholesterol is modified when excreted by the skin glands into *iso*cholesterol, or by the intestinal juices into coprosterol. Phytosterol is also converted into coprosterol in the intestine, and by excretion as in rubber into *iso*cholesterol. The term metasterols is suggested for the derived sterols coprosterol and *iso*cholesterol. Spongosterol (Henze) is probably in the same class. The position of stigmasterol (Windaus and Hauth, A., 1907, i, 129) and of brassicasterol (Windaus and Welsch, A., 1909, i, 229) is uncertain. Of the chemical relationships between cholesterol, phytosterol, and the metasterols little is known at present.

W. D. H.

The Oxidation of Coprosterol and Coprostanone. JOHN ADDY-MAN GARDNER and WILLIAM GODDEN (*Biochem. J.*, 1913, 7, 588—595).—When coprosterol ( $C_{27}H_{48}O$ ) is oxidised with the theoretical amount of chromic acid, the ketone coprostanone ( $C_{27}H_{46}O$ ) is produced, but the yield is only 60% (Dorée and Gardner, T., 1908, 93, 1628). In the present work, an excess of chromic acid was used, and the yield was 70%. The sodium hydroxide extracts on acidification also yielded an acid which was crystallisable (m. p.  $247^{\circ}$ ), and an oily substance which was not further investigated. Analysis of the acid and of its salts showed it had the composition  $C_{27}H_{46}O_4$ . Direct oxidation of coprostanone with chromic acid also gave a small yield of the same acid. After oxidation with ammonium persulphate, the products obtained were separated into three fractions, all of which were obtained in crystalline form. Some preliminary details are given of their properties, and further work is in progress.

W. D. H.

Molecular Rearrangements in the Camphor Series. XII. Derivatives of *iso*Camphoric Acid; Decomposition Products of Amino*isodihydrocampholytic* Acid. WILLIAM A. NOYES and LLOYD F. NICKELL (*J. Amer. Chem. Soc.*, 1914, 36, 118—127).—Noyes and Potter (A., 1912, i, 786) have studied the decomposition of aminodihydrocampholytic acid with nitrous acid. Similar work on amino*isodihydrocampholytic* acid has been carried out by Noyes and Knight (A., 1911, i, 111), but the products were not fully investigated. An improved method has now been devised for preparing the latter acid, and a further study has been made of its decomposition with nitrous acid.

Amino*isodihydrocampholytic* acid,  $CO_2H \cdot CH < \begin{matrix} CMe_2 \cdot CMe \cdot NH_2 \\ CH_2 - CH_2 \end{matrix}$ ,  
m. p.  $235-236^{\circ}$ ,  $[\alpha]_D^{21} - 32.9^{\circ}$ , furnishes a *hydrochloride*, m. p.  $296-298^{\circ}$

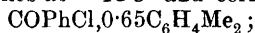


(decomp.),  $[\alpha]_D^{19} - 45.8^\circ$ , which when heated with acetic anhydride and sodium acetate is converted into the anhydride of *d*-aminodihydrocampholytic acid. On decomposing aminoisodihydrocampholytic acid with nitrous acid, the following products are obtained: *d*-campholytic acid, 35.8%; *l*-campholytolactone, 4.2%; *l*-trans-hydroxydihydrocampholytic acid, 19.1%; and a small quantity of isolaurolene. The Walden inversion occurs only to a slight extent in this decomposition.

*l*-Campholytolactone has m. p. 114–115°,  $[\alpha]_D - 8.2^\circ$  (in alcohol), and on hydrolysis is converted into *l*-cis-hydroxydihydrocampholytic acid, m. p. 117–118°,  $[\alpha]_D - 53.1^\circ$  (in alcohol). *d*-Campholytic acid has  $D_{25}^{25} 1.006$  and  $[\alpha]_D^{20} + 66.35^\circ$ . The formation of this acid in the decomposition furnishes direct evidence that it is the secondary asymmetric carbon atom of *d*-camphoric acid which rearranges to form *l*-isocamphoric acid. E. G.

**Halogen-nitro-derivatives of Benzoic Acid.** J. J. BLANKSMA (*Chem. Weekblad*, 1914, 11, 59–61).—Five halogen-nitro-derivatives of benzoic acid have been prepared. Bromination of 5-nitro-3-aminobenzoic acid yields 2:4:6-tribromo-5-nitro-3-aminobenzoic acid, reddish-brown crystals, m. p. 117°. The methyl ester of the former acid is converted by the diazo-method into methyl 3-bromo-5-nitrobenzoate, colourless crystals, m. p. 70°, converted by saponification into the corresponding acid. Acetylation of ethyl 5-nitro-3-aminobenzoate produces ethyl 5-nitro-3-acetylaminobenzoate, colourless crystals, m. p. 168°. Saponification of the former ester yields the corresponding 5-nitro-3-aminobenzoic acid, orange-red crystals, m. p. 208°. Bromination transforms ethyl 5-nitro-3-aminobenzoate into ethyl 2:4:6-tribromo-5-nitro-3-aminobenzoate, light brown crystals, m. p. 96°; and the diazo-method converts it into ethyl 3-chloro-5-nitrobenzoate, colourless crystals, m. p. 54°, saponifiable to the corresponding acid. Ethyl 3-bromo-5-nitrobenzoate is prepared analogously to the methyl ester, and has m. p. 44°. Saponification converts it into the corresponding acid. A. J. W.

**Investigation of Binary Systems Containing Benzoyl Chloride and Various Other Organic Compounds.** B. N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1701–1709).—The author has investigated the temperature-concentration diagrams of seven systems, all of which gave perfectly similar diagrams, no molecular compound being formed in any case. The different systems were composed of benzoyl chloride and (1) benzene: this showed, although not very clearly, a eutectic arrest corresponding with a eutectic point at  $-26.8^\circ$ , the composition being  $\text{COPhCl}, 1.03\text{C}_6\text{H}_6$ ; (2) *p*-xylene: the eutectic lies at  $-18.5^\circ$  and corresponds with



(3) mesitylene: the eutectic is situated at about  $-70^\circ$ , the corresponding composition being  $\text{COPhCl}, 4.7\text{C}_6\text{H}_3\text{Me}_3$ ; (4) chlorobenzene: eutectic point  $-54.2^\circ$ , composition  $\text{COPhCl}, 5.1\text{PhCl}$ ; (5) nitrobenzene:  $-20.5^\circ$  and  $\text{COPhCl}, 1.14\text{Ph}\cdot\text{NO}_2$ ; (6) diphenyl:  $-8^\circ$  and  $\text{COPhCl}, 0.2\text{C}_6\text{H}_5\text{Ph}$ ; (7) diphenylmethane:  $-15^\circ$  and  $\text{COPhCl}, 0.42\text{CH}_2\text{Ph}_2$ . The detailed results of the measurements are given in tabular form. T. H. P.

*p*-Nitroso-*N*-phenylglycine and *p*-Nitroso-*N*-*o*-carboxyphenylglycine. J. HOUBEN (*Ber.*, 1913, **46**, 3984—4000).—Previous attempts to cause phenylcarboxymethylnitrosoamine,  $\text{NO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , to undergo rearrangement into the corresponding *p*-nitrosophenylglycine have proved unsuccessful (Fischer and Hepp, A., 1887, 1115; Fischer, A., 1899, i, 349), the isolation of a considerable quantity of *p*-hydroxylaminobenzenediazonium chloride,  $\text{OH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ , indicating that the greater portion of the starting substance must have lost the nitroso-group without undergoing rearrangement.

The author regards the rearrangement which generally occurs, as the result of two reactions, the first involving the scission of the nitroso-radicle and the second its introduction into the nucleus, and finds that by the action of sodium nitrite and fuming hydrochloric acid the above *p*-nitrosophenylglycine can be produced in excellent yield. In a similar manner *o*-carboxyphenylcarboxymethylnitrosoamine can be converted into the hydrochloride of *p*-nitroso-*o*-carboxyphenylglycine.

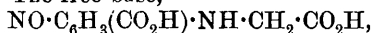
Phenylglycine was prepared by boiling 9.5 grams of aniline with 9.3 grams of chloroacetic acid in a solution of 4 grams of sodium hydroxide in 60 c.c. of water for a few minutes; the clear yellow solution obtained, when cooled in ice, deposited phenylglycine in approx. 85% yield. A solution of nitrosyl chloride was obtained by adding 50 grams of sodium nitrite to one litre of concentrated hydrochloric acid cooled in a freezing mixture, keeping the closed flask cold until most of the nitrite was decomposed and a deep reddish-yellow solution was produced. To 650 c.c. of this ice-cold solution 50 grams of finely granular phenylglycine was introduced, and the mixture shaken in the closed flask until the substance was entirely converted into a brownish-yellow powder, which was pure *p*-nitrosophenylglycine hydrochloride, the yield frequently attaining 80%. The conversion of phenylglycine into this nitroso-derivative can also be effected by the direct addition of sodium nitrite to a mixture of phenylglycine with concentrated hydrochloric acid, the yield being the same. The hydrochloride readily loses its acid, and when washed with water passes into the free *p*-nitrosophenylglycine, a sparingly soluble brown substance which decomposes explosively when warmed; with concentrated ammonia solution it gives a green colour, due to the green ammonium salt, which can be separated by the addition of alcohol. It is interesting to note that the isomeric 5-nitroso-*N*-methylantranilic acid is green, and the suggestion is made that the brown colour of the substance just described may be due to a quinonoid configuration  $\text{NOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

Preliminary experiments with *p*-nitrosophenylglycine show that it may be successfully used for the preparation of dyes, condensation with  $\alpha$ -naphthol,  $\alpha$ -naphthylamine, *m*-tolylenediamine, gallic acid, ethyl gallate, and  $\beta$ -naphthylamine producing respectively reddish-violet, violet-blue, blue, reddish-violet, red, and reddish-brown substances. Under the influence of sodium methoxide solution, condensation can be effected with *p*-nitrobenzyl cyanide to an azomethine compound, deep red needles from toluene solution.

*N*-Phenylmethylglycine is conveniently obtained by heating together

methylaniline and chloroacetic acid with sodium hydroxide solution for four hours; the resulting base is extracted with ether and precipitated as the hydrochloride; the yield is 74% of the theoretical; hydrochloride, m. p. 215—216° (compare Hinsberg and Rosenzweig, A., 1895, i, 144). Attempts to prepare a nitroso-derivative were unsuccessful, this result indicating that the introduction of a carboxyl group into one of the methyl radicles of dimethylaniline checks the formation of a para-nitroso-derivative. This view is supported by the action of sodium nitrite and concentrated hydrochloric acid on methyl dimethylantranilate, which gave rise only to a very small quantity of methyl 5-nitrosomonomethylantranilate.

Treatment of *o*-carboxyphenylglycine with nitrosyl chloride or sodium nitrite as described above for phenylglycine, effects almost quantitative conversion into the yellowish-brown *hydrochloride* of *p*-nitroso-*o*-carboxyphenylglycine, which decomposes above 100° without melting. The free base,



obtained by the action of sodium carbonate or acetate on the hydrochloride, is a green solid which rapidly changes when moist to a brown colour, possibly of a quinonoid form. It decomposes when heated and condenses with benzyl cyanide in the presence of sodium methoxide, giving a yellow azomethine *derivative*, malonitrile under similar conditions giving a blood-red azomethine compound; the azomethine compound,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{N} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , obtained with *p*-nitrobenzaldehyde, forms red needles, m. p. 256—258°. When the above hydrochloride is warmed in acetic acid with  $\alpha$ -naphthol,  $\beta$ -naphthol, gallic acid, *m*-tolylenediamine, and naphthylethylamine, *substances* are produced with blue, violet-red, violet, bluish-violet, and greenish-blue colours respectively.

[With TH. ARENDT.]—Methyl *o*-carbomethoxyphenylglycine, prepared by the interaction of methyl anthranilate and methyl bromoacetate, when treated with sodium nitrite and concentrated hydrochloric acid gives *methyl p*-nitroso-*o*-carbomethoxyphenylglycine,  $\text{NO} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me}) \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , green needles, m. p. 164—165°. *Ethyl p*-nitroso-*o*-carbomethoxyphenylglycine, prepared in an analogous manner, has m. p. 131° (decomp.).

By heating methyl anthranilate with ethyl bromoacetate, ethyl *o*-carbomethoxyphenylglycine, m. p. 48°, was obtained; this could be further converted in the usual manner with sodium nitrite into *ethyl p*-nitroso-*o*-carbomethoxyphenylglycine, green needles, m. p. 125° (decomp.). In a similar manner, *ethyl p*-nitroso-*o*-carboxyphenylglycine, green needles, m. p. 115—116° (decomp.), was obtained; this substance when treated in hydrochloric acid with oxidising agents gave with aniline and ethylaniline bluish-black precipitates, and with  $\beta$ -naphthylamine a reddish-brown substance; with benzyl and nitrobenzyl cyanides in alcoholic solution containing sodium methoxide, condensation occurs to yellow azomethine *compounds*; the action of sodium methoxide solution itself on the nitroso-ester causes the separation of a yellow substance, possibly the sodium salt of ethyl nitrosoindoxylcarboxylate.

Methyl *o*-carboxyphenylglycine is most conveniently prepared by

boiling together in aqueous solution for one hour potassium anthranilate and methyl chloroacetate; the action of sodium nitrite and concentrated hydrochloric acid causes its conversion into *methyl p-nitroso-o-carboxyphenylglycine*, a green solid, m. p. 115—116°.

D. F. T.

**Proof of the Chemical Isomerism of *allo*- and *iso*Cinnamic Acids.** HANS STOBBE and CURT SCHÖNBURG (*Annalen*, 1913, **402**, 187—259).—Whether *allocinnamic* acid, m. p. 68°, *isocinnamic* acid, m. p. 58°, and *isocinnamic* acid, m. p. 42°, are three chemically different isomeric compounds or three modifications of one chemical individual is a problem of very old standing. Since the results of numerous investigations of the physical properties of the three acids lead to the conclusion that they are different in the solid state, but alike in the fluid (dissolved or fused) state, Biilmann's theory that the three acids are three modifications of one trimorphous (*cis*-)cinnamic acid might be accepted were it not for a few observations of Liebermann and of Stobbe which cannot be brought into harmony with the theory. Stobbe, in particular, advances reasons for his belief that two chemically different isomeric acids exist, namely, the monomorphous *allo*-cinnamic acid, m. p. 68°, and the dimorphous *isocinnamic* acid, m. p. 58° and 42° (A., 1911, i, 859). On the contrary, Meyer (A., 1911, i, 975) supports Biilmann's theory. The objects of the present investigation are to find an explanation of the discordant experimental results obtained by Meyer and by Stobbe (*loc. cit.*), and evidence in favour of one or other of the two theories.

A sufficient proof of the chemical isomerism of the three acids will be obtained if it can be shown that (i) the acids exhibit differences in the fused or dissolved state; (ii) unlike mixtures of two acids in the fused or dissolved state can be prepared, and (iii) regularities obtain during the transformations of the acids.

The precautions which must be observed during the manipulation of the acids are emphasised; also it is essential that the 68°-acid be crystallised from petroleum, b. p. 30—33°, as well as from water.

Evidence of (i) is obtained as follows: Saturated aqueous solutions of the 68°-acid, prepared at temperatures not exceeding 30°, are heated for seven hours at 35°, 55°, and 70° in elongated closed glass tubes. The tubes are cooled, and after crystals have been deposited, each tube is inverted and the m. p. of the damp acid is observed; the tube is then opened in a desiccator and the m. p. of the dry acid determined in the usual manner. Similar experiments are performed with saturated solutions of the 68°-acid in petroleum, b. p. 30—33°. The results show that the 68°-acid is always obtained from the solutions which have been heated only at 35°, but from solutions which have been heated at 55° or 70°, generally the 68°-acid, occasionally the 42°-acid, never the 58°-acid, is obtained. Experiments on the 42°-acid under the same conditions show that the 42°-acid is always obtained from aqueous or petroleum solution.

In a second series of experiments, solutions of the 68°-acid in petroleum (b. p. 30—33°) of different concentrations are shaken for

half an hour at  $35^{\circ}$  in a closed vessel (shaped like a three-limbed star-fish) to ensure solution of all crystal seeds. The solution is then collected in one limb, and the solvent is distilled at  $35^{\circ}$  into a second limb. The m. p. of the residue, which is crystalline at once or becomes so after short cooling, is determined by immersing the limb in water at  $45^{\circ}$ ,  $60^{\circ}$ , or  $70^{\circ}$ . The residue is thus found always to consist of the  $68^{\circ}$ -acid. Similar experiments on the  $42^{\circ}$ -acid show that the  $42^{\circ}$ -acid is always obtained.

The results of seventy experiments by the two preceding methods prove that the stable  $68^{\circ}$ -acid and the metastable  $42^{\circ}$ -acid, in the absence of crystal-seeds, can be crystallised unchanged, the former, however, only with certainty when the temperature during the process of solution, and during the subsequent heating of the solution, does not attain to the m. p. of the acid, or to the m. p. of the acid depressed by the solvent (in other words, when fusion of the  $68^{\circ}$ -acid is avoided; if this occurs, the  $42^{\circ}$ -acid may be produced). Consequently, each acid retains its individuality in solution under definite conditions, and the two, therefore, are chemical isomerides.

Evidence of (ii) cannot be obtained by an examination of mixtures of the fused  $68^{\circ}$ - and  $42^{\circ}$ -acid, because the composition of the mixture is uncertain owing to the ease with which the fused  $68^{\circ}$ -acid changes to the  $42^{\circ}$ -acid. However, when a solution of the  $42^{\circ}$ -acid in petroleum is mixed with increasing quantities of a petroleum solution of the  $68^{\circ}$ -acid in the three-limbed vessel, with the necessary precautions against inoculation by crystal-seeds, the residue obtained by the distillation of the solvent at  $35^{\circ}$  has always m. p.  $42^{\circ}$ , until the amount of  $68^{\circ}$ -acid in the mixed solutions has been increased to about 3.5%; then the residue has m. p.  $68^{\circ}$ . Consequently the relative quantities of the components in the solution determine the character of the solutes and of the residue obtained by evaporation. Once again it is thus shown that the  $68^{\circ}$ -acid and the  $42^{\circ}$ -acid are not identical in the fluid state and are therefore chemical isomerides. The fact that the residues obtained by the evaporation of the mixed solutions always have m. p.  $42^{\circ}$  or  $68^{\circ}$  is explained as follows. The residues must be solid solutions of the two acids, because it is known that a heterogeneous mixture of the  $42^{\circ}$ - and  $68^{\circ}$ -acids is incapable of prolonged existence. When the solid solution contains about 3.5% or more of the  $68^{\circ}$ -acid, it is supersaturated with respect to this acid; solid  $68^{\circ}$ -acid separates and converts the remaining saturated solid solution entirely into the  $68^{\circ}$ -acid. When the solid solution contains less than about 3.5% of the  $68^{\circ}$ -acid, the mixed crystals are more stable, and heterogeneity occurs only after some, possibly a long, time, when, owing to the spontaneous change,  $42^{\circ}$ -acid  $\rightarrow$   $68^{\circ}$ -acid, so much  $68^{\circ}$ -acid has been produced that the limit of miscibility is exceeded.

Solid solutions of the two acids containing less than about 3.5% of the  $68^{\circ}$ -acid all have m. p.  $42^{\circ}$ , because the small amount of the  $68^{\circ}$ -acid present produces no, or only an inappreciable, depression of the m. p. A crystal having m. p.  $42^{\circ}$ , therefore, may be either the pure  $42^{\circ}$ -acid or a solid solution containing not more than about 3.5% of the  $68^{\circ}$ -acid; the more nearly this percentage of  $68^{\circ}$ -acid is present, the more readily will the " $42^{\circ}$ -acid" change to the  $68^{\circ}$ -acid. In this

manner an explanation is found of the conflicting statements of Liebermann, Büllmann, Stobbe and others regarding the "life" of the "42°-acid" at the ordinary temperature. The same considerations also serve to account for Stobbe and Reuss's remarkable observation (A., 1911, i, 859) that the velocity of transformation of the solid 42°-acid into the 68°-acid increases as the temperature falls; since the solubility of the solid 68°-acid in the solid 42°-acid decreases as the temperature falls, the mixed crystal must the more readily become heterogeneous the lower is the temperature.

Evidence in support of (iii) above has also been obtained. A systematic investigation of the conversion of the fused 68°-acid into the 42°-acid has hitherto not been undertaken. Büllmann attributes the transformation to the mere process of fusion (A., 1909, i, 382), whilst Liebermann ascribes the frequent failure of the transformation to a certain sluggishness of the 68°-acid. Now if the two acids are isomeric, the transformation must depend on the time of fusion and on the temperature of superheating. To ascertain the effect of the time of fusion, a large number of closed capillary tubes containing a little 68°-acid are heated at 70° for periods varying from 0.5 to sixty minutes. The result of 500 experiments shows that the longer the time of heating the greater is the number of cases in which the 42°-acid is produced. (The contents of a capillary tube after fusion do not form a coherent liquid, but a number of short liquid columns separated by air spaces; after the contents have solidified, it is not uncommonly observed that in one and the same tube some of the columns have m. p. 42°, and others, m. p. 68°.) The effect of superheating is exhibited in 625 experiments similar to the preceding, in which the capillary tubes are heated at 70°, 100°, 110°, 130° or 150°. The percentage number of cases in which the 42°-acid is produced increases with the temperature and reaches 100% when the tubes are heated at 130° for not less than two minutes. It is noteworthy that in no case has the 58°-acid been obtained. Since Meyer claims to have obtained 42°-acid, 58°-acid, and 68°-acid by the solidification of fused 42°-acid (A., 1911, i, 975; 1912, i, 32), 175 experiments have been performed with the 42°-acid for different periods of heating and at temperatures from 45° to 130°, but in no case has any acid other than the 42°-acid been obtained.

The acids, m. p. 42°, obtained in the previous experiments are not all identical substances, because some of them can be kept unchanged for a year, whilst others change to the 68°-acid at the ordinary temperature after a few minutes or hours. They are, in fact, solid solutions of the 42°-acid and 68°-acid, like those obtained by the evaporation of the mixed solutions in petroleum (see above). According to the results of those experiments, the least stable "42°-acids" are those which contain the greatest amount (up to about 3.5%) of the 68°-acid. So also in the preceding experiments on the heating of fused 68°-acid, it is proved that the most stable "42°-acids," that is, the solid solutions containing the smallest amounts of the 68°-acid, are those which have been prepared by heating the fused 68°-acid for the longest periods and at the highest temperatures. The proof is obtained by ascertaining the maximum amount of 68°-acid which can be added to the "42°-

acids" without changing the m. p. A second method of proving the same point is based on Stobbe and Reuss's observation that the change of the 42°-acid to the 68°-acid proceeds rapidly at low temperatures (*loc. cit.*). The "42°-acids" obtained from the fused 68°-acid in the previous experiments are kept at -14° for periods varying from 5 to 600 minutes, and the m. p.'s are then determined. The results of 110 such experiments show once again that the 68°-acid is obtained most frequently and in the shortest times from those "42°-acids" which have been obtained by heating the fused 68°-acid for short periods at the lower temperatures (70° and 110°), and which, therefore, are the solid solutions containing relatively the greatest amounts of the 68°-acid.

Experiments similar to the preceding at -14° have been performed with "42°-acids" after recrystallisation from water. Such recrystallised acids behave like the "42°-acids" obtained from the longest and most highly superheated 68°-acid fusions, that is, they are solid solutions containing very little 68°-acid.

Billmann and also Liebermann have observed (*loc. cit.*) that the change, liquid 68°-acid  $\rightarrow$  42°-acid, depends also on the amount of substance employed. This observation has been confirmed by heating portions of 10, 25, or 50 mg. of the 68°-acid at 70° for varying times and determining the m. p.'s of the solidified products. After short heating the 68° is recovered, by longer heating "42°-acids" of varying stability are obtained, and the change proceeds more slowly the greater is the quantity of material employed.

In this investigation the formation of the 58°-acid was first observed in the following series of experiments. Crystalline 42°-acid, prepared from the fused 68°-acid, is invariably converted into the 68°-acid by keeping at -75° for two minutes; the same result is obtained with 42°-acid crystallised from aqueous solution. Amorphous "42°-acids," prepared by heating the 68°-acid for five minutes at 110°, or for thirty minutes at 130°, solidifying, re-fusing at 45°, and finally cooling to -75°, yield sometimes the 68°-acid or the 58°-acid, or the 42°-acid, and occasionally in one and the same capillary tube mixtures of any two, or even of all three, acids. The results in general are similar to those obtained at -14°, with the very important difference, however, that the 58°-acid makes its appearance. The presence of 58°-acid in the "42°-acids" is due to the spontaneous change of the 42°-acid to the 58°-acid (see below), and its separation from the solid solutions at -75° is due, like that of the 68°-acid, to the decreased solubility of the 58°-acid in the 42°-acid at low temperatures. The fact that the 58°-acid is produced by the strong supercooling of amorphous, but not of crystalline, "42°-acids" is in complete agreement with the observations of Stobbe and Reuss (*loc. cit.*).

The proof that the 58°-acid is a chemical individual, different from, but isomeric with, the 68°-acid and the 42°-acid, has been established by the same methods as those employed above in the case of the 68°- and the 42°-acids, and to avoid repetition, only the results of the numerous experiments will be recorded. The 58°-acid retains its individuality in solution in water or petroleum, and can be crystallised therefrom unchanged, provided that the solution has not been heated

to a temperature at which fusion of the 58°-acid occurs. Determinations of the m. p.'s of the residues obtained by the evaporation of mixed solutions of the 58°- and the 68°-acids show that the residues having m. p. 58° may be either the pure 58°-acid or solid solutions (of the 68°-acid in the 58°-acid) having m. p. 58° (denoted by "58°-acid"). In such solid solutions, the maximum percentage of the 68°-acid is about 4 (certainly greater than the maximum solubility of the 68°-acid in the "42°-acids"); when this maximum is exceeded, heterogeneity occurs, and 68°-acid separates and converts the residual, saturated, solid solution into the 68°-acid. Since, therefore, the 58°-acid forms with the 68°-acid fluid mixtures and solid solutions, different from those produced by the 42°- and the 68°-acids, the 58°-acid must be isomeric with the 42°-acid, and all three acids are isomeric with one another. This conclusion is supported by the facts that the "58°-acids" change into the 68°-acid rapidly at low temperatures, and the velocity of the change at  $-75^{\circ}$  is smaller than that of the "42°-acids."

It has long been known that the 58°-acid changes into the 42°-acid by fusion. This change has been examined with "58°-acids" crystallised from solution, and is shown to depend on time and temperature. The higher the temperature and the longer the time during which the "58°-acid" is kept fused, the larger is the percentage number of cases (in 657 experiments) in which the "42°-acid" is produced. The "42°-acids" thus obtained are not all alike; some can be kept unchanged for years, others change to the 58°-acid at the ordinary temperature in a few minutes. The very important observations are made that a "42°-acid" obtained from liquid 58°-acid changes, if it changes at all, always to the (solid) 58°-acid, whilst a "42°-acid" prepared from liquid 68°-acid changes, if at all, always to the (solid) 68°-acid. The "42°-acids" obtained from the two different sources are, therefore, not identical; a "42°-acid" prepared from the 68°-acid is a solid solution of the 42°- and the 68°-acids only, whilst a "42°-acid" obtained from the 58°-acid contains 42°-acid, 58°-acid, and a very little 68°-acid.

In addition to the proof of the chemical isomerism of the 68°-, 58°-, and 42°-acids, the authors draw the following conclusions from the preceding experiments. Since the 58°- and the 42°-acids are metastable, it is probable that the two can never be obtained in a pure state; the relative amounts of the components in each are determined by the source and age of the specimens. The 68°-acid, which has the smallest solubility of the three acids, can be obtained practically pure provided it is old enough.

The phenomenon of "internal inoculation" is described. In the solid solution representing any "42°-acid," the changes, 42°-acid  $\rightarrow$  68°-acid and 42°-acid  $\rightarrow$  58°-acid, are continuously, although they may be slowly, proceeding. In course of time the solid solution becomes supersaturated with one or the other of the 58°- and 68°-acids; such acid separates and immediately sets up "internal inoculation" of the residual saturated solid solution. The effects of such internal inoculation of different types of "42°-acids" are discussed at length.

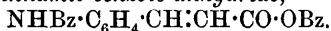


The paper closes with an explanation, in the light of the results of the preceding experiments, of the discordant observations of Stobbe and Meyer (*loc. cit.*). C. S.

**Anhydride Formation with Acylaminocarboxylic Acids.** GUSTAV HELLER (*Ber.*, 1913, **46**, 3974—3983).—The author has already observed certain cases of anhydride formation with amino-acids (compare Heller and Tischner, A., 1910, i, 770; 1913, i, 365), and now publishes further results in this direction.

*m*-Nitromandelic acid, prepared by the cyanohydrin synthesis from *m*-nitrobenzaldehyde, was reduced by ferrous hydroxide to *m*-aminomandelic acid, needles, m. p. 131—132° (decomp.); when treated with benzoyl chloride in pyridine solution, this acid gave a *benzoyl* derivative, granular crystals, m. p. 178°, unaccompanied by any anhydride.

In the action of benzoyl chloride on *m*-aminocinnamic acid in sodium carbonate solution, the resulting *benzoyl* derivative, needles, m. p. 229°, is accompanied by an insoluble substance, m. p. 148°, which appears to be *benzoyl-m-aminocinnamic benzoic anhydride*,



This reacts readily with phenylhydrazine, giving *benzoyl-m-aminocinnamic phenylhydrazide*, crystalline aggregates, m. p. 197—199°, and with sodium hydroxide solution on warming passes into *benzoyl-m-aminocinnamic acid*. The formation of the mixed anhydride is attributed to the primary formation of benzoic anhydride, which then enters into reaction with the second acid.

Similarly to the last case, *p*-aminobenzoic acid with benzoyl chloride in sodium carbonate solution gave *benzoyl-p-aminobenzoic benzoic anhydride*,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{OBz}$ , a granular substance which after melting at 128° resolidifies to re-melt near 210°. When heated with dilute sodium hydroxide solution the substance passes slowly into *benzoyl-aminobenzoic acid*, and when mixed with phenylhydrazine in ethereal solution gives a gradual deposition of *p-benzoylaminobenzoic phenylhydrazide*, leaflets, m. p. 248°.

In the light of the above results, the substance obtained by Heller and Tischner (*loc. cit.*) by heating *benzoyl-p-aminobenzoic acid* with acetic anhydride, and described as *benzoyl-p-aminobenzoic acid cycloid* with acetic anhydride of crystallisation, is in all probability *benzoyl-p-aminobenzoic acetic anhydride*; it does not react with phenylhydrazine.

The action of boiling acetic anhydride on *benzoyl-p-aminocinnamic acid* (needles, m. p. 274° with decomp.; obtained by benzylation of aminocinnamic acid in aqueous alkaline solution) for one hour gives *benzoyl-p-aminocinnamic acetic anhydride*, m. p. 149°, analogous to the last substance. It is slowly converted by hot dilute sodium hydroxide solution into the sodium salt of *benzoyl-p-aminocinnamic acid* and with phenylhydrazine gives no phenylhydrazide. Treatment with excess of benzoyl chloride in pyridine solution converts *p-aminocinnamic acid* into (polymeric?) *p-1-benzoyl-ψ-carbostyryl*, m. p. 285°.

When treated with benzoyl chloride and sodium carbonate solution, *o*-aminocinnamic acid gave an insoluble product, m. p. near 220°, which slowly dissolved in hot dilute sodium hydroxide, giving *benzoyl-p-aminocinnamic acid*, and gave no phenylhydrazide with

phenylhydrazine; the substance was therefore probably *benzoyl-o-aminocinnamic benzoic anhydride*, but was not pure. *Benzoyl-m-amino-benzoic benzoic anhydride*, obtained in a similar manner from *m*-amino-benzoic acid and benzoyl chloride, likewise could not be obtained pure.

By heating benzoyl-*o*-aminocinnamic acid for half an hour in boiling acetic anhydride, it is converted into *benzoyl-o-aminocinnamic anhydride*, needles, m. p. 194—195°, which when boiled with a mixture of acetic and hydrochloric acids slowly gives carbostyryl.

Treatment of *p*-aminohydrocinnamic acid with benzoyl chloride in sodium carbonate solution gave rise to the *benzoyl* derivative, leaflets, m. p. 194—195°, but the product from benzoylation in pyridine solution is a *substance*,  $2C_{16}H_{15}O_3N, C_5H_5N$  (compare Heller and Tischner, *loc. cit.*), m. p. near 240°. D. F. T.

**The Stereoisomeric Camphanecarboxylic Acids.** PH. BARBIER and V. GRIGNARD (*Bull. Soc. chim.*, 1914, 15, 26—37).—Having already investigated the liquid pinene hydrochloride by means of its organomagnesium derivative (compare A., 1910, i, 400) the authors have turned their attention to the solid hydrochloride, but although oxidation of the corresponding organomagnesium compound gives satisfactory results (compare *loc. cit.*; also Hesse, A., 1906, i, 375), the results obtained by treatment of the same compound with carbon dioxide have proved less decisive (compare Houben, A., 1906, i, 21).

The action of carbon dioxide on the organomagnesium derivative of solid pinene hydrochloride prepared by saturating an alcoholic solution of pinene at 75—80° with hydrogen chloride and collecting the crystals which separate from the fraction b. p. 80—82°/13 mm. on distillation, gave an acid product, b. p. 157—158°/16 mm. The original pinene had  $[\alpha]_D - 35.17^\circ$ , and the hydrochloride, m. p. 126°,  $[\alpha]_D - 21.66^\circ$ ; the resulting dihydropinenecarboxylic acid,  $C_{10}H_{17}\cdot CO_2H$ , consists of two isomerides, the more abundant forming needles, m. p. 76—78°, and yielding a dextrorotatory solution in methyl alcohol, whilst the other forms needles, m. p. 78—80°, and is probably identical with the racemic acid mentioned below.

Solid pinene hydrochloride prepared by saturating the same pinene in the cold with hydrogen chloride, and therefore comparable with the specimen used by Houben, gave the levorotatory acid, m. p. 73—74°, described by Houben (*loc. cit.*), which is doubtless a complex of two stereoisomerides.

The solid hydrochloride obtained from *dl*-pinene by the former method, when treated successively with magnesium and carbon dioxide, gave a racemic acid crystallising in needles, m. p. 78—80°.

The two specimens of active acid obtained above give the same anilide, needles, m. p. 179°, and *p*-toluidide, needles, m. p. 185°; also when heated alone, with alcoholic potassium hydroxide, aromatic amines or especially with mineral acids, they undergo isomerisation into one and the same levorotatory acid, m. p. 88—89°; the acid m. p. 73—74° is certainly more resistant to this treatment. These results are interpreted as due to the formation of a more stable geometrical isomeride, which is designated the  $\alpha$ - or *l*-camphanecarboxylic acid, whilst the less stable form is the  $\beta$ - or *d*-isocamphane-

carboxylic acid. The acid m. p. 76—78° is considered to be composed mainly of the  $\beta$ -acid associated with a small quantity of the  $\alpha$ -isomeride, whilst in the acid m. p. 73—74° the proportion of the  $\alpha$ -isomeride is greater. The  $\alpha$ - and  $\beta$ -acids thus possess the property of forming homogeneous crystalline mixtures. Under the influence of isomerising agents, the racemic acid, m. p. 78—80°, or *dl*-iso-camphanecarboxylic acid undergoes conversion into a stereoisomeric *d*-l-camphanecarboxylic acid, m. p. 93—94°.

From these results it would appear that, under the conditions of the two methods mentioned for the conversion of pinene into the solid hydrochloride, a certain amount of isomerisation similar to the above is effected, but it is also demonstrated that such isomerisation can also occur in the organomagnesium compound, as already suspected by Houben and Doescher (A., 1911, i, 61), the properties of the acid product being found to vary with differing conditions for the interaction of magnesium with the hydrochloride. D. F. T.

**Preparation of Chlorides of Hydroxy-acids.** EDUARD KOPETSCHNI and LADISLAUS KARZAG (*Ber.*, 1914, 47, 235—237; D.R.-P. 262883, 266351).—When the salts of hydroxycarboxylic acids are treated with thionyl chloride (*Ber.* and 1st patent) or carbonyl chloride (2nd patent) the acid chlorides are obtained. *Salicyloyl chloride* forms white needles, m. p. 17·5—18°.

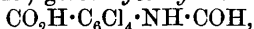
*m*- and *p*-*Hydroxybenzoyl chlorides* are oils having penetrating odours, which do not solidify at -15° to -20°.

*Glycolloyl chloride* is an oil of similar properties.

These chlorides are very reactive, giving, for example, with methyl alcohol the corresponding methyl esters of the acids. J. C. C.

**Preparation of Derivatives of Aromatic Hydroxycarboxylic Acids.** RICHARD WOLFFENSTEIN (D.R.-P. 267980. Compare this vol., i, 45).— $\beta\beta$ -*Trichloro-tert.-butyl 4-hydroxy-m-toluate*, prepared by the interaction of  $\beta\beta$ -trichloro-*tert.-butyl* alcohol and 4-hydroxy-*m*-toluic acid, has m. p. 97°.  $\beta\beta\beta$ -*Trichloro-tert.-butyl vanillate* has m. p. 130°, and  $\beta\beta\beta$ -*trichloro-tert.-butyl 1-naphthol-2-carboxylate* has m. p. 133°. These compounds have properties similar to those described in the chief patent (*loc. cit.*). J. C. C.

**Halogen Substituted Phthalic and Anthranilic Acids.** R. LESSER and R. WEISS (*Ber.*, 1913, 46, 3937—3946).—When heated with formic acid, tetrachloroanthranilic acid (compare Villiger and Blangley, A., 1909, i, 922) gives a *formyl* derivative,

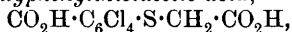


colourless needles, m. p. 304—306°, soluble in dilute sodium carbonate solution; the product obtained on heating with acetic anhydride is a

lactonic compound,  $\text{C}_6\text{Cl}_4\cdot\text{N}\begin{array}{c} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array}\text{CMe}$ , very pale yellow needles, m. p.

198—199°, which when heated with aqueous acetic acid becomes hydrated to the corresponding acid, *tetrachloro-o-acetylaminobenzoic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{Cl}_4\cdot\text{NH}\cdot\text{COMe}$ , needles, m. p. 240—241°, which easily reverts in the atmosphere to the original lactone (compare Mohr and Köhler, A., 1910, i, 116). Tetrachloroanthranilic acid is only

difficultly and incompletely diazotisable (compare Orndorff and Nicholls, A., 1913, i, 99); the solution of the diazo-compound was converted through the xanthate by treatment with chloroacetic acid into *tetrachloro-o-carboxyphenylthiolacetic acid*,



indistinct crystals, m. p.  $225^\circ$  (decomp.); this substance, of which the yield was poor, gives "*octachlorothioindigo*" when warmed with fuming sulphuric acid.

The action of bromine in acetic acid solution on isatoic acid gives rise to 3:5-dibromoanthranilic acid, colourless needles, m. p.  $234\text{--}235^\circ$  (compare Dorsch, A., 1886, 359), which is converted by acetic anhydride into an internal *anhydride* of the acetyl derivative (compare above), colourless needles, m. p.  $174\text{--}175^\circ$ , and can be made to pass through the stages diazo-compound and xanthate to 3:5-dibromo-2-carboxyphenylthiolacetic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , colourless prisms, m. p.  $186\text{--}187^\circ$  (decomp.). In the action of excess of bromine in hot acetic acid solution on isatoic acid there is obtained occasionally a *tribromoanthranilic acid*, colourless needles, m. p.  $245\text{--}246^\circ$  (decomp.); this acid when warmed with ammonia solution gives a red, insoluble *substance*, and also gives a crystalline *barium salt*. When treated with boiling acetic anhydride, tribromoanthranilic acid yields *tribromoanthranil*, needles, m. p.  $145\text{--}146^\circ$ .

The authors were unable to produce tetrabromoanthranilic acid by the action of bromine on isatoic acid (compare Dorsch, *loc. cit.*), but were able to obtain it by the action of potassium hypochlorite in alkaline solution on tetrabromophthalimide. *Tetrabromoanthranilic acid* forms colourless needles, m. p.  $204\text{--}205^\circ$ ; *barium salt*, crystalline; *silver salt*, amorphous. When heated with acetic anhydride it gives the internal *anhydride* of the *acetyl* derivative (see above), needles, m. p.  $257\text{--}258^\circ$ .

It is already known that phthalic anhydride can be converted by the theoretical amount of bromine into 4:5-dibromophthalic acid, m. p.  $208\text{--}209^\circ$ . This substance has now been converted through the imide, m. p.  $245\text{--}246^\circ$ , into 4:5-dibromoanthranilic acid, colourless needles, m. p.  $228\text{--}229^\circ$  (decomp.); *barium salt*, needles; *calcium salt*, needles; *silver salt*, amorphous and insoluble; the internal *anhydride* of the *acetyl* derivative forms microscopic needles, m. p.  $184\text{--}185^\circ$ . The diazotised solution of 4:5-dibromoanthranilic acid slowly deposits colourless needles of the *diazo*-compound; when boiled with alcohol and dilute sulphuric acid respectively, the *diazo*-solution gives rise to 3:4-dibromobenzoic acid, needles, m. p.  $234\text{--}235^\circ$ , and to 4:5-dibromosalicylic acid, m. p.  $217\text{--}218^\circ$ , probably identical with the isomeric acid of unknown constitution (Hübner, A., 1878, 148). The *diazo*-compound was also converted through the xanthate by means of chloroacetic acid into 4:5-dibromo-2-carboxyphenylthiolacetic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , needles, m. p.  $240\text{--}241^\circ$  (decomp.).

In one experiment on the bromination of phthalic anhydride, an exceptional result was obtained in the formation of another *dibromophthalic acid*, needles, m. p.  $194\text{--}195^\circ$ ; *anhydride*, needles, m. p.  $152\text{--}153^\circ$ ; *imide*, small rods, m. p.  $280\text{--}281^\circ$ .

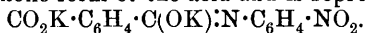
3:6-Dichloro-4:5-dibromophthalic acid is already known; its

anhydride, m. p. 269—270°, can be converted into the *imide*, yellow needles, m. p. 362—364°, which on treatment with alkaline sodium hypochlorite gives 3 : 6-dichloro-4 : 5-dibromoanthranilic acid, colourless needles, m. p. 193—194° (decomp.); *barium* salt, small rods; the *anhydride* of the *acetyl* derivative,  $C_9H_3O_2NCl_2Br_2$ , forms needles, m. p. 213—214°. The acid was not diazotisable. D. F. T.

### Isomeric Phenylphthalimides and Some Allied Compounds.

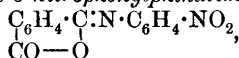
III. MITSURU KUHARA, SHIGERU KOMATSU, and ROKUHACHI NISHIYORI (*Mem. Coll. Sci. Eng. Kyōto*, 1913, 5, 343—363).—In an earlier paper (A., 1911, i, 205) it was shown that a mixture of a phthalamide with a colourless, normal, and a yellow, unsymmetrical, phthalimide results when phthalyl chloride reacts with an aromatic primary base at a low temperature. To account for this, it was assumed that the chloride exists as a mixture of the two forms, at the temperature of experiment. Pawlewski (A., 1895, i, 134, 414) and Dobrev (A., 1895, i, 360) prepared the nitrophenylphthalimides, but they obtained different substances. It is now shown that Pawlewski had isolated the white symmetrical compounds, whereas Dobrev had obtained the coloured *as*-isomerides. Both compounds are formed in the same operation, according to the above views. The *as*-nitrophenylphthalimides were also obtained by the action of acetyl chloride on the nitrophenylphthalamic acids. They are more soluble in alcohol than their isomerides, into which they are transformed by mineral acids.

The three nitrophenylphthalamic acids give coloured solutions in alkalis, those obtained from the *o*- and *p*-nitro-compounds being deep orange-red, whilst the meta-derivative gives a yellow solution. The ortho- and para-salts are therefore represented by the quinonoid formula  $CO_2K \cdot C_6H_4 \cdot CO \cdot N : C_6H_4 : NO \cdot OK$ , whilst the meta-salt is derived from the enolic form of the acid and is represented by

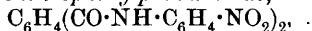


The behaviour of the phthalamic acids as pseudo-acids was investigated by the preparation of a number of salts. At low temperatures, disilver salts were obtained, from which dimethyl esters were prepared.

An ethereal solution of *o*-nitroaniline reacted with phthalyl chloride on warming and gave *as-o-nitrophenylphthalimide*,



canary-yellow needles, m. p. 152—153°, the *s*-isomeride, white, m. p. 198—200°, and *o-nitrophenylphthalimide*,



pale yellow, lustrous crystals, m. p. 187—189° (probably identical with Pawlewski's *o*-nitrophthalanilide). *as-p*-Nitrophenylphthalimide, m. p. 191—192°, and the *as-m*-derivative, m. p. 234—235°, were identified with Dobrev's compounds, and the symmetrical isomerides with Pawlewski's.

*Disilver phthalamate*,  $CO_2Ag \cdot C_6H_4 \cdot C(OAg) : NH$ , was obtained by adding silver nitrate (2 mols.) to ammonium phthalamate at  $-5^\circ$  as a white precipitate. It reacted with methyl iodide and the oily ester gave ammonia on hydrolysis. Ammonium phenylphthalamate was

converted into the *silver*, *disilver*, *barium*, and *lead* salts, the last three being derived from the acid in its enolic form.

*Dimethyl phenylphthalamate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OMe})\cdot\text{NPh}$ , was obtained in plates, m. p.  $90^\circ$ , which were hydrolysed to aniline and phthalic acid.

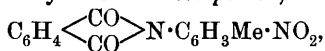
Silver and *disilver* salts of *m*- and *p*-tolylphthalamic acids; *silver* and *disilver* salts of *m*-xylylphthalamic acid; a *silver* and orange, lustrous *dipotassium* salt of *o*-nitrophenylphthalamic acid; a *silver* and yellow, lustrous, scaly *dipotassium* salt of *m*-nitrophenylphthalamic acid; and a *silver* and lustrous, orange-red *dipotassium* salt of *p*-nitrophenylphthalamic acid are described. Most of these phthalamic acids were discovered by Tingle and Rolker (A., 1909, i, 28). J. C. W.

#### Isomeric Phenylphthalimides and Some Allied Compounds.

IV. MITSURU KUHARA and SHIGERU KOMATSU (*Mem. Coll. Sci. Eng. Kyōtō*, 1913, 5, 363—366).—Phthalyl chloride has been condensed with 4-nitro-*m*-toluidine and with 6-nitro-*o*-toluidine and three products isolated in each case (compare preceding abstract).

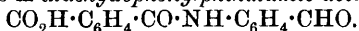
as-4-Nitro-*m*-tolylphthalimide,  $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$ , forms canary-

yellow needles, m. p.  $156\text{--}158^\circ$ ; the symmetrical *isomeride* crystallises in white needles, m. p.  $180\text{--}181^\circ$ , and 4-nitro-*m*-tolylphthalamic acid gives alkaline solutions which are orange-yellow when cold and orange-red when hot. The *silver* salt was analysed. as-6-Nitro-*o*-tolylphthalimide forms yellow needles, m. p.  $183\text{--}184^\circ$ ,  $231\text{--}232^\circ$  after solidification; the symmetrical compound,



has m. p.  $231\text{--}232^\circ$ , and 6-nitro-*o*-tolylphthalamic acid forms yellow crystals, and a *silver* salt. J. C. W.

Condensation Products of Phthalic Anhydride with *m*- and *p*-Aminobenzaldehyde, and their Derivatives. P. GELMO (*J. pr. Chem.*, 1913, [ii], 88, 810—828).—*m*-Aldehydophenylphthalimide,  $\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , prepared by heating phthalic anhydride with anhydro-*m*-aminobenzaldehyde at  $150^\circ$ , crystallises in lustrous, white, felted needles, m. p.  $177^\circ$  (corr.), and forms a *phenylhydrazone*, crystallising in small, yellowish-white needles, which become brown and decompose at about  $224^\circ$ ; the *oxime* forms lustrous, white leaflets, m. p.  $212^\circ$  (decomp., corr.). When heated with aqueous alkali hydroxides, it is hydrolysed to *m*-aminobenzaldehyde and phthalic acid; with aqueous sodium carbonate, containing a little sodium hydroxide, it yields *m*-aldehydophenylphthalamic acid,



This crystallises in flat, yellowish-white needles, m. p.  $157^\circ$  (decomp., corr.), and yields a *phenylhydrazone* as a light yellow, crystalline powder, m. p.  $216\text{--}217^\circ$ , with previous darkening and decomposition at  $207^\circ$ ; the *oxime* crystallises in small, yellowish-white leaflets, which begin to decompose at  $130^\circ$ , m. p.  $177\text{--}178^\circ$ ; the salts with the alkali-metals, together with the *barium*, *calcium*, *zinc*, and *silver* salts, are readily soluble in water.

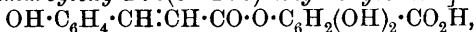
*p-Aldehydophenylphthalimide*, prepared from phthalic anhydride and *p*-aminobenzaldehyde at 160°, forms yellowish-white clusters of broad needles, m. p. 202° (corr.), and resembles the meta-isomeride in being readily hydrolysed by strong alkalis to phthalic acid and the original aminoaldehyde: the *phenylhydrazone* crystallises in long, slender, citron-yellow needles, m. p. 235—236°, with previous darkening and decomposition at 225°; the *oxime* forms yellowish-white leaflets, m. p. 227° (decomp., corr.). It is hydrolysed by aqueous sodium carbonate to *p-aldehydophenylphthalamidic acid*. This forms a citron-yellow, crystalline powder, m. p. 139—140° (decomp.), and yields a deep orange *phenylhydrazone*, which begins to decompose at 210°, m. p. 231—233°; the *oxime* crystallises in yellowish-white needles, m. p. 176°, with previous decomposition at 170°. F. B.

**Preparation of Dianthraquinonylaminocarboxylic Acids.** BADISCHE ANILIN- & SODA - FABRIK (D.R.-P. 268219).—Dianthraquinonylaminocarboxylic acids are prepared by heating halogen- or amino-anthraquinonocarboxylic acids with amino- or halogen-anthraquinones respectively in a solvent of high boiling point in the presence of a catalyst, such as copper, and an oxide or salt of the alkaline-earth metals. Examples are given illustrating the preparation of a dianthraquinonylaminocarboxylic acid from 1-chloroanthraquinone-2-carboxylic acid and 1-aminoanthraquinone, or alternately from 1-aminoanthraquinone-2-carboxylic acid and 1-chloroanthraquinone, of 2:2'-dianthraquinonylamine-3-carboxylic acid from 2-chloroanthraquinone-3-carboxylic acid and 2-aminoanthraquinone, and of 2:1'-dianthraquinonylamine-3-carboxylic acid from 2-aminoanthraquinone-3-carboxylic acid and 1-chloroanthraquinone. J. C. C.

**Constitution of Naringenin. Phloroglucinol Esters of Phenol-carboxylic Acids.** ADOLF SONN (*Ber.*, 1913, 46, 4050—4059).—Will (A., 1885, i, 906; 1887, i, 715) supposed naringenin to be an ester compounded of phloroglucinol and *p*-coumaric acid, whereas Tutin (T., 1910, 97, 2054), from analogy to eriodictyol and hesperitin, assumed that it has a ketonic structure. The ester from the above phenol and acid, synthesised by Fischer's method, is not identical with naringenin, which indirectly supports the alternative constitution.

*p*-Coumaric acid was prepared by Perkin's reaction at 175° in an open vessel, pressure being unnecessary. It was dissolved in *N*-alkali, treated with methyl chloroformate in a freezing mixture, and then the solution was acidified, when *p-methylcarbonatocinnamic acid*,  $\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$ , separated. It crystallised in thin prisms from acetone, m. p. 198—199°. The *chloride*,  $\text{C}_{11}\text{H}_9\text{O}_4\text{Cl}$ , formed white, silky prisms or needles, m. p. 137—138°, from which the *anilide* was obtained in pearly leaflets, m. p. 165—166°, which yielded *p-coumaranilide*, thin leaflets, m. p. 202°, when hydrolysed by dilute sodium hydroxide. Phloroglucinolcarboxylic acid was digested with *N*-sodium hydroxide (2 mols.) and then treated with the above *p-methylcarbonatocinnamoyl chloride* in acetone. The solution was acidified, poured into water, and the crude product treated with cold *N*-alkali (3—4 mols.), when the carbonato-group was hydrolysed. On

acidifying the deep yellow solution, *p*-coumaroylphloroglucinolcarboxylic [4(or 2)-*p*-coumaroyloxy-2:6(or 4:6)-dihydroxybenzoic] acid,



was isolated. It crystallised with  $1\frac{1}{2}\text{H}_2\text{O}$  in long, thin needles, m. p.  $194^\circ$ , and gave a deep violet coloration with ferric chloride. It was converted into *p*-coumaroylphloroglucinol [3:5-dihydroxyphenyl *p*-coumarate],  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , by heating in vacuum at  $200\text{--}220^\circ$ . A yellow, indefinite powder, m. p. about  $200^\circ$ , was thus obtained, almost insoluble in benzene, whereas naringenin forms well-defined crystals, m. p.  $248^\circ$ , and is soluble in benzene.

Similar phloroglucinol esters of the *p*-hydroxybenzoic acid derivatives were also prepared. *p*-Methylcarbonatobenzoylphloroglucinolcarboxylic acid was obtained from *p*-methylcarbonatobenzoyl chloride (E. Fischer, A., 1908, i, 892) and hydrolysed by cold sodium hydroxide to *p*-hydroxybenzoylphloroglucinolcarboxylic [4(or 2)-*p*-hydroxybenzoyloxy-2:6(or 4:6)-dihydroxybenzoic] acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{CO}_2\text{H}$ . The latter crystallised in thin, tufted needles, m. p.  $215^\circ$ , and gave a deep violet-red coloration with ferric chloride. When maintained for a short time in vacuum, above its melting point, it yielded *p*-hydroxybenzoylphloroglucinol [3:5-dihydroxyphenyl *p*-hydroxybenzoate],  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , which was obtained in white, moss-like masses of needles, m. p.  $218^\circ$ .

*p*-Coumaric acid was also reduced to  $\beta$ -*p*-hydroxyphenylpropionic acid, and the crude ethereal extract of the latter was condensed, as above, with methyl chlorocarbonate.  $\beta$ -*p*-Methylcarbonatophenylpropionic acid,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , forms thin, glistening tablets, m. p.  $86\text{--}87^\circ$ . The crude chloride was condensed with phenetidine in the cold. The phenetide,  $\text{C}_{19}\text{H}_{21}\text{O}_5\text{N}$ , crystallised in prisms, m. p.  $142\text{--}143^\circ$ , and was hydrolysed to  $\beta$ -*p*-hydroxyphenylpropionophenetide,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , which formed thick prisms, m. p.  $175\text{--}176^\circ$ . The above chloride was also condensed with glycine in the presence of the theoretical amount of *N*-alkali hydroxide. The colourless oil obtained on acidifying was extracted with ether and hydrolysed by cold alkali, and finally  $\beta$ -*p*-hydroxyphenylpropionylglycine,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , was obtained in glistening prisms from hot water, m. p.  $179^\circ$ . It may be a constituent of normal urine, since  $\beta$ -*p*-hydroxyphenylpropionic acid is.

J. C. W.

**Oxides and Isomerides of Trithiobenzaldehyde.** O. HINSBERG (*J. pr. Chem.*, 1913, [ii], 88, 800—810).—Baumann and Fromm (A., 1890, 25) have shown that trithiobenzaldehyde exists in two isomeric forms, termed  $\beta$ - and  $\gamma$ -trithiobenzaldehydes, which are considered to be stereoisomerides of the *cis-trans*-type. By the successive oxidation of the  $\beta$ -form with hydrogen peroxide and reduction with hydriodic acid, the author has obtained a third isomeride, which he terms  $\delta$ -trithiobenzaldehyde. The new isomeride is converted into the  $\beta$ -form by crystallisation from glacial acetic acid, benzene, or chloroform.

The author suggests that the  $\beta$ - and  $\delta$ -forms are sulphur isomerides of the same type as the  $\alpha$ - and  $\beta$ -trimethylene sulphides (compare A.



1913, i, 818), whilst the  $\beta$ - and  $\gamma$ -forms are to be considered as *cis-trans*-isomerides. The different behaviour of the  $\beta$ - and  $\gamma$ -forms on oxidation is, however, difficult to reconcile with this view; on oxidation with hydrogen peroxide,  $\beta$ -trithiobenzaldehyde is converted into a tetroxide belonging to the  $\delta$ -series, whilst the  $\gamma$ -isomeride gives rise to a pentoxide. Further, both the  $\delta$ -tetroxide and  $\gamma$ -pentoxide on oxidation with potassium permanganate yield the same trisulphone.

$\delta$ -Trithiobenzaldehyde tetroxide ( $\delta$ -tribenzylidenedisulphoxidesulphone),  $\text{CHPh} \begin{smallmatrix} \text{SO} \cdot \text{CHPh} \\ \text{SO} \cdot \text{CHPh} \end{smallmatrix} \text{SO}_2$ , prepared by oxidising  $\beta$ -trithiobenzaldehyde with hydrogen peroxide for several days at the ordinary temperature in glacial acetic acid solution, crystallises in slender, colourless needles, m. p. 256—257° (decomp.), but slowly decomposes on prolonged heating at 130—140°. When kept in contact with hydriodic acid (D 1.96) for several days, it is reduced to  $\delta$ -trithiobenzaldehyde, which forms a pale brown, crystalline powder, m. p. 180°.

$\gamma$ -Trithiobenzaldehyde pentoxide ( $\gamma$ -tribenzylidenesulphoxidedisulphone),  $\text{CHPh} \begin{smallmatrix} \text{SO}_2 \cdot \text{CHPh} \\ \text{SO}_2 \cdot \text{CHPh} \end{smallmatrix} \text{SO}$ , obtained by oxidising  $\gamma$ -trithiobenzaldehyde under the same conditions as given above for the oxidation of the  $\beta$ -isomeride, crystallises from glacial acetic acid in small, colourless needles (decomp. 254°), and is reduced by hydriodic acid to  $\beta$ -trithiobenzaldehyde.

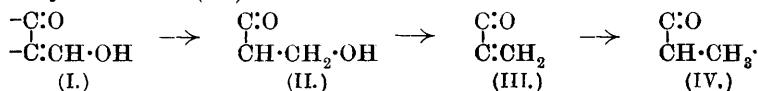
Tribenzylidenetrisulphone,  $\text{CHPh} \begin{smallmatrix} \text{SO}_2 \cdot \text{CHPh} \\ \text{SO}_2 \cdot \text{CHPh} \end{smallmatrix} \text{SO}_2$ , prepared by oxidising the  $\delta$ -tetroxide or  $\gamma$ -pentoxide with potassium permanganate and sulphuric acid, crystallises from ethyl acetate in small needles, which are not fused at 300°. It differs from the  $\delta$ -tetroxide and  $\gamma$ -pentoxide in not being reduced by hydriodic acid, and in forming a *sodium* salt, which undergoes no change when boiled with aqueous sodium peroxide.

F. B.

**Methylation of Ketones.** J. D. RIEDEL, AKT.-GES. (D.R.-P. 266405).—Methyl derivatives of ketones, aldehydes, and esters are readily prepared by reducing the corresponding hydroxymethylene compounds with hydrogen by the aid of colloidal palladium as catalyst. Examples are given of the preparation in this way of 1-methylcyclohexan-2-one, methylcamphor, and ethyl methylacetoacetate [compare following abstract].

J. C. C.

**A New Method of Methylation: Methyl Compounds from Hydroxymethylene Compounds.** A. KÖTZ and E. SCHAEFFER (*J. pr. Chem.*, 1913, [ii], 88, 604—640).—The method is only applicable for the methylation of aliphatic and hydroaromatic ketones, and esters of ketonic acids. It consists in converting the ketone into the hydroxymethylene derivative (I) and reducing the latter by means of hydrogen in the presence of colloidal palladium to the corresponding methyl derivative (IV):



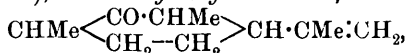
It is probable that ketone-alcohols of the type (II) are formed as intermediate products in the reduction, and that these readily lose water, yielding unsaturated compounds (III), which then undergo further reduction. Evidence in support of this view is furnished by the isolation of a ketone-alcohol of this type in the reduction of hydroxymethylenedihydrocarvone, although attempts to reduce  $\beta$ -hydroxybutaldehyde, which contains the grouping shown in (II), were unsuccessful.

On account of their marked acid character, the hydroxymethylene compounds often precipitate the palladium from its colloidal solutions, and in these cases the reduction cannot be carried out by the usual methods of Paal and Skita. The following method, however, was found to be very serviceable where precipitation of the palladium occurred: a methyl-alcoholic solution of the hydroxymethylene compound is placed in the absorption vessel, and an aqueous solution of palladous chloride (without any protective colloid) carefully introduced below this solution. On vigorously shaking, a rapid absorption of hydrogen takes place, and although the palladium is very soon precipitated, the reduction is complete, provided that only small quantities of the hydroxymethylene compound are employed; for large quantities, successive treatment with palladous chloride in this manner is necessary.

The following compounds have been prepared by reduction of hydroxymethylene compounds in this manner or according to Skita's method.

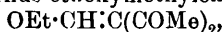
1:3-Dimethylcyclohexan-2-one from 3-hydroxymethylene-1-methylcyclohexan-2-one; methylcyclohexan-2-one from hydroxymethylene-cyclohexan-2-one; 1:4-dimethylcyclohexan-3-one from 4-hydroxymethylene-1-methylcyclohexan-3-one; methylmenthone, 1-methylcyclopentan-2-one, and methyleamphor from the corresponding hydroxymethylene compounds; methylisothujone (1:3:5-trimethyl-2-isopropyl- $\Delta^1$ -cyclopenten-4-one),  $\text{CMe} \begin{array}{c} \text{CO}-\text{CMe} \\ | \\ \text{CMe}:\text{CPr}^s \end{array}$ , an oil, b. p. 103—105°/11 mm. and 229—230° under ordinary pressure.

The reduction of hydroxymethylenedihydrocarvone yields hydroxymethyldihydrocarvone,  $\text{CHMe} \begin{array}{c} \text{CO} \cdot \text{CH}(\text{CH}_2 \cdot \text{OH}) \\ | \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$ , which was isolated in the form of its benzoyl derivative (lustrous crystals, m. p. 111°), and methyldihydrocarvone,



a liquid, b. p. 226—227°, having an odour resembling that of menthone (*semicarbazone*, m. p. 168°).

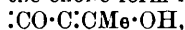
Hydroxymethylene compounds of diketones and ketonic esters can be reduced by this method, but not those derived from esters of dicarboxylic acids. Thus ethoxymethyleneacetylacetone,



and ethyl hydroxymethyleneacetoacetate yield  $\alpha\alpha$ -diacetyethane and ethyl methylacetoacetate respectively, whereas the hydroxymethylene derivatives of ethyl malonate and ethyl succinate do not undergo reduction.

Of the ethers and esters of hydroxymethylene compounds, only those which are readily hydrolysed by water can be reduced by this method; the ethyl ethers of ethyl hydroxymethyleneacetoacetate and hydroxymethyleneacetylacetone, being readily hydrolysed by water, are quantitatively reduced to the corresponding methyl derivatives, whilst methoxymethylenecamphor and ethyl ethoxymethylenemalonate, which are not readily hydrolysed, cannot be reduced. Similar results were obtained in the case of the acetyl derivatives. The reduction of the iron and copper salts, and also the amide, imide, and anhydride of hydroxymethylenecamphor, was investigated, but with negative results. On the other hand, the chloromethylene derivatives of camphor and ethyl succinate are readily reduced to methylcamphor and ethyl methylsuccinate respectively.

The behaviour of acetylacetone, acetylcamphor, and 4-acetyl-1-methylcyclohexan-3-one, which in the enolic form have a structure,



similar to that of the hydroxymethylene compounds, has also been investigated, but no reduction was found to take place; a similar negative result was obtained with the enolic form of dibenzoylacetylmethane,  
F. B.

**Influence of the Substituent on the Interaction of Benzene and its Derivatives with Benzoyl Chloride in Presence of Antimony Trichloride.** B. N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1710—1738).—In preceding papers (1911 and 1912), the author has shown, for a number of substituents, the immense influence these exert on the capacity of aromatic compounds of combining with antimony trichloride and tribromide and on the properties of the products of such combination. In order to obtain a greater insight into this influence, the investigation has now been extended to a more complex reaction, that of benzoyl chloride on benzene and its near derivatives in presence of antimony trihaloids.

This reaction proceeds with less ease than in presence of aluminium chloride, and all the experiments were carried out at 150—155°, at which temperature evolution of hydrogen chloride proceeds with moderate rapidity. The temperature-concentration diagrams of binary systems composed of benzoyl chloride and a number of aromatic hydrocarbons indicate in no case the formation of a molecular compound (this vol., i, 170).

Preliminary experiments were made at 150—155° in absence of antimony trichloride, but only with mesitylene did the reaction, hydrocarbon + benzoyl chloride = ketone + hydrogen chloride, take place to an appreciable extent, and even in this case the velocity was very small. In the presence of antimony trichloride, these reactions proceed readily and give good yields of ketone. The first phase in the reaction consists in the formation of a compound of antimony trichloride with the hydrocarbon,  $2\text{SbCl}_3\cdot\text{C}_6\text{H}_5\text{R}$ ; this is then acted on by the benzoyl chloride, the result being a compound of antimony chloride with the ketone,  $\text{SbCl}_3\cdot\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{R}$ , which decomposes into its constituents at the temperature of the experiment; the

antimony trichloride thus liberated may then react with fresh quantities of hydrocarbon and benzoyl chloride. The total reaction, expressed by the equation  $\text{ArH} + \text{C}_6\text{H}_5\cdot\text{COCl} + \text{SbCl}_3 = \text{Ar}\cdot\text{CO}\cdot\text{C}_6\text{H}_5 + \text{HCl} + \text{SbCl}_3$ , proceeds to an end and gives results in accord with the equation representing a bimolecular equation, the hydrocarbon and the benzoyl chloride being taken always in molecular proportions. The velocity of the reaction varies directly as the square of the concentration of the antimony trichloride.

With benzene and its monoalkyl derivatives the velocity constants of the reaction in presence of  $2\text{SbCl}_3$  and  $1\text{SbCl}_3$  are as follows:

	$2\text{SbCl}_3$ .		$1\text{SbCl}_3$ .	
$\text{C}_6\text{H}_6$ .....	0·000224	1	0·0000546	1
$\text{C}_6\text{H}_5\text{Me}$ .....	0·00272	12	0·00067	12
$\text{C}_6\text{H}_5\text{Et}$ .....	0·00466	21	0·00111	20
$\text{C}_6\text{H}_5\text{Pr}$ .....	0·0051	23	0·0012	22
$\text{C}_6\text{H}_5\cdot\text{C}_5\text{H}_{11}$ .....	0·0052	23	—	—

These figures indicate the great influence of the benzene substituent on the velocity of the reaction. The identity of the results for propyl- and *iso*amyl-benzenes seems to indicate the attainment of a limiting velocity of reaction, but the explanation, perhaps, lies in the marked resinification accompanying the reaction in these two cases.

With dialkylbenzenes the results are as follows:

	$2\text{SbCl}_3$ .		$1\text{SbCl}_3$ .	
$\text{C}_6\text{H}_6$ .....	0·000224	1	0·0000546	1
<i>p</i> - $\text{C}_6\text{H}_4\text{Me}_2$ .....	0·00476	21	0·00112	21
<i>o</i> - $\text{C}_6\text{H}_4\text{Me}_2$ .....	0·00725	32	0·00176	32
<i>m</i> - $\text{C}_6\text{H}_4\text{Me}_2$ .....	0·0178	80	0·00446	81
<i>p</i> - $\text{C}_6\text{H}_4\text{MePr}$ .....	0·0089	40	0·0022	40

The influence of the position of the second substituent is very marked (compare Menschutkin, A., 1898, i, 186; 1900, i, 335, 341; de Bruyn and Steger, A., 1899, i, 744), whilst the increasing magnitude of the influence as the size of the substituent increases is seen on comparing the results for *p*-dimethyl- and *p*-methyl*isopropyl*-benzenes.

The effect of a third substituent is shown by the following figures:

	$2\text{SbCl}_3$ .		$1\text{SbCl}_3$ .	
$\text{C}_6\text{H}_6$ .....	0·000224	1	0·0000546	1
$\text{C}_6\text{H}_5\text{Me}$ .....	0·00272	12	0·00067	12
<i>m</i> - $\text{C}_6\text{H}_4\text{Me}_2$ .....	0·0178	80	0·00446	81
1:3:5- $\text{C}_6\text{H}_3\text{Me}_3$ ...	0·107	478	0·0269	493
1:2:4- $\text{C}_6\text{H}_3\text{Me}_3$ ...	0·0316	141	0·00760	139

The constants for 1:3:5- and 1:2:4-trimethylbenzene are in the ratio 3·4 with  $2\text{SbCl}_3$ , 3·5 for  $1\text{SbCl}_3$ , and 3·6 for  $0·5\text{SbCl}_3$ . The constant for mesitylene is lowered from 0·107 at  $155^\circ$  to 0·0049 at  $84^\circ$  when  $2\text{SbCl}_3$  is taken, and from 0·0269 at  $155^\circ$  to 0·0169 at  $125^\circ$  and to 0·0059 at  $105^\circ$  when  $1\text{SbCl}_3$  is used.

In presence of  $2\text{SbCl}_3$ , the following constants were obtained: diphenylmethane, 0.0175; diphenyl, 0.0035; triphenylmethane, 0.0030, but in these cases marked resinification and blackening occur.

For benzene, chlorobenzene, bromobenzene, and nitrobenzene, the constants are in the proportions 1 : 0.1 : 0.022 : 0.02.

The results of the series of measurements made with each compound are given in full. T. H. P.

**Synthesis of 2:3-Dihydroxyacetophenone.** HEINRICH VON KRANNICHFELDT (*Ber.*, 1913, 46, 4016—4025).—The synthesis of 2:3-dihydroxyacetophenone has been accomplished by the methods of Klages (A., 1904, i 45) and Posner (A., 1912, i, 453). Incidentally, typical derivatives of 2:3-dimethoxybenzaldehyde have been prepared [with M. HAARSMAN].

2:3-Dimethoxy-1- $\alpha$ -hydroxyethylbenzene (Klages, *loc. cit.*) was added to a solution of potassium dichromate and sulphuric acid at  $30^\circ$ , when the resulting yellow oil was immediately removed by steam. 2:3-Dimethoxyacetophenone,  $\text{C}_{10}\text{H}_{12}\text{O}_3$ , was thus obtained as an almost colourless, refractive, mobile, faintly smelling liquid, b. p.  $143\text{--}144^\circ/14\text{ mm.}$  The semicarbazone formed white prisms, m. p.  $166\text{--}167^\circ$ , and the oxime crystallised in white, glistening scales, m. p.  $96\text{--}97^\circ$ . The methoxy-groups were replaced by hydroxyl by heating with hydriodic acid or with powdered aluminium chloride in chlorobenzene. 2:3-Dihydroxyacetophenone (*v*-acetocatechol),  $\text{C}_8\text{H}_8\text{O}_3$ , formed dark yellow prisms, m. p.  $97\text{--}98^\circ$ , which gave yellow solutions in alkalis and concentrated sulphuric acid. It is best purified by the hydrolysis of the acetyl derivative,  $\text{C}_{12}\text{H}_{12}\text{O}_5$ , which crystallises in white leaflets, m. p.  $109^\circ$ .

The above oxime was also obtained by boiling 2:3-dimethoxycinnamic acid,  $\text{C}_{11}\text{H}_{12}\text{O}_4$ , with hydroxylamine (Posner's method). This acid was obtained from *o*-veratraldehyde by Perkin's method in white, silky crystals, m. p.  $180\text{--}181^\circ$ , which sublime in beautiful needles. The dibromide forms colourless prisms, m. p.  $152^\circ$ , and the ethyl ester crystallises in colourless, glistening scales, m. p.  $44\text{--}45^\circ$ .  $\beta$ -2:3-Dimethoxyphenylpropionic acid,  $\text{C}_{11}\text{H}_{14}\text{O}_4$ , was obtained by reduction, in colourless crystals, m. p.  $63^\circ$ . The chloride is a pale yellow, mobile oil, b. p.  $165\text{--}166^\circ/15\text{ mm.}$ , and the anilide forms white needles, m. p.  $106\text{--}107^\circ$ .

2:3-Dimethoxybenzaldehyde was also converted into the bisulphite compound, and this was filtered, washed with alcohol, and treated with a saturated solution of potassium cyanide. On pouring the product into water, 2:3-dimethoxymandelonitrile solidified. It crystallised in white, microscopic tablets and prisms, m. p.  $76^\circ$ , and was hydrolysed to 2:3-dimethoxymandelic acid,  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , by solution in concentrated hydrochloric acid. This acid crystallises in microscopic, white prisms, m. p.  $93^\circ$ , and forms an acetyl derivative, m. p.  $114^\circ$ . The nitrile was also heated with hydriodic acid, but the 2:3-dihydroxyphenylacetic acid could not be purified, and was therefore methylated by methyl sulphate and the ester hydrolysed. 2:3-Dimethoxyphenylacetic acid,  $\text{C}_{10}\text{H}_{12}\text{O}_4$ , was then obtained in white needles, m. p.  $82\text{--}83^\circ$ .

[With E. ROSSELET.]—Attempts were also made to obtain 2:3-dihydroxyacetophenone by the action of aluminium chloride on guaiacol chloroacetate (compare Fries and Finck, A., 1909, i, 42), but rearrangement into the para-position resulted, the product being  $\omega$ -chloro-3:4-dihydroxyacetophenone (Mannich and Hahn, A., 1911, i, 649). The above compound was prepared by heating guaiacol with chloroacetyl chloride, and obtained in white needles, m. p.  $60^{\circ}$  (compare Einhorn, A., 1903, i, 90, and Dzierzgovsky, A., 1894, i, 74). Creosol chloroacetate (Einhorn, *loc. cit.*) was prepared by the same method. When heated to  $100^{\circ}$  with aluminium chloride it yields 3:4-dihydroxy-o-tolyl chloromethyl ketone,  $C_9H_9O_3Cl$ , which crystallises in almost colourless, microscopic prisms, m. p.  $130^{\circ}$ , provokes to sneezing, and gives dark green colorations with ferric chloride. 3:4-Dihydroxy-o-tolyl methyl ketone,  $C_9H_{10}O_3$ , was prepared from the compound by the action of zinc dust in acetic acid. It formed white needles, m. p.  $168-169^{\circ}$ , and gave a dark green coloration with ferric chloride. The chloroacetyl group was eliminated from the above chloroacetates and also from *p*-creosol chloroacetate (Fries and Finck, *loc. cit.*) by the action of aniline in cold ethereal solution, when  $\omega$ -chloroacetanilide was obtained.

J. C. W.

**Dinaphthyl Ketones and Dinaphthyl Ketimines.** A. E. TSCHITSCHIBABIN and S. I. KORJAGIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1823—1829).—The authors have prepared the three dinaphthyl ketimines by the method given by Moureu and Mignonac (A., 1913, i, 873), and have converted them by boiling with dilute hydrochloric acid into the corresponding ketones, which are obtained in good yields.

*Di- $\beta$ -naphthyl ketimine*,  $C(C_{10}H_7)_2:NH$ , crystallises in white plates, m. p.  $121.5-122.5^{\circ}$ , and is a moderately strong base; its *hydrochloride* and *picrate*, m. p.  $230.5-232^{\circ}$  (decomp.), were prepared.

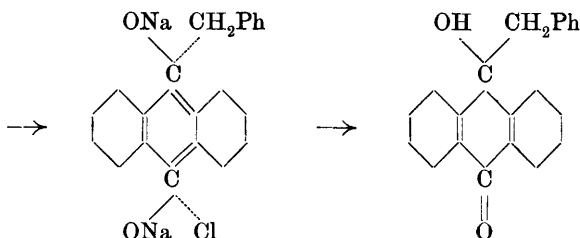
*$\alpha$ -Naphthyl  $\beta$ -naphthyl ketimine*,  $C(C_{10}H_7)_2:NH$ , crystallises in hemispherical masses of prismatic needles, m. p.  $103-104^{\circ}$ ; the *hydrochloride* and *picrate*, m. p.  $223.5-225.5^{\circ}$  (decomp.), were prepared.

*Di- $\alpha$ -naphthyl ketimine*,  $C(C_{10}H_7)_2:NH$ , forms white, prismatic needles, m. p.  $87-88^{\circ}$ ; its *hydrochloride* and *picrate*, m. p.  $191-192.5^{\circ}$  (decomp.), were prepared.

*Di- $\alpha$ -naphthyl ketone* forms a *picrate*, crystallising in large prisms, m. p.  $121.5-122^{\circ}$ . T. H. P.

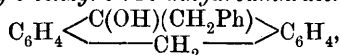
**Benzyl Derivatives of Anthraquinone and of Indigotin.** M. TSCHILIKIN [with E. PAULSEN] (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1834—1845).—The author has investigated the interaction of anthraquinone and phenylbenzyltrimethylammonium chloride in presence of sodium hydroxide and hyposulphite. According to the results of Holt (*Färbte Zeitung*, 1910, 244) and of Porai-Koschic (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1079), this reaction would be expected to lead to ethers of anthraquinol (oxanthranol), the latter being formed by the reduction of the anthraquinone. The product obtained is, however,

analogous to that obtained by Liebermann (A., 1882, 855), and must be regarded not as an ether of oxanthranol, but as an alkyl derivative, namely, benzyloxanthrone. In its formation, the anthraquinone is first converted into the disodium derivative of anthraquinol, which is a red, unstable compound, and readily undergoes re-oxidation to anthraquinone. From this disodium compound the reaction proceeds thus:



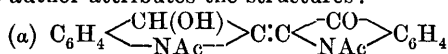
This compound has the properties ascribed to it by Liebermann (*loc. cit.*), Levi (A., 1885, 1140) and Bach (A., 1890, 1144), and on treatment with concentrated sulphuric acid the  $>\text{C}(\text{CH}_2\text{Ph})\cdot\text{OH}$  group is transformed into  $>\text{C}:\text{CHPh}$ , the compound thus formed having m. p.  $117^\circ$ , and not  $127^\circ$  as stated by Levi (*loc. cit.*).

In addition to benzyloxanthrone, the above reaction gives yellow needles of 9-hydroxy-9-benzyl-9:10-dihydroanthracene,

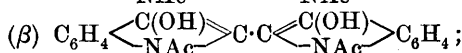


m. p.  $135\text{--}136^\circ$ , which Bach (A., 1890, 1425) described as 10-hydroxy-9-benzyl-9:10-dihydroanthracene, m. p.  $130\text{--}140^\circ$ .

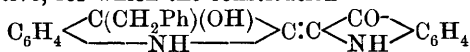
The above results throw a new light on the structure of the benzyl derivatives of leucoindigotin and ethers of indigotin in general, as well as on the whole reaction of benzylation, which is of great technical interest. That two isomeric leucoindigotins exist may be regarded as indicated by the existence of two diacetyl derivatives, to which the author attributes the structures:



and



only one tetra-acetyl derivative is known, corresponding with the  $\beta$ -form. Leucoindigotin is assumed to consist of an equilibrated mixture of the ketonic and enolic isomerides corresponding with the above diacetyl compounds, the enolic modification always being formed in the larger quantity. Etherification by the action of benzyl chloride, either alone or in presence of dimethylaniline, or by the action of phenylbenzyltrimethylammonium chloride (leucotrope), yields only one benzyl derivative, for which the constitution



is proposed. Evidence, such as the identity of this compound with that obtained from the organo-magnesium compound, is quoted in support of this structure.

T. H. P.

**Preparation of  $\beta$ -Nitro-derivatives of Acyl-*p*-diaminoanthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (O.R.-P. 267445).—When 1:4-dibenzoyldiaminoanthraquinone is treated with nitric acid in nitrobenzene suspension at 90°, it yields 2-nitro-1:4-dibenzoyldiaminoanthraquinone, orange needles, which on hydrolysis gives 2-nitro-1:4-diaminoanthraquinone, greenish-blue needles. Similarly, 1:4-diaminoanthraquinoneurethane gives 2-nitro-1:4-diaminoanthraquinoneurethane, orange-red prisms, which on hydrolysis yields the above 2-nitro-1:4-diaminoanthraquinone. The urethane of 1:4:5:8-tetra-aminoanthraquinone yields a 2-nitro-derivative which on hydrolysis furnishes 2-nitro-1:4:5:8-tetra-aminoanthraquinone.

J. C. C.

**The Constituents of Oil of Calamus.** H. THOMS and R. BECKSTROEM (*Ber.*, 1913, 46, 3946—3948).—The divergence between the results of the authors (A., 1901, i, 396; 1902, i, 809, 810) and those recently published by Semmler and Spornitz (this vol., i, 69) is attributed to the different origin of the samples investigated, that of the latter investigators being a Russian oil, whilst that of the authors was Japanese.

D. F. T.

**The Constituents of Ethereal Oils. (The Sesquiterpene Fraction of Java Citronella Oil.)** F. W. SEMMLER and K. E. SPORNITZ (*Ber.*, 1913, 46, 4025—4029).—A specimen of the sesquiterpene fraction of Java citronella oil was freed from methyleugenol by washing with dilute alcohol. It then had the constants, b. p. 153—156°/15 mm.,  $D_{20}$  0.8659,  $n_D$  1.50386, and the analysis suggested the presence of some sesquiterpene alcohol. After boiling with sodium, followed by several fractionations, *sesquicitronellene*,  $C_{15}H_{24}$ , was obtained; b. p. 138—140°/9 mm.,  $D_{20}$  0.8489,  $n_D$  1.53252,  $n_D + 0.36^\circ$ . The exaltation of the molecular refraction, 74.53 instead of 69.6, the reduction by sodium and alcohol to inactive *dihydrosesquicitronellene*,  $C_{15}H_{26}$ , b. p. 131—133°/12 mm.,  $D_{20}$  0.8316,  $n_D$  1.4800, and the reduction by hydrogen in presence of platinum to inactive *octahydrosesquicitronellene*,  $C_{15}H_{32}$ , b. p. 115—117°/9 mm.,  $D_{20}$  0.7789,  $n_D$  1.43518, indicate that the oil is an aliphatic sesquiterpene with two conjugated double linkings, homologous with the aliphatic terpene, ocimene (Enklaar, A., 1906, i, 377).

*cycloSesquicitronellene*,  $C_{15}H_{24}$ , was obtained by heating the aliphatic oil with concentrated formic acid. It had b. p. 129—132°/15 mm.,  $D_{20}$  0.8892,  $n_D$  1.5069,  $n_D + 56^\circ$ . It could no longer be reduced by sodium and alcohol, but reduction with hydrogen and platinum did not conclusively prove whether the compound is mono- or di-cyclic.

The washed, starting material was also ozonised, and among the products of subsequent hydrolysis was found a *paraffin*,  $C_{20}H_{38}$ , b. p. 165—167°/15 mm.,  $D_{20}$  0.8387,  $n_D$  1.46370. It is uncertain whether the substance is a normal constituent or due to sophistication of the citronella oil with petroleum. The above-mentioned *sesquiterpene alcohol*,  $C_{15}H_{26}O$ , was isolated. It is tertiary, contains conjugated double linkings, and readily submits to ring formation. J. C. W.



Review of the Pioneer Work on the Synthesis of Caoutchouc. FRANCIS J. POND (*J. Amer. Chem. Soc.*, 1914, 36, 165—199).—The literature relating to the early work on the synthesis of caoutchouc is reviewed in detail.

The author has repeated Bouchardat's experiment, but has failed to obtain any product which could be regarded as caoutchouc.

E. G.

The Oleo-resins of Jeffrey and Singleleaf Pines. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1913, 5, 971—973).—The volatile oil of *Pinus monophylla* contains from 80 to 85% of *d*- $\alpha$ -pinene; 4 to 5% of *l*- or *i*-limonene; 4 to 6% of *d*-cadinene; losses by polymerisation, etc., 4.5%. The colophony contains 7.22% of resen and resin acids isomeric with abietic acid. The volatile oil of *Pinus jeffreyi* consists of about 95% of *n*-heptane and 5% of an aldehyde, apparently citronellal. The colophony contains 12.5% of resen and resin acids isomeric with abietic acid.

W. P. S.

The Main Constituent of Japanese Lac. IV. Some Derivatives of Hydrourushiol. RIKO MAJIMA and IKUYA NAKAMURA (*Ber.*, 1913, 46, 4080—4088. Compare A., 1912, i, 883).—Further derivatives of hydrourushiol confirm the assumption that it contains two ortho-hydroxyl groups and a straight side-chain, para to one of the hydroxyl groups. The nature of this alkyl substituent is shown by oxidation with permanganate in cold aqueous acetone to palmitic acid. The side-chain should therefore be  $C_{15}H_{31}$ , and not  $C_{14}H_{29}$ , as was originally suggested. In another paper (this vol., i, 167) the preparation of 1-tetradecyl- and 1-pentadecyl-3:4-dimethoxybenzenes is described. Unfortunately, neither of these products is identical with dimethoxyhydrourushiol, although they seem to be nearly related to it.

The following derivatives of hydrourushiol are described: lead salt; dibenzoyl derivative, colourless needles, m. p. 59—60.5°; di-*m*-dinitrobenzoyl derivative, white, spherical tufts, m. p. 93°; bromodiacetylhydrourushiol, colourless, m. p. 35—43°, dibromohydrourushiol, a brown powder, m. p. 60—66°.

Dimethoxyhydrourushiol was nitrated, and further derivatives were obtained from the nitro-compounds. Fuming nitric acid in acetic acid solution yielded nitrodimehoxyhydrourushiol in long needles, m. p. 72—73°, which were dissolved in fuming nitric acid, and thus converted into a dinitro-derivative, which formed almost colourless, long, flat crystals, m. p. 83°. The mononitro-derivative was readily reduced by zinc dust and glacial acetic acid to aminodimehoxyhydrourushiol, which yielded small, purple granules, m. p. 65—66.5°. The white hydrochloride had m. p. 152—153°; the platinichloride formed slender, yellow prisms, m. p. 178°, and the acetyl derivative had m. p. 66—67°.

Diacetylhydrourushiol was very difficult to nitrate. When warmed with a mixture of fuming nitric acid and sulphuric acid it yielded dinitromonoacetylhydrourushiol, which formed colourless needles, m. p. 69—70.5°, and gave a yellow potassium salt. It was hydrolysed to

*dinitrohydrourushiol*, pale yellow needles, m. p. 122—122.5°, and this was converted into the *diacetyl* derivative, pale brown granules, m. p. 72.5—73.5°. The analyses of all these derivatives give values which agree with either  $C_{15}H_{31}$  or  $C_{14}H_{29}$  for the side-chain.

On heating hydrourushiol over a free flame or at 350—400° in a sealed tube, only catechol could be isolated from the decomposition products. J. C. W.

**Synthesis of Picein, the Glucoside of the Pine (*Pinus picea*); New Artificial Glucoside.** F. MAUTHNER (*J. pr. Chem.*, 1913, [ii], 88, 764—770).—The gluco-*p*-hydroxyacetophenone obtained by the condensation of  $\beta$ -acetobromoglucose with *p*-hydroxyacetophenone and hydrolysis of the resulting tetra-acetogluco-*p*-hydroxyacetophenone (A., 1912, i, 574) is now found to be identical with picein, the glucoside isolated by Tanret (A., 1894, i, 616) from the needles of the pine.

The preparation of tetra-acetogluco-*p*-hydroxyacetophenone is best accomplished by the gradual addition of aqueous sodium hydroxide to a solution of *p*-hydroxyacetophenone and  $\beta$ -acetobromoglucose in acetone, the temperature not being allowed to rise above 16°.

*Tetra-acetogluco-p-hydroxybenzophenone*,  $C_{27}H_{28}O_{11}$ , prepared by shaking an ethereal solution of  $\beta$ -acetobromoglucose with *p*-hydroxybenzophenone, dissolved in aqueous sodium hydroxide, crystallises in colourless needles, m. p. 167—168°, and is hydrolysed by barium hydroxide at the ordinary temperature to *gluco-p-hydroxybenzophenone*, which forms colourless needles, m. p. 178—179°,  $[\alpha]_D^{20} - 55.58^\circ$  in alcoholic solution.

*Methyl tetra-acetogluco-m-hydroxybenzoate*,  $C_{22}H_{26}O_{12}$ , prepared from  $\beta$ -acetobromoglucose and methyl *m*-hydroxybenzoate in acetone solution in the presence of sodium hydroxide, has m. p. 114—115° and is hydrolysed by aqueous barium hydroxide to *gluco-m-hydroxybenzoic acid*,  $C_{13}H_{16}O_8$ , crystallising in colourless needles, m. p. 143—144°,  $[\alpha]_D^{20} - 68.41^\circ$  in aqueous solution. F. B.

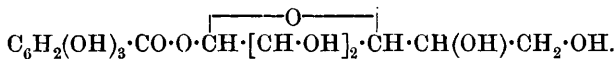
**“Crystallised Rhein” of Commerce.** O. A. OESTERLE and E. R. HAUGSETH (*Arch. Pharm.*, 1913, 251, 550—552).—“Crystallised rhein” of commerce is insoluble in cold aqueous sodium carbonate and does not contain a methoxy-group, and therefore does not contain rhein (1:8-dihydroxyanthraquinone-3-carboxylic acid) or emodin methyl ether. Its m. p. is 192° and, after recrystallisation from benzene, 196°; its acetyl derivative has m. p. 208°. These constants are those of chrysophanic acid and its acetyl derivative respectively. “Crystallised rhein,” therefore, is almost pure chrysophanic acid; the analytical data correspond with the formula  $C_{14}H_5MeO_2(OH)_2$ .

C. S.

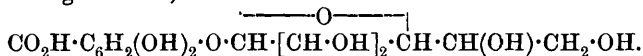
**Comparative Examination of the Constitution of Tannin from Turkish and from Chinese Gall-nuts.** K. FEIST and H. HAUN (*Arch. Pharm.*, 1913, 251, 468—526).—A comprehensive survey is given of the chemistry of tannin since its discovery by Scheele in 1787.

Finely powdered Chinese gall-nuts are dried at  $100^{\circ}$  and then extracted successively with chloroform, benzene, and ether. (The last solvent removes a crystalline substance which proves to be gallic acid.) The tannin is then extracted from the galls by means of acetone. The tannin is obtained from the acetone extract as an amorphous powder, and yields, by hydrolysis with boiling dilute sulphuric acid, 93.5% of gallic acid and about 5.5% of dextrose (identified by its reducing properties, rotatory power, fermentibility, and in the form of its osazone, m. p.  $205^{\circ}$ ). Hence tannin from Chinese gall-nuts, like that from Turkish, contains chemically bound dextrose; the latter contains more dextrose than the former. Turkish tannin, freed as completely as possible from glucogallic acid, yields by hydrolysis gallic acid and about 9% of dextrose.

Since tannin, therefore, is apparently a compound (or several compounds) of gallic acid and dextrose, the most rational method of ascertaining its constitution is an examination of the "simplest tannin," that is, the crystalline substance, glucogallic acid, which is extracted by ether from Turkish galls after they have been extracted with chloroform and with benzene. Glucogallic acid has a molecular weight about 320 (by titration and by the ebullioscopic method in acetone) and yields about equal molecular quantities of gallic acid and dextrose by hydrolysis with boiling dilute sulphuric acid. By methylation by an excess of ethereal diazomethane, glucogallic acid yields a *substance*, m. p.  $77^{\circ}$ , softening at  $60^{\circ}$ , yellow crystals, which does not develop a coloration with ferric chloride, does not reduce Fehling's solution even after boiling for a short time, contains 49% of methoxyl, and is hydrolysed, not by boiling dilute sulphuric acid, but by methyl alcoholic potassium hydroxide, yielding gallic acid trimethyl ether. Hence in glucogallic acid the dextrose cannot have condensed with the gallic acid at a phenolic hydroxyl group. Glucogallic acid, therefore, is an ester of dextrose and gallic acid. The following considerations determine at what point of the dextrose molecule ester formation has occurred. Glucogallic acid reduces Fehling's solution (this does not prove the presence of an aldehyde group, because gallic acid, contrary to statements in the literature, also reduces Fehling's solution), but does not form an osazone; moreover, methylated glucogallic acid does not reduce Fehling's solution. Hence glucogallic acid does not contain a free aldehyde group, and therefore has the constitution



It is quite different in its behaviour from Fischer and Strauss's  $\beta$ -glucosidogallic acid,



Attempts have been made to synthesise glucogallic acid by means of bromotetra-acetylglucose. In the first place it is shown that bromotetra-acetylglucose in ether reacts with an excess of silver phosphate or arsenate in the sense of the equation  $\text{C}_6\text{H}_7\text{OBr}(\text{OAc})_4 + \text{AgA} = \text{AgBr} + \text{C}_6\text{H}_7\text{O}(\text{OAc})_4\text{A}$  (where A denotes an acid radicle). Silver triacetylglallate cannot be prepared, but by shaking an ethereal solution

of bromotetra-acetylglucose and triacetylgallic acid with silver carbonate, silver bromide and silver acetate are formed, and an amorphous substance is produced which is probably incompletely acetylated glucogallic acid; the evidence for this deduction, however, is by no means satisfactory. Attempts to acetylate glucogallic acid have been unsuccessful, as also have been attempts to hydrolyse the preceding amorphous substance, both decomposing during the respective operations.

By treatment with an excess of ethereal diazomethane, Chinese and Turkish tannins have been converted into methylated derivatives which have been separated into fractions containing different percentages of methoxy<sup>1</sup>. This result is regarded as yet another proof of the heterogeneity of tannin. The same conclusion is drawn from the results of an investigation of the rotatory powers, in water and in 96% alcohol, of various samples of commercial tannin.

Although glucogallic acid cannot be extracted from Chinese gall-nuts and is not produced by the hydrolysis of Turkish tannin, the authors regard it as highly probable that this acid is the basis of the Turkish and the Chinese tannin molecules. Both are esters of gallic acid and dextrose; in Chinese tannin the percentage of gallic acid is much greater than that of dextrose. In agreement with this, the molecular weight of Turkish tannin in acetone is very much smaller than that of Chinese tannin, and all the fractions of methylated Turkish tannin contain a greater percentage of methoxyl than the corresponding fractions of methylated Chinese tannin.

The fraction of methylated Chinese tannin which is insoluble in cold absolute alcohol is identical with Herzig's methylotannin; it is not an individual substance, however, its percentage of methoxyl corresponding with that required by a mixture of methylated undeca- and dodeca-galloyldextrose. The fraction of methylated Turkish tannin which is soluble in cold absolute alcohol is, excluding glucogallic acid, the only crystalline derivative of tannin hitherto obtained; it again, however, is not an individual substance, but is a mixture of methylated mono-, di-, and tri-galloyldextrose. C. S.

**Combination of Caffeine with Phenols.** A. BAUMANN (*Chem. Zentr.*, 1913, 2, 2036—2037; from *Arb. Pharm. Inst. Univ. Berlin*, 10, 127—147).—Chlorocaffeine has been condensed with a number of phenols, reaction being carried out in the presence of alkali hydroxide in aqueous solution under reflux, sometimes at higher temperatures under pressure, and sometimes in the presence of xylene. The *phenol* compound of caffeine,  $C_{14}H_{14}O_3N_4$ , forms needles, m. p. 143°, which are soluble in concentrated hydrochloric acid without decomposition, and are stable towards 15% aqueous sodium hydroxide. The *guaiacol* compound, prepared by heating the requisite materials in aqueous solution at 140°, consists of colourless needles of faintly bitter taste, m. p. 151—152°. The *thymol* compound,  $C_{18}H_{22}O_3N_4$ , needles, m. p. 130—132°, is prepared in xylene solution at 155°. With the three cresols in aqueous solution, chlorocaffeine yields the *o-cresol* compound,  $C_{15}H_{16}O_3N_4$ , needles, m. p. 150—151°, the *m-cresol* compound, needles, m. p. 144—145°, and the *p-cresol* compound, needles, m. p. 138—139°

The *eugenol* compound,  $C_{18}H_{20}O_4N_4$ , consists of needles, m. p. 119—120°, whilst the *carracrol* compound, needles, has m. p. 145—146°.

The catechol-monocaffeine compound [*o*-hydroxyphenoxycaffeine],  $C_{14}H_{14}O_4N_4$ , crystallises in needles, m. p. 215°, which are soluble in dilute sodium hydroxide, and yield an *acetyl* derivative,  $C_{16}H_{16}O_5N_4$ , needles, m. p. 186—187°. The corresponding di-caffeine compound has m. p. 280—281°, and is insoluble in dilute sodium hydroxide. In a similar manner, resorcinol yields a monocaffeine compound, needles, m. p. 197—198° (*acetate*, m. p. 123—124°), and a dicaffeine compound, m. p. 288—289°. Analogously, quinol gives a monocaffeine compound, m. p. 206—207° (*acetate*, m. p. 210—211°), and a dicaffeine compound, m. p. 285°. *p*-Hydroxybenzoic acid likewise condenses with chlorocaffeine to yield the substance,  $C_{15}H_{14}O_5N_4$ , m. p. 243—244°, needles of slightly bitter taste, soluble in dilute sodium carbonate solution. *o*-Hydroxybenzoic acid and methyl salicylate could not be condensed with chlorocaffeine in the presence of alkali, whilst hydroxy-caffeine could not be condensed with phenols.

The phenol and thymol compounds of caffeine are stable towards boiling concentrated hydrochloric acid, and are not attacked at 160° by a solution of hydrogen chloride in ether or xylene. They are, however, decomposed by concentrated aqueous hydrochloric acid at 160° into phenol or thymol and hydroxycaffeine. A similar decomposition is caused by heating with aqueous, more rapidly with alcoholic, sodium hydroxide.

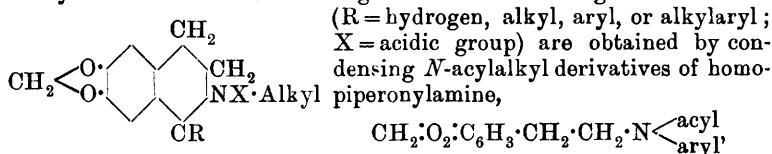
H. W.

**Fermentative Decomposition of Creatinine.** II. D. ACKERMANN (*Zeitsch. Biol.*, 1913, 63, 78—82. Compare A., 1913, i, 1049).—*N*-Methylhydantoin could not be detected as a product of the decomposition of creatinine by means of macerated cat's liver in the presence of toluene.

When creatinine is decomposed by putrefactive bacteria for a period of four weeks, sarcosine is formed. It is considered that the sarcosine is derived from *N*-methylhydantoin, but other possibilities of its formation are suggested also.

E. F. A.

**Preparation of Salts of Hydrastinine and its Homologues.** HERMAN DECKER (D.R.-P. 267699. Compare A., 1911, i, 906).—Salts of hydrastinine and its homologues of the annexed general formula



and converting the dihydroisoquinoline derivatives so obtained into their salts.

*N*-Formylmethylhomopiperonylamine, when condensed by means of phosphoric oxide, yields hydrastinine; *N*-formylethylhomopiperonylamine gives *N*-ethylnorhydrastinine (*platinichloride*, brown prisms, m. p. 195—197° decomp.) and benzoyl-*N*-methylhomopiperonylamine, m. p. 80—81°, furnishes 1-phenylhydrastinine, which forms

white needles, m. p. 152—153° (decomp.). The *picrate* of the latter base forms silky needles, m. p. 98—99°. J. C. C.

**Strychnos Alkaloids. XIX. Some New Oxidation Products of Brucine.** HERMANN LEUCHS and HUBERT RAUCH (*Ber.*, 1913, 46, 3917—3922).—In addition to brucinonic acid and dihydrobrucinonic acid (Leuchs and Brewster, A., 1912, i, 210), the oxidation of brucine by potassium permanganate in acetone solution gives rise to a mixture of neutral substances which amounts to 10% of the brucine used.

By a complex process of extraction and recrystallisation with various solvents, the amorphous mixture could be made to yield three new crystalline substances. The chief of these appears to have the composition  $C_{23}H_{24}O_7N_2$ , and the name trihydroxydehydrobrucine is suggested; it crystallises in cubes or prisms, which are very sparingly soluble in chloroform and benzene, and has  $[\alpha]_D^{20} + 87.4^\circ$  (in hydrochloric acid, D 1.19) and m. p. 336° (decomp.). It is of interest that the solution in acetic acid exhibits no optical activity.

The second product, which has the composition,  $C_{23}H_{26}O_7N_2$ , of a trihydroxybrucine, and so is possibly a dihydro-derivative of the previous compound, crystallises from benzene solution in needles or prisms, m. p. 130—135° (decomp.), which contain benzene of crystallisation; the product recrystallised from water has m. p. 240° (decomp.). In acetic acid solution the substance has  $[\alpha]_D^{20} + 5.66^\circ$ .

The third substance,  $C_{21}H_{22}O_6N_2$ , crystallises from acetic acid in pale green, quadratic pyramids, m. p. 290° (decomp.),  $[\alpha]_D^{20} + 72.8^\circ$  (in acetic acid).

All three substances give the well-known colour reaction with nitric acid. D. F. T.

**Synthesis of Hygrine. II. Synthesis of Racemic Hygrine. A New Oxidation Method. Further Remarks on the Catalytic Reduction of Pyrrole Derivatives.** KURT HESS (*Ber.*, 1913, 46, 4104—4115. Compare A., 1913, i, 1378).—In the former paper an account was given of the preparation of two isomeric 1-methylpyrrolidylpropanols, one of which should yield hygrine on oxidation to the ketone. Difficulty was then experienced in the methylation of the pyrrolidyl derivative. For this purpose, formaldehyde has now been employed, with the unexpected result that oxidation of the hydroxyl group also took place during the one operation, so that almost quantitative yields of the desired ketones were obtained. A comparison of these compounds with hygrine establishes the alkaloid as  $\alpha$ -1-methylpyrrolidyl-2-propane- $\beta$ -one,  $CH_2 \begin{matrix} \swarrow CH_2 \cdot NMe \\ \searrow CH_2 \cdot CH \cdot CH_2 \cdot COMe \end{matrix}$  although the resolution of the synthetic substance and the racemation of the natural product are yet to be accomplished. Willstätter's assumption (A., 1900, i, 405) is therefore justified.

The oxidation of hydroxy-amines to amino-ketones (according to the scheme  $:C \cdot NHR \cdots CH(OH) \cdots + CH_2O = :C \cdot NMeR \cdots CO \cdots + H_2O$ ) seems to be of general application, and is the subject of future work

by the author. The preparation of diacetonmethylamine from diacetonalkamine is now described.

$\alpha$ -2-Pyrrolidylpropan- $\alpha$ -ol was acidified with hydrochloric acid and heated with 40% formaldehyde at 115—120° in a sealed tube. The product,  $\alpha$ -1-methylpyrrolidyl-2-propane- $\alpha$ -one,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{NMe} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COEt} \end{smallmatrix}$ , was dried over barium oxide and obtained as a colourless, mobile, hygroscopic oil, b. p. 70—75°/12 mm., bath 90—95°, 69—74°/14 mm., bath 85—90°, 80—82°/21 mm., bath 95—100°. It has a powerful basic and narcotic odour, is very soluble, and gives the pyrrole reaction. It reduces alkaline, but not acid, permanganate, and also silver nitrate and neutral gold chloride, but from an acid solution of the latter, the *aurichloride* was obtained in yellow, microscopic needles, m. p. 106° (corr.). The *oxime*,  $\text{C}_8\text{H}_{16}\text{ON}_2$ , was obtained as a clear syrup, b. p. 140°/16 mm., which did not form a picrate. The *picrate*,  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_4$ , of the ketone formed long, yellow needles, which sintered at 95° (corr.) and had m. p. 103° (corr.).

Similarly,  $\alpha$ -2-pyrrolidylpropane- $\beta$ -ol was converted by formaldehyde into  $\alpha$ -1-methylpyrrolidyl-2-propane- $\beta$ -one (formula above), which forms a colourless oil, b. p. 79—83°/14 mm., bath 90—100°, 89—92°/21—22 mm., bath 100—110°. It is not so mobile as the isomeride, is not discoloured by light, and its poppy-like odour is not so unpleasant. The *picrate* forms slender, yellow needles, which sinter at 162° (corr.) and have m. p. 176° (corr.). The picrate from a specimen of natural hygrine, with b. p. 79—81°/11—12 mm., bath 90—95°,  $[\alpha]_D^{20}$  1.2°, had m. p. 158° (corr.). The *oxime* had m. p. 125° (corr.), and the picrate of the oxime agreed exactly with that of the oxime of natural hygrine (Liebermann and Kühling, A., 1893, i, 446).

Attention is again called to the influence of traces of oxygen on the spongy platinum used in the catalytic reductions. Much better results are obtained when the preparation is not dried in vacuum, but is simply washed with the solvent which is subsequently employed. Admission of air to the catalyst causes a rise of temperature and cohesion of the finely divided metal. Using spongy palladium as catalyst, complete reduction of the pyrrol alcohols to  $\alpha$ -2-pyrrolidylpropane [2-propylpyrrolidine],  $\text{C}_7\text{H}_{15}\text{N}$ , was effected. This compound is very volatile in steam, and could thus be fractionated from the less volatile, partially-reduced products. It is a clear, mobile, narcotic oil, b. p. 145—150°/765 mm.

Diacetonamine, prepared by Heintz's method (A., 1874, 1080), was successfully distilled in a high vacuum; b. p. 25°/0.14 mm. It was reduced by sodium and alcohol to diacetonalkamine (Kahan, A., 1897, i, 494), b. p. 70—75°/16 mm., and this was heated with 40% formaldehyde at 115—120°. *Diacetonmethylamine*,  $\text{C}_7\text{H}_{15}\text{ON}$ , was then obtained as a colourless, mobile, very soluble oil, b. p. 50—53°/15 mm. It has a peculiar, menthol-like, overpowering odour. J. C. W.

**A New Method for the Preparation of 1-Substituted Isatins.** R. STOLLÉ (*Ber.*, 1913, 46, 3915—3916).—A preliminary account of the formation of 1-substituted isatins by the intra-

molecular condensation of oxalic amide chlorides [chloroglyoxylamides] of the type  $\text{COCl}\cdot\text{CO}\cdot\text{NRPh}$ , which are obtainable by the interaction of oxalyl chloride and mono-substituted anilines under suitable conditions.

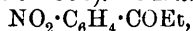
*Chloroglyoxylodiphenylamide*,  $\text{COCl}\cdot\text{CO}\cdot\text{NPh}_2$ , needles, m. p.  $70^\circ$ , when treated with water forms *diphenyloxamic acid*, needles, m. p. near  $146^\circ$  (decomp.), and with alcohol produces the corresponding *ethyl ester*, platelets, m. p.  $87^\circ$ . If a bimolecular proportion of diphenylamine is taken with oxalyl chloride the product is *oxalo-diphenylamide*, plates, m. p.  $169^\circ$ , which often accompanies the amide chloride as by-product.

The intramolecular condensation of chloroglyoxylodiphenylamide gives 1-phenylisatin, which when treated with alkalis is converted into the sodium salt of the corresponding isatic acid; this regenerates 1-phenylisatin on the addition of acids. When heated with phosphorus pentachloride, phenylisatin gives a *dichloro*-derivative, leaflets, m. p.  $100^\circ$ .

Ethylaniline reacts in carbon disulphide solution with oxalyl chloride in the presence of aluminium chloride, forming 1-ethylisatin, m. p.  $95^\circ$ .

D. F. T.

*o*-Aminopropiophenone, its Acyl Derivatives, and Their Condensation to 2- and 4-Hydroxyquinolines. E. WOHLICH (*Arch. Pharm.*, 1913, 251, 526—550).—*o*-Nitropropiophenone,



b. p.  $175^\circ/25$  mm., a viscous, yellow liquid, is obtained in 42—46% yield by treating an ethereal solution of *o*-nitrobenzoyl chloride with an ethereal suspension of ethyl sodiomethylacetoacetate and hydrolysing the resulting ethyl *o*-nitrobenzoylmethylacetoacetate by boiling dilute sulphuric acid. By reduction with tin and concentrated hydrochloric acid on the water-bath, it is converted into *o*-aminopropiophenone, m. p.  $45$ — $46^\circ$ , yellowish-white leaflets, from which the following acyl derivatives have been prepared by the action of the respective acid anhydrides: *acetyl* derivative,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{COEt}$ , m. p.  $71^\circ$ , colourless plates; *propionyl* derivative, m. p.  $51^\circ$ , stout rhombohedra; *butyryl* derivative, m. p.  $39$ — $40^\circ$ , large, rhombohedral crystals, and *benzoyl* derivative, m. p.  $130^\circ$ , colourless needles.

In accordance with Camps' rule (A., 1900, i, 115, 310; 1902, i, 178, 396), the preceding *o*-acylaminopropiophenones, except the last, yield 2- and 4-hydroxyquinoline derivatives by condensation with the calculated quantity of sodium hydroxide in boiling aqueous alcohol. The 4-hydroxyquinoline derivatives exhibit distinctly basic and acidic properties and develop red colorations with ferric chloride, whilst 2-hydroxyquinoline derivatives do not give a ferric chloride reaction and are feebly acidic and basic. Thus *o*-acetylaminopropiophenone yields Konrad and Limpach's 4-hydroxy-2:3-dimethylquinoline (A., 1892, 78) and 2-hydroxy-4-ethylquinoline, m. p.  $197^\circ$ , small prisms (*hydrochloride*, long needles; *platinichloride*,  $2\text{C}_{11}\text{H}_{11}\text{ON}, \text{H}_2\text{PtCl}_6, \text{H}_2\text{O}$ , decomp.  $199$ — $200^\circ$ , pale yellow needles; *picrate* m. p.  $149$ — $150^\circ$ , yellow needles). *o*-Propionylaminopropiophenone yields 4-hydroxy-3-methyl-2-ethylquinoline, m. p.  $297^\circ$  (*hydrochloride*, m. p.  $180$ — $185^\circ$ ;



*picrate*, m. p. 184°, yellow needles; *platinichloride*,  
 $2C_{12}H_{13}ON, H_2PtCl_6, 2H_2O$ ,  
 decomp. 218° [rapidly heated], reddish-yellow needles), and 2-hydroxy-3-methyl-4-ethylquinoline, m. p. 188°, colourless needles (*picrate*, m. p. 183°; *hydrochloride*, m. p. 120—130°). *o*-Butyrylamino-*prop*iophenone yields 2-hydroxy-3:4-diethylquinoline, m. p. 174—175° (*picrate*, m. p. 156—157°, small, yellow needles; *platinichloride*,  
 $2C_{13}H_{15}ON, H_2PtCl_6, 2H_2O$ ,  
 m. p. 194—195°, red needles), and 4-hydroxy-3-methyl-2-propylquinoline, m. p. 275 (*picrate*, m. p. 179°; *platinichloride*,  
 $2C_{13}H_{15}ON, H_2PtCl_6, 2H_2O$ ,  
 m. p. 201—202°).

Only one quinoline derivative can be formed by the condensation of *o*-benzoylamino-*prop*iophenone. 4-Hydroxy-2-phenyl-3-methylquinoline, m. p. 276°, develops a coloration with ferric chloride, but is only feebly basic.

By treatment with phosphorus pentachloride, the preceding hydroxyquinolines are converted into the corresponding chloro-derivatives; by reducing the latter by hydrogen iodide in glacial acetic acid or by distillation with zinc dust, the corresponding alkylated quinolines are obtained. It is found that chlorine in position 4 is more difficultly removed than chlorine in position 2; the difficulty increases with the number of carbon atoms in the alkyl groups, so that the halogen can be eliminated from the higher 4-chloroalkylquinolines only by distillation with zinc dust. 4-Chloro-2:3-dimethylquinoline has m. p. 78° (decomp.). 2-Chloro-4-ethylquinoline, m. p. 76—77°, crystallises in colourless prisms. 4-Chloro-3-methyl-2-ethylquinoline and the corresponding iodo-compound have m. p. 22—23° and 64—65° respectively. By distillation with zinc dust under diminished pressure, 4-hydroxy-3-methyl-2-propylquinoline yields two substances, one of which is probably 3-methyl-2-propylquinoline, m. p. 59° (*platinichloride*, m. p. 228°), whilst the other, m. p. 65—70°, is possibly an indole derivative, since it responds to the pine-shaving test. 2-Chloro-3-methyl-4-ethylquinoline, m. p. 72—73°, is converted into 2-iodo-3-methyl-4-ethylquinoline, m. p. 103°, by hydriodic acid, potassium iodide, and amorphous phosphorus, but is reduced by hydrogen iodide in glacial acetic acid at 275° to 3-methyl-4-ethylquinoline, b. p. 172—173°/27—28 mm. (*picrate*, m. p. 196—197°; *platinichloride*, m. p. 230°, reddish-yellow needles). In a similar manner, 2-chloro-3:4-diethylquinoline, b. p. 203—205°/24—25 mm., is reduced to 3:4-diethylquinoline, b. p. 177—178°/25 mm. (*picrate*, m. p. 179°, yellow needles; *platinichloride*, m. p. 230° [decomp.], yellowish-red needles).

Equal molecular quantities of *o*-aminopropiophenone and ethyl acetoacetate react at 160—165° to form only 2-hydroxy-3-acetyl-4-ethylquinoline, m. p. 198—199°, colourless needles, which is quite devoid of basic character, whilst under similar conditions *o*-aminopropiophenone and ethyl benzoylacetate yield 2-hydroxy-3-benzoyl-4-ethylquinoline, m. p. 213°, about 8—10% of the intermediate substance,  $CH_2Bz \cdot CO \cdot NH \cdot C_6H_4 \cdot COEt$ , m. p. 94—95°, also being obtained; the latter is converted into the former by aqueous alcoholic sodium hydroxide.

C. S.

**Preparation of Anthraquinoneacridinecarboxylic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 262469).—1-Anilinoanthraquinone-2-carboxylic acid, when heated with sulphuric acid (60°Bé) to 90–100°, yields a mixture of anthraquinone-1:2-acridone and 1-acridineanthraquinone-2-carboxylic acid. Similarly, 1-*p*-chloroanilinoanthraquinone-2-carboxylic acid gives 1-*p*-chloroacridineanthraquinone-2-carboxylic acid, and a corresponding acid is produced by the condensation of 1-*p*-toluidinoanthraquinone-2-carboxylic acid. J. C. C.

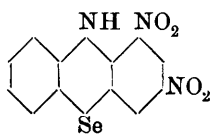
**The Decomposition of Phenylbenzylideneisooxazolone by Phenylhydrazine.** ANDRÉ MEYER (*Bull. Soc. chim.*, 1913, [iv], 13, 1106–1107. Compare Dains and Griffin, A., 1913, i, 1086).—1-Phenyl-4-benzylideneisooxazol-5-one is decomposed by boiling in alcoholic solution with phenylhydrazine, giving phenylbenzylidenehydrazone. Hydroxylamine and bases capable of combining with aldehydes and ketones can take the place of the phenylhydrazine. The reaction is general to such isooxazolones as the above. W. G.

**Preparation of Anthraquinone-*N*:1:1'-oxazines.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 266945, 266946).—Anthraquinone-*N*:1:1'-oxazines are obtained by heating a mixture of 1-halogen-anthraquinones having the 2-position free and 2-halogen-1-aminoanthraquinones in nitrobenzene solution with sodium acetate (to fix mineral acid) and a catalyst.

*Anthraquinone-N:1:1'-oxazine*,  $C_{14}H_6O_2 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C_{14}H_6O_2$ , is prepared from 1-chloroanthraquinone and 2-bromo-1-aminoanthraquinone, using copper acetate as catalyst. It separates from quinoline as a brownish-violet, crystalline powder. The compound is also obtained (second patent) by heating a mixture of 1-nitro-2-hydroxyanthraquinone and 1-chloroanthraquinone in nitrobenzene solution with metallic copper. J. C. C.

**Preparation of Anthraquinonethiazoles.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 267523. Compare this vol., i, 87).—When 2-aminoanthraquinones containing a free ortho-position are heated with sulphur or sulphur-yielding substances and benzylidene chloride (instead of benzotrichloride as previously described, *loc. cit.*), anthraquinonethiazoles are produced. These are yellow, crystalline powders, which dye cotton in yellow shades from the hyposulphite vat. J. C. C.

**Preparation of Phenazselenonium Colouring Matters.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 261969).—The interaction of potassium selenocyanate and *o*-nitrodiazobenzene yields *o*-nitroselenocyanobenzene, which with alkalis gives *o*-nitroselenophenol, and this, on reduction, furnishes *o*-aminoselenophenol. The latter

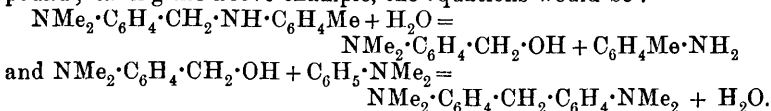


condenses with di- or tri-nitrohalogenbenzenes to nitroselenazines, which on reduction and subsequent oxidation give phenazselenonium colouring matters.

1:3-Dinitrophenoselenazine (annexed formula), prepared from picryl chloride and *o*-aminoseleno-

phenol, is a deep red powder, m. p. 195°. It yields by the above treatment, 1:3-diaminophenazselenonium chloride, dark olive needles. On nitration, dinitrophenoselenazine gives 1:3:6-trinitrophenoselenazine a red powder, m. p. 180°, and the 1:3:6-triaminophenazselenonium chloride prepared from it forms needles with a metallic lustre. J. C. C.

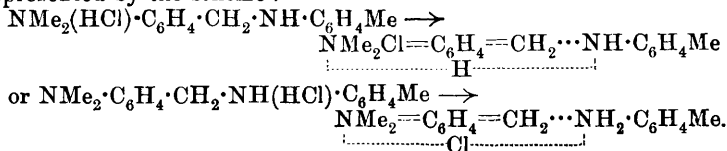
The Mechanism of the Rearrangement of Aminobenzylanilines into Diphenylmethane Bases. A Contribution to the Partition of Chemical Valency. J. VON BRAUN and O. KRUBER (*Ber.*, 1913, 46, 3952—3965).—*p*-Aminobenzylaniline and its derivatives when warmed with aromatic amines in acid solution become converted into *pp'*-diaminodiphenylmethane derivatives in the manner represented by the equation:  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{Me} + \text{C}_6\text{H}_5\text{NMe}_2 = \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 + \text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ , but little is known of the mechanism of the change. A suggestion has been made (von Braun, A., 1908, i, 684) that the action occurs in two stages, the first involving the fission of the molecule of the *p*-aminobenzylaniline derivative by the action of water, the second stage being the condensation of the *p*-aminobenzyl alcohol derivative formed with the aromatic amine producing the diaminodiphenylmethane compound; taking the above example, the equations would be:



This view of the change has proved a useful working hypothesis (compare von Braun and collaborators, A., 1912, i, 968; 1913, i, 1327, 1330), but as aminobenzyl alcohol compounds with a tertiary nitrogen atom cannot be made to give the condensation assumed above, the explanation must be sought in an entirely different direction.

New facts have now been discovered concerning the rearrangement. The solutions used must not be too acidic, otherwise the yield will be far from satisfactory; the amount of acid should be that required for dissolving the reagents. It is found that such a solution, for example, of the dihydrochloride of a *p*-aminobenzylaniline, has characteristic properties, and on warming or adding a little alkali, a reddish-yellow colour appears which disappears when a large excess of acid is introduced. *m*-Aminobenzylaniline derivatives do not produce this colour change, neither do they give the rearrangement with aromatic amines.

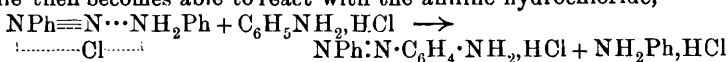
The conclusion is therefore drawn that it is those molecules of the *p*-aminobenzylaniline derivative which are less rich in acid which enter into the action, and that the lack of acid must exert a weakening effect on the linking C·N in the centre of the molecule. The colour reaction mentioned above also indicates that the same influence causes a tendency to alteration to some quinonoid configuration. The only explanation which appears to be compatible with the evidence is that represented by the scheme:



The weakening thus produced at the C·N linking in the centre of the molecule renders possible the interaction with an aromatic amine to produce a diaminodiphenylmethane derivative. It is considered that the balance of the evidence is decidedly in favour of the latter of the two possibilities for the first stage.

It is possible that the conversion of diazoamino-compounds into aminoazo-compounds in the presence of the hydrochloride of an aromatic amine depends on a similar preliminary disturbance of the N·NH linking, thus:  $\text{NPh:N} \cdot \text{NHPh}, \text{HCl} \rightarrow \text{NPh} \equiv \text{N} \cdots \text{NH}_2\text{Ph}$ . The mole-

cule then becomes able to react with the aniline hydrochloride,



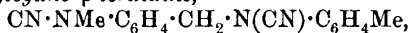
(compare Goldschmidt and Reinders, A., 1896, ii, 515, 556).

The following substances are described: *m*-Aminobenzylaniline hydrochloride has m. p. 63° (compare Purgotti and Monti, A., 1901, i, 22).

*p*-Dimethylaminobenzyl-*p*-toluidine dihydrochloride forms colourless needles, m. p. 186—187°, and can be converted into a *platinichloride*, m. p. 189°; when heated in the crystalline condition or in solution, the dihydrochloride assumes a reddish-yellow colour; this is not due to a fission of the molecule into *p*-toluidine and a quinonoid substance of the type  $\text{NMe}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2$ , for no appreciable amount of *p*-toluidine is formed.

By the action of  $\beta$ -naphthalenesulphonyl chloride on an aqueous acetone solution of dimethylaminobenzyltoluidine in the presence of alkali at the ordinary temperature, the *naphthalenesulphonyl* derivative,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{SO}_2 \cdot \text{C}_{10}\text{H}_7) \cdot \text{C}_6\text{H}_4\text{Me}$ , needles, m. p. 137°, is obtained; its *hydrochloride* and *sulphate* are sparingly soluble in water.

If finely divided dimethylaminobenzyltoluidine is shaken with an equal quantity of powdered cyanogen bromide, *dimethylaminobenzylcyano-p-toluidine*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{CN}) \cdot \text{C}_6\text{H}_4\text{Me}$ , a colourless, crystalline mass, m. p. 135°, is obtained (*hydrochloride*, leaflets, m. p. 165°; *platinichloride*, m. p. 116—118°), which is accompanied by some *methylcyanoaminobenzylcyano-p-toluidine*,



m. p. 140°; this is also obtainable by the action of cyanogen bromide on the monocyano-derivative. The monocyano-compound is easily hydrolysed by warm dilute hydrochloric acid, giving *as-p-tolyl-dimethylaminobenzylcarbamide*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{CO} \cdot \text{NH}_2) \cdot \text{C}_6\text{H}_4\text{Me}$ , m. p. 178—179°; like the cyano-compound this is a mono-acid base; *platinichloride*, m. p. 169°.

*p*-Dimethylaminobenzyl-*p*-toluidine gives a *p*-nitrobenzoyl derivative, deep red needles, m. p. 144°; *hydrochloride*, m. p. 65—66° (decomp.); *platinichloride*, m. p. 153—154°.

The above acyl derivatives of *p*-dimethylaminobenzyl-*p*-toluidine combine fairly readily with methyl iodide; the monocyano-derivative gives a *methiodide*,  $\text{NMe}_3\text{I} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{CN}) \cdot \text{C}_6\text{H}_4\text{Me}$ , m. p. 95—100° (decomp.); the corresponding *methiodides* of the nitrobenzoyl and of the benzoyl derivatives have m. p. 120—121° and 150—151° respectively. The *methiodide*, colourless leaflets, m. p. 162°, of the acetyl derivative was converted by silver chloride into the corresponding

*methochloride*, m. p.  $188^{\circ}$ ; *platinichloride*, m. p.  $210^{\circ}$  (decomp.). On repeatedly evaporating its solution in concentrated hydrochloric acid to dryness, this methochloride compound loses its acetyl group with production of *p*-dimethylaminobenzyl-*p*-toluidine *methochloride hydrochloride*,  $\text{NMe}_3\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH}(\text{HCl}) \cdot \text{C}_6\text{H}_4\text{Me}$ , a colourless powder, m. p.  $177^{\circ}$ ; *platinichloride*, m. p.  $199^{\circ}$ . This methochloride hydrochloride, as also the acyl derivatives of *p*-dimethylaminobenzyl-*p*-toluidine, do not give a colour reaction when their aqueous solutions are warmed or treated with alkali, and they do not undergo the condensation with aromatic amines, thus confirming the authors' view as to the mechanism of this condensation. D. F. T.

**Aminohydrazines. II. Benzylidene-*p*-aminophenylhydrazine (Benzaldehyde-*p*-aminophenylhydrazone).** HARTWIG FRANZEN and B. VON FÜRST (*Ber.*, 1913, 46, 3965—3974. Compare Franzen, A., 1907, i, 321).—It has already been shown that benzaldehyde-*o*-nitrophenylhydrazone can be reduced by sodium hyposulphite in ammoniacal alcoholic solution to benzaldehyde-*o*-aminophenylhydrazone, but this product could not be hydrolysed to the free hydrazine on account of its conversion under the influence of acid into 2-phenylbenziminazole. As the para-isomeride could not be capable of this condensation, it has now been submitted to investigation.

When an aqueous solution of sodium hyposulphite is gradually introduced into a boiling alcoholic solution of benzaldehyde-*p*-nitrophenylhydrazone to which one-fifth its bulk of a cold saturated alcoholic solution of ammonia has been added, reduction is effected to *benzaldehyde-p-aminophenylhydrazone*, yellow needles or leaflets, m. p.  $133$ — $134^{\circ}$  (decomp.), which rapidly darken. This substance when treated with benzaldehyde in boiling alcoholic solution is converted into its *benzylidene* derivative,  $\text{CHPh}:\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}:\text{N}:\text{CHPh}$ , golden-yellow leaflets, m. p.  $163$ — $164^{\circ}$ , which is also obtained occasionally as a product of the above reduction. In a similar manner, *p*-anisaldehyde and *m*-nitrobenzaldehyde condense with benzaldehyde-*p*-aminophenylhydrazone, producing the *p*-anisylidene and *m*-nitrobenzylidene derivatives, a yellowish-brown, crystalline powder, m. p.  $148^{\circ}$ , and an intense yellow powder, m. p.  $158^{\circ}$ , respectively. With phenylthiocarbimide the benzaldehyde-*p*-aminophenylhydrazone yields a *thiocarbanilide* derivative,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}:\text{N}:\text{CHPh}$ , an almost colourless, crystalline mass, m. p.  $157^{\circ}$ .

Unlike the ortho-isomeride (*loc. cit.*), benzaldehyde-*p*-aminophenylhydrazone when added in hot alcoholic solution to dilute hydrochloric acid at  $-10^{\circ}$  gives a violet-red, powdery *hydrochloride*, m. p.  $179$ — $181^{\circ}$ , which is unstable in a moist condition; on the addition of concentrated ammonia solution the hydrochloride regenerates the original benzaldehyde-*p*-aminophenylhydrazone. The *sulphate* can be obtained in a similar manner, and shows similar properties. The suggestion is made that these strongly coloured salts are possibly of an azo-structure, for example,  $\text{NH}_2(\text{HCl}) \cdot \text{C}_6\text{H}_4 \cdot \text{N}:\text{N} \cdot \text{CH}_2\text{Ph}$ , or a quinonoid structure,  $\text{NH}_2 > \text{C}_6\text{H}_4 \cdot \text{N}(\text{HCl}) \cdot \text{N}:\text{CHPh}$ .

When benzaldehyde-*p*-aminophenylhydrazone is treated in boiling

alcoholic solution with 2*N*-sulphuric acid, a deep-coloured solution is obtained which, after the addition of water and subsequent cooling, gives a deposit of almost colourless leaflets of a *sulphate*; the lack of colour is indicative of a normal structure and confirms the occurrence of a rearrangement in the formation of the coloured salts just described.

Under the action of a hot alcoholic solution of hydrogen chloride, the behaviour of benzaldehyde-*p*-aminophenylhydrazone is quite different; instead of a hydrochloride or of the likely hydrolytic products benzaldehyde and *p*-aminophenylhydrazine, there is obtained *p*-phenylenediamine together with benzaldehyde and ammonia. This result indicates a fission of the molecule at the N-N linking instead of at the C:N linking as might be expected, and throws light on the intramolecular condensation of the ortho-isomeride under the influence of acid. In the latter case, the primary products are probably *o*-phenylenediamine, benzaldehyde, and chloroamine, of which the two former condense to a dihydrobenziminazole; this is then oxidised by the chloroamine to benziminazole itself.

D. F. T.

#### Crystallography of Some Aromatic Nitrogen Compounds.

JULIEN DRUGMAN (*Zeitsch. Kryst. Min.*, 1913, 53, 266—270).—The following compounds, prepared by F. D. Chattaway, were measured. Bismethylphenylazimethylene (monoclinic,  $a : b : c = 1.3335 : 1 : 1.1667$ ;  $\beta = 103^\circ 44'$ ). *N*-Dichlorobenzylidenediacetamide (T., 1912, 101, 1207). *N*-Chlorophthalimide (rhombic-bisphenoidal,

$$a : b : c = 0.3000 : 1 : 0.275).$$

*N*-Dichlorobenzenesulphonimide (monoclinic,  $a : b : c = 0.7213 : 1 : 1.2009$ ;  $\beta = 100^\circ 29'$ ).

L. J. S.

Constitution of Acetylacetonecarbamide [4:6-Dimethyl-dihydropyrimid-2-one]. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1914, 36, 104—115).—Acetylacetonecarbamide exists in two modifications, one colourless, the other yellow. It has been suggested by Haan (A., 1908, i, 577) that the former is 4:6-dimethyl-2:3-dihydropyrimid-2-one,  $\text{CH} \begin{smallmatrix} \text{CMe}=\text{N} \\ \text{CMe}\cdot\text{NH} \end{smallmatrix} \text{CO}$ , and the latter, 4:6-dimethyl-

2:5-dihydropyrimid-2-one,  $\text{CH}_2 \begin{smallmatrix} \text{CMe}\cdot\text{N} \\ \text{CMe}\cdot\text{N} \end{smallmatrix} \text{CO}$ . Both compounds crystallise with  $2\text{H}_2\text{O}$ , and have m. p.  $197^\circ$ .

A *potassium* salt can be prepared from an aqueous solution of either of these compounds, and is completely decomposed by the carbon dioxide of the atmosphere. On adding silver nitrate to a solution of either modification, a white *silver* salt is precipitated, which reacts with methyl iodide with formation of a red, crystalline methyl iodide additive *compound* of a trimethylpyrimidone. Mercuric chloride also yields an insoluble salt with the dimethyldihydropyrimidone. When a solution of the yellow acetylacetonecarbamide in methyl alcohol is boiled with methyl iodide, the additive *compound*,  $\text{C}_6\text{H}_8\text{ON}_2\cdot\text{MeI}$ , is produced in the form of colourless crystals which gradually become red when left in the air.

If diazomethane vapour is passed into a cold solution of acetyl-

acetonecarbamide in chloroform, 3 : 4 : 6-*trimethyl-2 : 3-dihydropyrimid-2-one*, m. p. 63°, is obtained which forms colourless crystals. The same compound can be prepared by the condensation of methylcarbamide with acetone; its *hydrochloride* crystallises in colourless prisms. The conclusion is drawn that acetylacetonecarbamide does not contain a hydroxyl group and that the tautomeric forms must have the constitutions ascribed to them by Haan. E. G.

**Preparation of 5-Mono- and -di-allylbarbituric Acids.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE (D.R.-P. 268158).—The interaction of allyl bromide and barbituric acid, according to the quantities used, leads to the production of 5-*allylbarbituric acid*, m. p. 162°, and 5-*diallylbarbituric acid*. The latter forms colourless leaflets, m. p. 169—170°, and has a stronger hypnotic action than the corresponding diethyl derivative (veronal). J. C. C.

**Constitution of Benzoylhydrazicarbonyl.** R. STOLLE and K. O. LEVERKUS (*Ber.*, 1913, 46, 4076—4080. Compare A., 1913, i, 898).—The authors have carried out the proposed condensations of nitrobenzoylhydrazicarbonyl with benzoyl chloride and benzoylhydrazicarbonyl with nitrobenzoyl chloride, and have obtained different products. This argues against the hydrazicarbonyl structure for these derivatives.

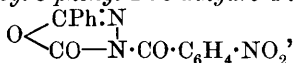
The formation of 2 : 5-diphenyl-1 : 3 : 4-oxadiazole by the action of heat on dibenzoylhydrazicarbonyl and the preparation of ethyl dibenzhydraziodoformate by the action of sodium ethoxide (A., 1913, i, 97) agree with the alternate oxadiazole formula. The tautomeric formulæ :



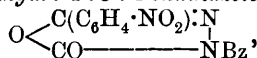
most nearly correspond with the behaviour of "benzoylhydrazicarbonyl" and its substitution products.

On this basis, the compound is re-named 2-keto-5-phenyl-2 : 3-dihydro-1 : 3 : 4-oxadiazole; "dibenzoylhydrazicarbonyl" is called 2-keto-3-benzoyl-5-phenyl-2 : 3-dihydro-1 : 3 : 4-oxadiazole; and Schestakov's methyl derivative of "benzoylhydrazicarbonyl" (A., 1913, i, 97), which yields benzoylhydrazine on heating with water, and therefore exists in the tautomeric form corresponding with (II), is re-named 2-methoxy-5-phenyl-1 : 3 : 4-oxadiazole.

2-Keto-3-*p*-nitrobenzoyl-5-phenyl-2 : 3-dihydro-1 : 3 : 4-oxadiazole,



was obtained by heating "benzoylhydrazicarbonyl" with *p*-nitrobenzoyl chloride in pyridine, in leaflets, m. p. 195°. 2-Keto-3-benzoyl-5-*p*-nitrophenyl-2 : 3-dihydro-1 : 3 : 4-oxadiazole,



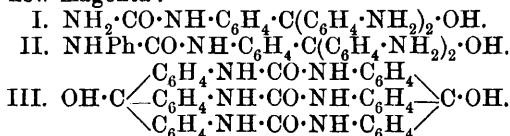
formed glistening needles and leaflets, m. p. 196°. A mixture of the isomerides melted about 30° lower. Both compounds yielded *benzoyl-p*-nitrobenzoylhydrazine, C<sub>14</sub>H<sub>11</sub>O<sub>4</sub>N<sub>3</sub>, on warming with dilute sodium

hydroxide and precipitating with acids. The compound was also prepared from *p*-nitrobenzoylhydrazine and benzoyl chloride. It is a white powder, m. p. 236°. On heating alone, they also gave the same *phenyl-p-nitrophenyl*-1:3:4-*oxadiazole*,  $C_{14}H_9O_3N_3$ , the evolution of carbon dioxide being quantitative. This compound was also obtained by heating benzoyl-*p*-nitrobenzoylhydrazine with thionyl chloride. It forms glistening leaflets, m. p. 209°. J. C. W.

**The Formation of Methenylbis[phenylmethylpyrazolone] from Phenylmethylpyrazoloneglyoxylic Acid.** WILHELM WISLICENUS and OTTO BILFINGER (*Ber.*, 1913, **46**, 3948—3949).—A correction. The substance recently obtained by heating an alcoholic solution of 1-phenyl-3-methyl-5-pyrazolone-4-glyoxylic acid (Wislicenus, Elvert, and Kurtz, A., 1913, i, 1387), and described as 1-phenyl-3-methyl-4-methylene-5-pyrazolone, is in reality methenylbis[phenylmethylpyrazolone],  $\begin{matrix} \text{NPh} \cdot \text{CO} \\ | \\ \text{N} = \text{CMe} \end{matrix} > \text{CH} \cdot \text{CH} : \text{C} < \begin{matrix} \text{CO} - \text{NPh} \\ | \\ \text{CMe} : \text{N} \end{matrix}$  (compare Betti and Mundici, A., 1907, i, 543). D. F. T.

**Preparation of 1:7-Dimethylguanine.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 262470).—2:4:5-Triamino-6-pyrimidone is converted into the 5-formyl derivative by treatment with dilute formic acid at a moderate temperature, the latter methylated, and the 1-methyl derivative boiled with concentrated formic acid, whereby 1-methylguanine,  $\begin{matrix} \text{NMe} - \text{CO} - \text{C} \cdot \text{NH} \\ | \\ \text{C}(:\text{NH}) \cdot \text{NH} \cdot \text{C} - \text{N} \end{matrix} \geq \text{CH}$ , crystallising in needles, is produced. On methylation, 1:7-dimethylguanine, needles, m. p. 337—339°, is obtained. J. C. C.

**Carbamides of the Rosaniline Series.** GUIDO MAYER (*J. pr. Chem.*, 1913, [ii], **88**, 699—730).—An account of the preparation and properties of carbamide derivatives of the following three types from pararosaniline, rosaniline, and tri-*p*-aminophenyldi-*m*-tolylcarbinol, the dye-base of new-magenta:



The compounds of the first type are obtained in the form of their hydrochlorides (1) by the addition of potassium cyanate to aqueous solutions of the hydrochlorides of the dyes, and (2) by fusing the dye-bases with carbamide and heating the product with hydrochloric acid. The following compounds were prepared in this manner:

4':4''-Diamino-4-carbamidotriphenylcarbinol hydrochloride,  $\text{NH}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , from pararosaniline; 4':4''-diamino-4-carbamidodiphenyl-*m*-tolylcarbinol hydrochloride from rosaniline, and 4':4''-diamino-4-carbamidophenyldi-*m*-tolylcarbinol hydrochloride from the dye base of new-magenta.



The corresponding *bases*, which probably have a quinonoid structure, are obtained by heating the hydrochlorides with dilute aqueous potassium hydroxide for several days at 90—95°.

The compounds described above decompose, when heated, with the evolution of ammonia and aniline, give red colorations on treatment with strong mineral acids, and yield diazonium compounds, which couple with resorcinol and R-salt to form yellow azo-dyes. They are reduced to the corresponding leuco-compounds with zinc and hydrochloric acid, and give characteristic colorations with potassium chlorate and hydrochloric acid and other oxidising agents; the *picrates* and *mercurichlorides* are mentioned. When the sulphate of the carbamide, derived from pararosaniline, is treated with acetic acid and solid sodium nitrite, and the resulting solution diluted with water, an unstable, flesh-coloured *diazonium* compound,

$\text{NH}_2 \cdot \text{CO} \cdot \text{N}(\text{NO}) \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})(\text{C}_6\text{H}_4 \cdot \text{NH}_2) \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$ , is precipitated. The diazonium compound rapidly loses nitric oxide, yielding a product from which 4'-amino-4'-hydroxy-4-carbamidotriphenylcarbinol hydrochloride,

$\text{NH}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , is obtained by boiling with water and subsequent treatment with hydrochloric acid. When boiled, the filtrate from the above unstable diazonium compound yields aurin and 4':4''-dihydroxy-4-carbamidotriphenylcarbinol,  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , a black substance which gives intensely violet solutions in dilute aqueous potassium hydroxide.

The phenylcarbamides of type II are obtained in the form of their hydrochlorides by fusing the dye bases with phenylcarbamide and dissolving the product in hydrochloric acid. The *hydrochlorides* of 4':4''-diamino-4-phenylcarbamidotriphenylcarbinol,

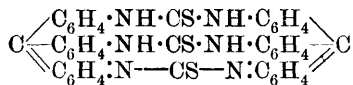
$\text{NH}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , from pararosaniline, of 4':4''-diamino-4'-phenylcarbamidodiphenyl-m-tolylcarbinol, from rosaniline, and 4':4''-diamino-4-phenylcarbamidophenyldi-m-tolylcarbinol, from the dye base of new-magenta, were prepared in this manner; the corresponding imino-bases are formed by heating the hydrochlorides with aqueous potassium hydroxides.

The above phenylcarbamides form *picrates* and *mercurichlorides*, can be diazotised, and give characteristic colorations on treatment with strong mineral acids and oxidising agents. When heated they decompose without melting.

The *tricarbamides* of type III are obtained in the form of their *hydrochlorides* (annexed formula) by passing carbonyl chloride into a hydrochloric acid solution of the dyes; the hydrochlorides are sparingly soluble in water and decompose when heated with evolution of aniline and ammonia. The free *bases* are also described. F. B.

Some Thiocarbamides of the Rosaniline Series. SIEGFRIED HILLER (*J. pr. Chem.*, 1913, [ii], 88, 731—743. Compare preceding abstract).—When heated with carbon disulphide in alcoholic solution

in the presence of a little sulphur, pararosaniline is converted into a *trithiocarbamide* of the annexed constitution; similar compounds,



and  $\text{C}_{43}\text{H}_{32}\text{N}_6\text{S}_3$  have also been prepared from rosaniline and 4:4':4''-

triaminophenyldi-*m*-tolylcarbinol.

The three compounds are brownish-red to blackish-red substances, having a metallic lustre, yield in acetic acid solution metallic precipitates with picric acid, copper sulphate and mercuric chloride, and are decomposed by hot acids with liberation of hydrogen sulphide. On treatment with sodium hydroxide, their solutions in acetic acid yield the corresponding red *carbinol bases*.

When heated with benzoic acid and aniline, the trithiocarbamides from pararosaniline and rosaniline yield blue *phenyl* derivatives, which yield reddish-brown solutions in strong acids.

Attempts to prepare the trithiocarbamide, derived from pararosaniline, by the addition of ammonium thiocyanate to a hot alcoholic solution of pararosaniline hydrochloride, gave *tri-p-aminotriphenylcarbinol thiocyanate*,  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{S}$ , as a lustrous, green, metallic precipitate.

4:4'-Diamino-4''-phenylthiocarbamidotriphenylcarbinol,

$\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ ,

4:4'-diamino-4''-phenylthiocarbamidodiphenyl-*m*-tolylcarbinol,

$\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2) \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ ,

and 4:4'-diamino-4''-phenylthiocarbamidophenyldi-*m*-tolylcarbinol,

$\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2) \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ ,

are obtained by heating phenylthiocarbimide with alcoholic solutions of pararosaniline, rosaniline, and tri-*p*-aminophenyldi-*m*-tolylcarbinol respectively. They are amorphous, violet substances, which give orange-red solutions in sulphuric acid, and when heated with dilute acids or water are partly resolved into their components and partly converted into the corresponding carbamides with evolution of hydrogen sulphide.

When heated with benzoic acid and aniline they yield blue *phenyl* derivatives. The *hydrochlorides*, ( $\text{BHCl}$ ), prepared by the direct union of phenylthiocarbimide and the hydrochlorides of the original dye bases, form red aqueous or alcoholic solutions from which the corresponding *carbinol bases* are precipitated on the addition of sodium hydroxide.

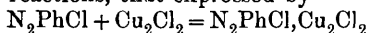
F. B.

**The Kinetics of the Sandmeyer Reaction.** P. WAENTIG and JOHANNA THOMAS (*Ber.*, 1913, 46, 3923—3937. Compare Heller, A., 1910, i, 240; Heller and Tischner, A., 1911, i, 243).—The cuprous haloid employed in the Sandmeyer reaction is fairly generally believed to form an intermediate additive compound with the diazo-compound, although various views are held as to the details of the mechanism of the change.

Cryoscopic experiments with a solution of cuprous chloride in dilute hydrochloric acid give probability to the view that it is the double molecule  $\text{Cu}_2\text{Cl}_2$  and not  $\text{CuCl}$  which is involved in the change.

By adding a concentrated solution of benzenediazonium chloride at  $-17^{\circ}$  gradually to a saturated solution of cuprous chloride in 25% hydrochloric acid at  $-60^{\circ}$ , the authors have obtained an unstable, bulky, red precipitate of composition,  $C_6H_5N_2Cl, Cu_2Cl_2$ , analogous to the cuprous bromide compound isolated by Hantzsch (A., 1895, i, 516).

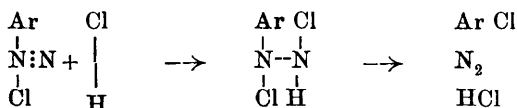
Measurements of the velocity of the decomposition of benzenediazonium and *p*-toluenediazonium chloride solutions at  $0^{\circ}$  in the presence of an approximately equimolecular quantity of cuprous chloride dissolved in hydrochloric acid, by means of the volume of liberated nitrogen, show that the *p*-toluenediazonium salt decomposes much more slowly than the benzenediazonium salt. The constants calculated for a unimolecular change in any one experiment were satisfactory, but the higher the initial concentration of diazonium salt and cuprous chloride the greater the constants obtained. This effect appears to be due to the cuprous chloride, and the deduction may be drawn that of the two successive reactions, that expressed by



is of measurable velocity and seems to be unimolecular on account of the constancy of the concentration of the cuprous chloride during an experiment, whilst the change  $N_2PhCl, Cu_2Cl_2 = PhCl + N_2 + Cu_2Cl_2$  is very rapid. The simplicity of this view is somewhat discountenanced by the impossibility of obtaining satisfactory constants when the diazonium salt and cuprous chloride are present in other than equimolecular proportions, and by the authors' discovery that with equimolecular proportions of diazonium and cuprous salts the velocity of the reaction is very considerably depressed by increased concentration of the hydrochloric acid present.

A rise of  $10^{\circ}$  in the temperature of the reaction increases the velocity to twice its original value. This result indicates that in the preparation of a phenol from a diazonium salt (for which the temperature-coefficient is above 3.5), a high temperature will be advisable, whilst a lower temperature should prove more satisfactory for the formation of an aryl haloid.

It is suggested that the decomposition of the diazonium haloids may to some extent follow the course:



analogous to the well-known explanation of phenol formation, for the investigation of which it will be necessary to investigate the velocity of decomposition with various concentrations of acid in the absence of the disturbing effect of cuprous chloride.

D. F. T.

**The Nature of the Free Amino-groups in Proteins.**  
DONALD D. VAN SLYKE and FREDERICK J. BIRCHARD (*J. Biol. Chem.*, 1914, 16, 539—547).—In various native proteins (hæmoglobin, caseinogen, gelatin, edestin, gliadin, etc.), the amount of free amino-nitrogen is equal to one-half the lysine nitrogen; in gliadin there is a difference of 0.7%. The period required for complete reaction of the

proteins with nitrous acids (thirty minutes) is longer than that required by  $\alpha$ -amino-acids (three to four minutes), but corresponds with that found for lysine with an  $\alpha$ -amino-group free. The conclusion is drawn that the same group is free in the protein molecule; and this group practically represents the entire amount of free  $\text{NH}_2$  determinable in native proteins by this method. All the others are condensed into peptide linkings. With the primary proteoses the relations are different, the free  $\text{NH}_2$  exceeding half the lysine nitrogen by 3 to 5%.

W. D. H.

**The Colloidal State of the Mixed Protein and Gold Sols.** FRIEDRICH JACOBS (*Biochem. Zeitsch.*, 1913, 58, 343—351).—The effect of the addition of gold sols to protein solutions was investigated by measurement of the changes in the viscosity and osmotic pressure of the solutions. Under the conditions of the experiments, this addition caused no appreciable change in the viscosity. It produced, however, a lowering of the osmotic pressure, which was 7.4% in the case of albumin and 3.9% in that of hæmoglobin. In the case of globulin, no change could be detected, owing to the small absolute pressure.

S. B. S.

**The "Gold Numbers" of the Proteins of the Blood.** W. HEUBNER and FR. JACOBS (*Biochem. Zeitsch.*, 1913, 58, 352—361).—The "gold numbers" of various fractions of albumin, globulin, and hæmoglobin were determined. The variations in different preparations of the same substance were, however, somewhat large. The "gold numbers" cannot be used, therefore, for the identification of any given blood-protein.

S. B. S.

**Some Protein Derivatives.** KARL LANDSTEINER (*Biochem. Zeitsch.*, 1913, 58, 362—364).—The products obtained from proteins of horse-serum, precipitated therefrom by alcohols, by treatment with acetic anhydride, with alcohol in the presence of hydrochloric and sulphuric acids, and with diazomethane are described. The first and third of these products, when tested by the complement-deviation method, were found to have lost their species specificity.

S. B. S.

**The Clotting of Caseinogen Solutions.** SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1913, 7, 568—575).—Casein prepared by the use of pepsin (or rennin) differs from metacaseinogen, a product obtained by the action of water at 37° on caseinogen, in that it cannot be converted by solution in alkali hydroxide and reprecipitation into a more soluble product which dissolves in calcium hydroxide to yield clottable solutions. Pancreatin clots caseinogen only in the presence of soluble calcium salts; the casein produced has only half the solubility in half-saturated lime water of the casein prepared by pepsin. Caseins are regarded as combinations of the protein and enzyme. The action of the enzymes is not an ordinary proteoclastic one; the same view has also been expressed by van Slyke and Bosworth. "Natural caseinogen" is probably not a calcium salt.

W. D. H.

**The Hexone Bases of Caseinogen.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1914, 16, 531—538).—The following figures were obtained by Kossel's and by the author's methods :

	Kossel's method.	Nitrogen distribu- tion method.
Histidine .....	4.1—4.5	6.2
Arginine.....	7.5—7.8	7.4
Lysine.....	8.7—9.3	10.3

The loss of histidine in Kossel's method is ascribed to adsorption by barium phosphotungstate. The results with arginine are practically the same in both methods. The Kossel-Patton method as modified by Osborne, Leavenworth, and Brautlecht gives more consistent results for histidine.

W. D. H.

**Ovo-mucoid and Metallic Hydroxides.** J. NEUMANN (*Zeitsch. physiol. Chem.*, 1914, 89, 149—150).—Ovo-mucoid can be completely precipitated by zinc hydroxide in the presence of potassium hydroxide or sodium carbonate. This is attributed to the formation of a hydrate; other metallic hydroxides act in the same way, and there is in the quantity used an inverse proportion between it and the molecular weight of the metallic hydroxide. Primary proteins and proteoses act in the same way, but not peptone.

W. D. H.

**Enzyme Action, Facts and Theory.** HENDRIK PIETER BARENDRECHT (*Biochem. J.*, 1913, 7, 549—561).—A criticism of some of the recent researches on the kinetics of enzyme action. The radiation theory of enzyme action (Barendrecht, A., 1904, ii, 551) is extended. Enzyme action spreads like radiation from a centre. The radiation may be absorbed by the substrate, by the products of action, or by any other foreign substance. The enzyme particle extends its catalytic action in a sphere as regards both hydrolysis and synthesis.

A new isomeride of dextrose, enzyme made, is postulated, the transformation of which to stable dextrose is a balanced action.

E. F. A.

**The Auto-catalysis of Trypsinogen.** H. M. VERNON (*J. Physiol.*, 1913, 47, 325—338).—When once trypsinogen is activated, that is, converted into trypsin by enterokinase, the view is taken that further activation is mainly due to trypsin itself (auto-catalysis), or rather to a variety of trypsin called "unstable trypsin."

W. D. H.

**Behaviour of Diastase in the Presence of a Specific Precipitate.** AGNES ELLEN PORTER (*Biochem. J.*, 1914, 7, 599—603).—The action of diastase is accelerated by the presence of serum. In the presence of antigen (dilute egg-white solutions) the enzyme is more active with normal rabbit serum than when rabbit serum immunised against egg-white is used: hence the immune serum exercises the greater absorption. A similar difference is observed when horse-serum is used as the antigen.

Taka-diastase displayed no tendency to become absorbed by a specific precipitate. Serum from which the globulins had been precipitated by saturation with carbon dioxide and removed after centrifuging, retained most of the original enzyme activity.

E. F. A.

**Hydrolysis of Glycogen by Diastatic Enzymes. II. Influence of Salts on the Rate of Hydrolysis.** ROLAND VICTOR NORRIS (*Biochem. J.*, 1913, 7, 622—629. Compare A., 1913, i, 308).—A dialysed extract of pig's pancreas has practically no hydrolysing action when added to a dialysed glycogen solution. The addition of small quantities of neutral salts restores the activity of the enzyme. The most effective salts are those of the halogen acids, the activity diminishing in the order: chloride, bromide, iodide. Potassium, sodium, and also calcium, barium and magnesium chlorides produce quantitatively the same acceleration. Nitrates have a slight accelerating action, but sulphates are almost without action in restoring activity to the dialysed enzyme. They have no depressing action neither do they hinder the acceleration produced by sodium chloride.

The concentration of salt required to produce a maximum degree of hydrolysis rises with increasing enzyme concentration, but appears to be independent of the glycogen concentration. The anion is much more concerned in the reaction than the cation, and the action of the salts is chiefly confined to the enzyme. E. F. A.

**The Preparation of Protein-free Emulsin.** KOHSHI OHTA (*Biochem. Zeitsch.*, 1913, 58, 329—338).—If the commercial preparation of emulsin is digested with one-tenth part of its weight of pancreatin in 100 times its weight of water, rendered slightly alkaline with ammonia, a considerable amount of protein passes into solution. If the digest is dialysed, concentrated, and precipitated with alcohol, a product is produced which is somewhat more active than the original emulsin, and which is quite free from proteins. The substance thus obtained contains calcium, magnesium and phosphorus, and yields a reducing substance on hydrolysis with acids. Whilst the protein-free emulsin hydrolyses amygdalin and salicin, it is free from other ferments which are present in the crude product. S. B. S.

**The Optimum Temperature of Salicin Hydrolysis by Enzyme Action is Independent of the Concentration of Substrate and Enzyme.** ARTHUR COMPTON (*Proc. Roy. Soc.*, 1913, B, 87, 245—254).—The temperature of the greatest activity of sweet-almond emulsin acting on salicin is determined under different conditions according as the concentration of the substrate and that of the enzyme are varied separately or together. The optimum is shown to be constant at about 34°. E. F. A.

**The Reduction Ferments. V. The Co-ferment of Perhydridase. Formation of Aldehydes from Amino-acids.** A. BACH (*Biochem. Zeitsch.*, 1913, 58, 205—212).—It has been shown that erepton (a commercial digestion product of protein) acts as a co-ferment to perhydridase. It is now found that this preparation yields aldehyde when its solution is submitted to distillation. The aldehyde appears entirely in the first third of the distillate. If the residue is kept for twenty-four hours and again distilled, a quantity of aldehyde equal to that given in the first distillation is obtained. If the distillation is now continued in a current of air, aldehyde is again produced, each fraction of the distillate containing approximately

the same amount of aldehyde. Strecker's reaction will explain the formation of aldehyde from erepton, which can be imitated very nearly when aniline is distilled with *p*-benzoquinone. The oxidation of the amino-acid is effected by the water, and the hydrogen thus set free reduces the "acceptor." In a current of air the latter is again oxidised. The action of erepton as a co-ferment to perhydri-dase can therefore be explained by the fact that under certain conditions it can give rise to a simple aldehyde, which is the true co-ferment. Perhydri-dase is a true aldehydase. S. B. S.

**The Conditions of Action of Rennin.** L. MICHAELIS and A. MENDELSSOHN (*Biochem. Zeitsch.*, 1913, 58, 315—328).—The optimal precipitation point of caseinogen by acid from either pure solution or milk lies at  $[H^+] = 2.5 \times 10^{-5}$ . In presence of lime it is shifted in the acid direction, and is then less distinct at about  $[H^+] = 3 \times 10^{-4}$ . The optimal coagulation point by rennin in the presence of lime lies between  $[H^+] = 4 \times 10^{-7}$  and  $1 \times 10^{-6}$ , but cannot be determined with greater accuracy. The points  $[H^+] = 3 \times 10^{-6}$  and  $[H^+] = 1 \times 10^{-7}$  are certainly outside the region of optimal activity. Between the optimal point of acid precipitation and of rennin action there exists a zone which lies outside the optimal conditions for both these actions. This indicates that the rennin action and the acid precipitation are distinct actions, a conclusion which is confirmed by the fact that the calcium ion action in rennin clotting cannot be replaced by increased hydrogen-ion concentration. S. B. S.

**Preparation of Organic Arsenic Compounds.** HEINRICH BART (D.R.-P. 267082).—3-Carbethoxyamino-4-hydroxyphenylarsine (annexed formula), prepared by the electrolytic reduction of the corresponding arsenic acid, is a colourless, crystalline powder, m. p. 155—160°; on treatment with sulphurous acid and subsequent hydrolysis, it furnishes a base which is useful for the preparation of therapeutically active compounds. J. C. C.

**Preparation of Organic Arsenic Compounds.** HEINRICH BART (D.R.-P. 268172).—3-Carbethoxyamino-4-hydroxyphenylarsinic acid is prepared by adding a solution of diazotised 5-amino-2-hydroxyphenylurethane (m. p. 130°) to a solution of sodium arsenite and sodium hydroxide to which copper paste has been added. Sodium *p*-hydroxyphenylarsinate is similarly obtained from *p*-aminophenol. J. C. C.

**Preparation of Aromatic Stibino-compounds, Aromatic Stibine Oxides, and their Derivatives.** CHEMISCHE FABRIK VON HEYDEN, AKT.-GES. (D.R.-P. 268451).—Aromatic stibino-compounds and stibine oxides are prepared by reducing the corresponding mono-arylstibinic acids. Stibinobenzene,  $C_6H_5 \cdot Sb \cdot Sb \cdot C_6H_5$ , is obtained by reducing phenylstibinic acid with sodium hyposulphite in sodium hydroxide solution; *m*-aminophenylstibine oxide,  $NH_2 \cdot C_6H_4 \cdot SbO$ , by reducing *m*-nitrophenylstibinic acid with stannous chloride (the intermediate compound, *m*-aminophenylstibine chloride hydrochloride,

$\text{HCl} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SbCl}_2$ , has m. p.  $215^\circ$ ); *di-m-aminostibinobenzene* from the intermediate compound just mentioned, and sodium hyposulphite, or hypophosphite, and *mm'-diamino - pp' - dihydroxystibinobenzene* from *m-nitro-p-hydroxyphenylstibinic acid* and sodium hyposulphite.

J. C. C.

**Preparation of Secondary Aromatic Stibine Oxides and their Derivatives.** CHEMISCHE FABRIK VON HEYDEN, AKT.-GES. (D.R.-P. 269206).—Secondary aromatic stibine oxides are prepared by reducing the chlorides of the corresponding stibinic acids with sulphur dioxide in methyl-alcoholic solution. *m-Aminodiphenylstibine oxide*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SbPh} \cdot \text{O} \cdot \text{SbPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , is a faintly-coloured powder which sinters at  $70^\circ$ .

J. C. C.

**Preparation of Aromatic Nitrohydroxystibinic Acids.** CHEMISCHE FABRIK VON F. HEYDEN, AKT.-GES. (D.R.-P. 262236. Compare A., 1913, i, 1122).—Nitrohalogenarylstibinic acids are treated with alkali hydroxides and furnish nitrohydroxystibinic acids. *p* Chlorophenylstibinic acid, prepared from diazotised *p*-chloroaniline and antimony oxide, yields, on nitration, *4-chloro-3-nitrophenylstibinic acid*, the aqueous solution of which, with hydrochloric acid, gives the *chloride*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SbOCl}_2$ . On warming the acid with potassium hydroxide solution, *potassium 3-nitro-4-hydroxyphenyl-1-stibinate* is produced as a scarlet, crystalline powder, from which the yellow *3-nitro-4-hydroxyphenyl-1-stibinic acid* is obtained on acidification (compare *loc. cit.*).

J. C. C.

**Preparation of Aromatic Stibinic Acids.** CHEMISCHE FABRIK VON HEYDEN, AKT.-GES. (D.R.-P. 269205. Compare A., 1913, i, 416).—Secondary and tertiary stibinic acids are prepared by treating an aromatic diazonium salt with a mono- or di-aryl substituted antimony oxide in the presence of alkali hydroxide. The interaction of benzenediazonium chloride and *m*-aminophenylstibine oxide furnishes *m-aminodiphenylstibinic acid*, a faintly-coloured powder. *Chloro-m-phenylenestibinic acid*, a brown powder, is obtained by decomposing diazotised *p*-chloro-*m*-aminophenylstibine chloride with cold sodium hydroxide, and by a similar method, *phenyl-m-phenylenestibinic acid*,  $\text{C}_6\text{H}_4 \cdot \text{SbPh}(\text{OH})_2$ , a brown powder, is prepared from *m*-aminodiphenylstibine oxide.

J. C. C.



### Physiological Chemistry.

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**The Removal of Diffusible Substances from the Circulating Blood by Dialysis.** JOHN J. ABEL, LEONARD G. ROWNTREE, and B. B. TURNER (*J. Pharmacol. expt. Ther.*, 1914, **5**, 275—316).—The artery of an animal (previously treated with hirudin) is connected to an apparatus consisting of tubes made of cellodin, outside of which

is Ringer's solution; the blood thus subjected to dialysis is returned to a vein of the animal. The blood is thus in part freed from diffusible substances, and the operation does no harm to the animal. Quantitative results with salicylic acid show that the rate of removal of this from the blood compares not unfavourably with the kidney. The method is regarded as one of great promise, even from the therapeutic point of view.

W. D. H.

**"Sucre Virtuel" and Blood Glycolysis.** R. LÉPINE (*J. Biol. Chem.*, 1914, 16, 559—561).—Polemical against Macleod (A., 1913, i, 1258), who is stated to have insufficiently or incorrectly quoted the author's writings. The main point is that after the blood is removed, an increase of sugar in it may occur at 58° before glycolysis sets in.

W. D. H.

**The Sugar of the Blood Plasma.** H. BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1914, 158, 61—64).—The authors have determined the amounts of free and combined sugar in the plasmas from venous and arterial blood drawn simultaneously from horses and dogs, and from arterial blood from chicken. Except in two cases, the animals were bled without an anæsthetic, and it was found that the venous plasma was richer in combined sugar than the corresponding arterial plasma. An examination of the nature of the reducing sugar obtained by hydrolysis of the serum points to it being dextrose. Possibly a little glucosamine is present.

W. G.

**A New Vaso-constrictor Substance in the Blood, and Adrenal Cortex.** CARL VOEGTLIN and DAVID I. MACHT (*J. Amer. Med. Assoc.*, 1913, 61, 2136—2138).—From the blood of men and other animals a crystalline substance was isolated, which had a powerful and lasting vaso-constrictor effect. The blood or serum was dried, and extracted with chloroform; on evaporating the extract, the residue was extracted with methyl alcohol; on evaporating off the alcohol, the substance in question was obtained. It is probably related to cholesterol. The same material was also obtained from the adrenal cortex. It has a digitalis-like action on the heart.

W. D. H.

**Fibrinogen. I. Its Origin and Destruction in the Body.** G. H. WHIPPLE (*Amer. J. Physiol.*, 1914, 33, 50—69).—The amount of fibrinogen in dog's blood varies greatly, but is not influenced by feeding or fasting; the variations in human blood are smaller. The amount of fibrinogen rises in pneumonia and septicæmia, and it falls even to zero in acute liver injury; it is usually low in most (but not all) cachetic conditions. It has no relationship to activity or disease of the bone marrow. If the circulation of the blood is confined to head and thorax by tying the aorta, the fibrinogen rapidly disappears, as it is used by the tissues and the source of supply is cut off. If the liver is removed from the circulation, the fibrinogen does not fall appreciably, some other organ (the

intestine) continuing the supply. In chloroform poisoning of the liver, the fibrinogen drops rapidly; probably the injured liver cells effect a drain on the blood fibrinogen. No enzyme able to destroy fibrinogen could be isolated from them. W. D. H.

**Fibrinogen. II. Association of Liver and Intestine in Regeneration of Fibrinogen.** E. W. GOODPASTURE (*Amer. J. Physiol.*, 1914, 33, 70—85).—In young dogs, regeneration of fibrinogen after the blood has been defibrinated is rapid, occurring in about half-an-hour. Ligation of the hepatic artery and spleen pedicle causes a slight delay, and of the intestines, a marked delay in regeneration. If the intestines are entirely removed, fibrinogen returns to the normal within eight hours. Chloroform anaesthesia also causes great delay. The conclusion is drawn that the production of fibrinogen is the result of the combined activity of the liver and intestine. W. D. H.

**The Influence of Phosphatides on Blood Coagulation.** C. A. PEKELHARING (*Zeitsch. physiol. Chem.*, 1914, 89, 22—38).—Some recent workers have stated that phosphatides hasten blood-clotting, and have suggested that thrombokinase is a phosphatide. The present experiments with lecithin and blood-plasma, or solutions of fibrinogen, show that this phosphatide does not hasten the process, or in cases where the clotting time is shortened the result can be explained in other ways. W. D. H.

**Distribution, Inhibition, and Acceleration in Hæmolysis.** SVANTE ARRHENIUS and FRAN BUBANOVIĆ (*Medd. K. Vet. Nobelinstitut.*, 1913, 2, No. 32, 1—22).—Observations have been made with reference to the influence of various salts on the hæmolytic action of different substances on red blood corpuscles. From a comparison of the hæmolytic effects produced by the alkaline earth-metal chlorides, it is found that the activity increases with increasing atomic weight. The hæmolytic action of benzene is increased by calcium chloride, whilst that of chloroform is diminished when hypotonic solutions are employed in the comparison. Potassium oxalate reduces the activity of chloroform and ammonium chloride in hypotonic solution, but has no appreciable influence on the activity of saponin and of acetone in isotonic solution. Sodium fluoride is also without effect on the action of saponin in isotonic solution.

Other observations refer to the hæmolytic action of various organic substances, and from these it appears that the hæmolysis is inhibited by weak hæmolysts if the action takes place in hypotonic solution.

The distribution of the hæmolytic substances methyl, ethyl, and *isoamyl* alcohol, ethyl ether, and acetone between the blood corpuscles and the surrounding solution has been examined, and the results show that the ratio of distribution is about 3 for methyl alcohol and acetone, 3·3 for ethyl alcohol and ethyl ether, and 5·5 for *isoamyl* alcohol. The absorption capacity of the blood corpuscles for these weak hæmolysts is therefore very much smaller

than for the strong hæmolysts, for which the distribution ratio is of the order 100—1000. H. M. D.

**The Hæmolytic Action of Mixtures of Cyclamin and Cholesterol.** HERMANN LUMMERZHEIM (*Meld. K. Vet. Nobelinstitut.*, 1913, 2, No. 28, 1—21).—From observations on the hæmolytic action of mixtures of cyclamin and cholesterol, it would appear that these substances combine to form a dissociating complex compound. For a given quantity of cyclamin, the hæmolytic effect decreases as the amount of cholesterol present increases.

Consistent values can only be obtained when the observations are made with one and the same solution of blood corpuscles. The divergences are attributed to the presence of serum, which reduces the hæmolytic effect of the cyclamin. H. M. D.

**The Secretion of Gastric Juice in the Cat.** A. J. CARLSON, J. S. ORR, and W. F. BRINKMAN (*Amer. J. Physiol.*, 1914, 33, 86—94).—The experiments on cats with a Pavlov stomach pouch showed that the "appetite secretion" is practically identical with that in the dog. The drinking of water if the animals are thirsty causes secretion of gastric juice; this secretion is only partly "psychic." W. D. H.

**The Ferments of the Pancreas. III. The Properties of Trypsin, Trypsinogen, and Enterokinase.** JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1913, 47, 339—360).—The effects of destructive agents on trypsin, trypsinogen, and enterokinase show great variations. The only effective agents for preserving trypsin at 38° are salts of the alkaline earths, especially calcium. In alkaline solutions (N0·16-sodium carbonate) trypsin is destroyed within forty-five minutes at 50° and within five minutes at 60°. In acid solution (N0·025-hydrochloric acid) destruction is much slower, and some remains undestroyed even after boiling for five minutes. Trypsinogen keeps indefinitely in N0·16-sodium carbonate at room temperature, but is destroyed in five minutes at 65°. Hydrochloric acid (N0·25) has no effect on it at 40°, and even at 100°, for five minutes, 30% of it is undestroyed. In the presence of neutral salts the temperature of destruction varies. The most marked property of enterokinase is its immediate destruction in the presence of free acid (N0·01-hydrochloric acid) at 16°. In water or N0·5-sodium chloride solution, five minutes' heating at 65° destroys it; the same strength of calcium chloride raises this temperature to 75°. Albumin, peptone, and amino-acids protect trypsin from heat destruction at 50° in varying degrees. The effect of amino-acids is small. The duration of protection is related to the length of time taken by the trypsin to digest the added protein.

Serum contains anti-trypsin and anti-enterokinase, but no anti-trypsinogen. The trypsin-antitrypsin compound cannot be broken up so as to liberate the trypsin. Enterokinase occurs in the greatest quantity in the mucous membrane of the first 2/7 of the small

intestine, and especially in the superficial layers. There is evidence that it is not formed by Brunner's glands. It is found in small amounts in almost every tissue of the body.

The general view taken of the action of the various enzymes on one another is the following: Enterokinase and trypsin are destroyed by the hydrochloric acid of the gastric juice, but trypsinogen is not acted on. Trypsinogen, however, is destroyed by pepsin and hydrochloric acid. Trypsin has no effect on enterokinase or trypsinogen. Enterokinase has no effect on trypsin, but activates trypsinogen. Pepsin is destroyed by the alkali of pancreatic juice.

W. D. H.

#### The Adaptation of Entero-amylase to Chemical Stimulation.

L. J. TE GROEN (*Zeitsch. physiol. Chem.*, 1914, **89**, 91—100).—Intestinal juice collected from a Vella's fistula is amylolytic, even when the secretion is excited by a non-specific substance such as sodium cholate. In the omega double fistula of Lombroso, there is more such action in the oral than in the aboral half. On regular diets, the amount of amylase is constant, but stimulation of the intestinal mucous membrane with starch solution increases the amount of amylase formed.

W. D. H.

**Fasting Studies. XII. Ammonia, Phosphate, Chloride, and Acid Excretion of a Fasting Man.** D. W. WILSON and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, **36**, 137—146).—An experiment is described which was undertaken with the object of ascertaining the relation between the ammonia, phosphate, chloride, and acid excreted in the urine during a seven-day fast, and during a subsequent low-feeding period of four days and a high-feeding period of five days. During a preliminary period of four days, the subject was given a uniform diet containing 21.86 grams of nitrogen per day. The daily routine work of the subject (a laboratory instructor) was continued during the fast.

In the course of the fast, the ammonia excreted rose rapidly, reaching a maximum on the sixth day; the acidity increased to a maximum on the third day and then gradually diminished; the phosphate increased until the third day and then decreased, the relative decrease being closely parallel to that of the acidity; the amount of chloride excreted decreased rapidly for three days and afterwards more slowly.

During the low-feeding period, the subject received a diet containing 5.23 grams of nitrogen per day. The ammonia nitrogen was higher during the first day of this period than on the last day of the fast, but subsequently decreased, although the minimum value was somewhat higher than any value observed in the preliminary period. The acidity fell immediately to a value lower than any noted in the preliminary period and continued to decrease until the fourth day. The phosphate diminished slightly on the first day, and considerably on the second, and subsequently increased to about half the value found in the preliminary period. The chloride decreased greatly on the first day, reached a minimum

on the second day, and remained at this value for the remainder of the period.

In the final period, the amount of food given was increased to that of the preliminary period. The ammonia continued to decrease for the first two days, increased greatly on the third, and decreased on the fourth and fifth days to a value rather above that of the preliminary period. The acidity increased on the first day to a value somewhat below the normal and did not vary greatly subsequently. The amount of phosphate increased rapidly, was above the normal on the second and third days, but for the remainder of the period was a little below the average of the preliminary period. The chloride increased during the first three days and all the values were higher than those of the preliminary period.

These results are discussed in their relation to the metabolic processes. E. G.

**Fasting Studies. XIII. Output of Fæcal Bacteria as Influenced by Fasting and by Low and High Protein Intake.** N. R. BLATHERWICK and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, 36, 147—152).—In the preceding paper, Wilson and Hawk have given an account of the study of the ammonia, phosphate, chloride, and acid excretion of a subject undergoing a seven-day fast. During the course of the same experiment, observations were made of the amount of fæcal bacteria excreted. It was found that the daily excretion of bacterial nitrogen was reduced from 1.571 grams to 0.101 gram, whilst the actual weight of the excreted bacterial substance fell from 14.336 grams to 0.920 gram per day. The proportion of the fæcal nitrogen present as bacterial nitrogen was diminished from 55.82% to 32.29% as a result of the fast. The percentage of dry bacteria in the fæces was slightly increased.

During the period of the low protein diet, the amounts of bacterial nitrogen and of bacterial substance excreted were approximately the same as during the fast, but, on the resumption of a high protein diet, the amounts immediately underwent a considerable increase. The proportion of the fæcal nitrogen consisting of bacterial nitrogen was about the same in both the high and low protein feeding periods. No definite relation could be traced between the excretion of fæcal bacteria and that of urinary indican. The ingestion of 5.23 grams of nitrogen after the fast was followed by an excretion of fæcal bacteria which was only one-fourteenth as great as that produced before the fast when four times as much nitrogen was ingested. E. G.

**The Influence of Drinking on Digestion.** FRANZ GRÖBBELS (*Zeitsch. physiol. Chem.*, 1914, 89, 1—21).—The observations recorded relate to the rate of outflow of the contents of the stomach in dogs. This increases the more fluid is administered; pure water leaves the stomach most easily. Alcoholic drinks and coffee slow the output in comparison. Thirst, and the taking of fluid to allay it, delays the digestion of a meal. W. D. H.

**Water Drinking. XV. The Output of Fæcal Bacteria as Influenced by the Drinking of Distilled Water at Meal Times.** N. R. BLATHERWICK and P. B. HAWK (*Biochem. Bull.*, 1913, 3, 28—40).—Two subjects were fed for a month on a uniform diet; in the fæcal nitrogen, the bacterial nitrogen constituted 57·5%; the proportion of dry bacteria in dry fæces was 30%, and the weight of dry bacteria 6·2 grams a day. When 500 c.c. of distilled water were added to the usual water ingestion (100 c.c.) at each meal, there was a decrease in bacterial nitrogen; when the amount was increased to 850 c.c. per meal, this decrease was more pronounced. The addition of water leads to better utilisation of proteins, and better digestion and absorption; this beneficial result continued during the periods after the water ingestion. Copious water drinking lessens the urinary indican. W. D. H.

**Studies in Water Drinking. XVI. Influence of Distilled Water Drinking with Meals on Fat and Carbohydrate Utilisation.** N. R. BLATHERWICK and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, 36, 152—157).—Mattill and Hawk (A., 1912, ii, 64) observed a slight improvement in the utilisation of fat when large volumes of freshly-prepared, softened water were taken with meals. In an experiment now described, two young men were given a uniform diet and the effect of the copious ingestion of distilled water was studied. It was found that the utilisation of fat and carbohydrate was not appreciably affected. E. G.

**Studies in Water Drinking. XVII. Ammonia Output as an Index of the Stimulation of Gastric Secretion following Water Ingestion.** F. WILLS and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, 36, 158—165).—A study of the effect on two men of drinking water with meals showed that an increase took place in the amount of ammonia excreted which was directly proportional to the extra volume of water ingested. Evidence is adduced which indicates that this increase was directly due to the stimulation of gastric secretion by the water. It is suggested that the uniform relation between the water ingested and the ammonia excreted may be regarded as indicating an attempt on the part of the gastric cells to maintain a uniform acid concentration. The increased amount of ammonia excreted per 100 c.c. of water ingested was a little higher when moderate quantities of water were drunk than when very large volumes were taken. The increase in the output of ammonia by one subject was 100% greater than in the case of the other, in spite of the fact that the ingestion of water was increased by the same amount in each instance. During the period of the ingestion of large volumes of water, reduced indican values were observed, which indicates that the increase in the ammonia excretion did not arise from intestinal putrefaction. E. G.

**Intermediary Purine Metabolism. I. The Purine Store in the Liver and its Relationship to Uric Acid Excretion.** HANS ROSENBERG (*Chem. Zentr.*, 1913, ii, 1691—1692; from *Zeitsch. expt. Path. Ther.*, 1913, 14, 245—254).—Certain purine derivatives can be

removed from the surviving liver of a dog by perfusion, even when the animal has been kept on a purine-free diet. The amount can be altered (*a*) before the perfusion (with blood) by the alteration of the diet, the amount being diminished by a purine-free diet and increased by a purine-rich diet; (*b*) during the perfusion by drugs. Atophan and adrenaline increase the amount. The author draws the conclusion that the liver can store purine substances in the same manner as it does glycogen and fats. When the amount reaches a certain limit, the organ becomes saturated and the purine substances enter the circulation. This fact will explain the variations in the uric acid excretion with purine-free and purine-rich diets. In gouty subjects, the saturation point is raised, owing to the slow action of enzymes. Atophan can influence these pathological (and also the physiological) conditions by making the flow of purine substances from the liver continuous. S. B. S.

**Intermediary Purine Metabolism. II. Uric Acid Piqure.** EDGAR MICHAËLIS (*Chem. Zentr.*, 1913, ii, 1692; from *Zeitsch. exp. Path. Ther.*, 1913, 14, 255—261).—The Claude Bernard *piqure* produces in rabbits a transient, but very marked, increase in the allantoin excretion, and a change in that of the other nitrogenous substances. The author believes that the sugar centre also controls the purine metabolism of the liver and has a marked influence on the general metabolism. S. B. S.

**The Influence of Diet on the Formation of Indole in the Organism.** D. M. BERTRAND (*Ann. Inst. Pasteur*, 1913, 27, 76—82).—It was found that rabbits, when fed with carrots, excreted no indole derivatives in the urine, whereas those fed on potatoes contained these substances. Detailed examination of the bacterial flora of the intestine failed to reveal any marked difference between the animals fed on different diets. It is known that *B. coli*, in the presence of a medium from which indole can be produced, do not give rise to this substance when sugar is added. They attack, by preference, the latter, producing acidity, and do not degrade the proteins to indoles. The difference of indole production, when the animals are fed on carrots and potatoes, may be due, therefore, to the differences in the degradation of the carbohydrates, and the presence or absence of acids in the intestine. S. B. S.

**Retention of Nitrogen after Feeding on Ammonium Salts and Urea.** E. GRAFE (*Zeitsch. physiol. Chem.*, 1913, 88, 389—424).—A discussion of the way in which the nitrogen is retained in the body after feeding on ammonium salts and urea. Further experiments on pigs are described which lead to the conclusion that the form in which the nitrogen is retained must be in combination as protein or protein-like substances. W. D. H.

**Fat Absorption. III. Changes in Fat During Absorption.** W. R. BLOOR (*J. Biol. Chem.*, 1914, 16, 517—529).—During absorption the lowering of melting point of fats of high melting point



points to an addition of an unsaturated (probably oleic) acid. An elevation of the melting point and lowering of iodine value in fats of low melting point points to an addition of saturated fatty acids. In cocoanut oil, which consists mainly of glycerides of saturated fatty acids, there is addition of oleic acid without change in the melting point. In cod liver oil, which contains a large percentage of glycerides of highly unsaturated fatty acids, lowering of the iodine value occurs. The intestine shows a tendency in producing these changes to bring about a chyle fat of uniform nature, presumably the characteristic body fat of the animal. W. D. H.

**The Rate of Absorption of Cholesterol from the Digestive Tract of Rabbits.** EDWIN P. LEHMAN (*J. Biol. Chem.*, 1914, 16, 495—503).—It is possible by giving rabbits small doses of cholesterol by the mouth to demonstrate in the majority of experiments an increase of this substance in the blood in the course of a few hours. W. D. H.

**Fatty Acids of Hen's Eggs.** V. H. MOTTRAM (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, 47, xviii—xix).—The iodine values of the fatty acids from hen's eggs show that in the eggs from any one hen there is great constancy, yet the value differs widely in different hens even of the same stock. In the first week of incubation, whether the eggs are fertile or infertile, the iodine value rises. Here there is a case in which the desaturation of fatty acids occurs independently of the action of the liver. W. D. H.

**The Galactosides of the Brain.** I. OTTO ROSENHEIM (*Biochem. J.*, 1913, 7, 604—610).—A new method for the preparation of the two galactosides of the brain by means of pyridine is described, and evidence is adduced that they exist in the brain in the preformed state. W. D. H.

**The Sugar Consumption in the Surviving Normal and Diabetic Heart.** E. W. H. CRUICKSHANK and S. W. PATTERSON (*J. Physiol.*, 1913, 47, 381—388).—There are wide variations in the amount of dextrose disappearing from the fluid perfusing normal hearts, and in diabetic hearts the glycogen content is inversely proportional to the disappearance of sugar. In one case of a diabetic heart no sugar disappeared, and at the end of the experiment the heart still contained 0.4% of glycogen. In another case, no sugar consumption occurred until the second hour; this is ascribed to a failure in the glycogen store, thus throwing the heart on to the sugar in the circulating fluid. Both in normal and diabetic hearts the heart uses up its local store of glycogen in preference to drawing on the sugar circulating through it. As the local store varies, so variations in the utilisation of the circulating fluid occur. In diabetic hearts, there is no abolition of the power to utilise sugar, but there may be a diminution in this power. W. D. H.

**The Influence of Carbon Dioxide on the Heart in Varying Degrees of Anæsthesia.** E. P. CATHCART and G. H. CLARK (*J. Physiol.*, 1913, **47**, 393—406).—When anæsthesia is deep and carbon dioxide has no effect on the amplitude of the heart beat, there is no rise of blood-pressure, although according to Starling and von Anrep the gas should provoke the secretion of adrenaline. With light anæsthesia when the amplitude of the heart is increased, the rise of blood-pressure occurs. Further work is in progress before generalisations are possible. W. D. H.

**Glycogen and Sugar Formation in the Isolated Livers of Warm-blooded Animals.** HERMANN K. BARRENSCHEEN (*Biochem. Zeitsch.*, 1913, **58**, 277—314).—It is possible under suitable experimental conditions (with the use of the Mendel-Friese perfusion apparatus) to produce glycogen in the surviving livers of rabbits and dogs. This happens when dextrose and lævulose are added to the perfusing blood. Under these conditions glycogen is not produced when lactic acid, glyceric acid, glycerol, and glycol-aldehyde are substituted for the above-mentioned sugars. They give rise, however, to sugar when perfused through the livers of dogs which have been rendered glycogen-free by phloridzin treatment. Pyruvic acid, alanine, and serine do not give rise to sugar in the isolated liver. Livers removed from animals five to thirty-two days after removal of the pancreas are no longer capable of forming glycogen from dextrose or lævulose when added to the perfusion blood (taken from normal animals) even after addition of extract of pancreas to the perfusion fluid. If the pancreas is only partly removed, the glycogen-forming function remains intact. The destruction of the liver function is not due to the effects of operation, and neither laparotomy nor adrenaline poisoning destroys the glycogenic functions. On the other hand, phloridzin poisoning does prevent the liver from forming glycogen, although the sugar-forming function (from lactic acid, glycerol, etc.) remains intact. The destruction of the glycogenic function by phloridzin is not due, therefore, to the fatty infiltration into the liver.

S. B. S.

**The Change of Lævulose into Dextrose in the Artificially Perfused Liver.** S. ISAAC (*Zeitsch. physiol. Chem.*, 1914, **89**, 78—90).—In liver perfusion, lævulose is changed into dextrose with great rapidity. Lævulose may therefore quite well be an intermediate substance in dextrose formation, as Embden and others have suggested. In lævulosuria it is possible that the conversion does not occur. W. D. H.

**Negative Experiments on the Influence of the Pancreas on Acetoacetic Acid Formation in the Liver.** H. D. DAKIN and H. W. DUDLEY (*J. Biol. Chem.*, 1914, **16**, 515—516).—The addition of pancreas extract to blood perfused through dogs' livers had no marked effect on acetoacetic acid formation from butyric acid, homogentisic acid, or tyrosine. The experiments were undertaken

in the hope of clearing up the relationship between acetoacetic acid excretion and extirpation of the pancreas. W. D. H.

**Glyoxalase.** IV. H. D. DAKIN and H. W. DUDLEY (*J. Biol. Chem.*, 1914, **16**, 505—513).—Glyoxalase is present and antiglyoxalase absent in all the glands of the body examined, except the pancreas and the abdominal lymphatic glands; the anti-action of the latter is, however, trifling compared with the pancreas. The antiglyoxalase of the pancreas is a specific function of that organ, and acts mainly by way of an internal secretion.

Contrary to Neuberg's statement, it was found that glyoxal may be converted into glycollic acid by enzyme action. Glyoxalase is not the same as aldehydemutase (Neuberg), for the latter is unaffected by extracts of the pancreas. W. D. H.

**The Iodine Content of the Thyroid and of Some Branchial Cleft Organs.** A. T. CAMERON (*J. Biol. Chem.*, 1914, **16**, 465—473).—Further support is given to the view that iodine is an invariable constituent of thyroid tissue; it is found in the thyroids of pigeon, alligator, frog, and dogfish. Iodine is absent in the ventral branchial body of the frog. In the parathyroids of the dog the iodine is probably due to contamination with thyroid tissue. There is doubtless a differentiation of function between the two organs. W. D. H.

**The Action of Leucocytes and of Kidney Tissue on Amino-acids.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1914, **16**, 555—557).—The authors previously found that leucocytes and kidney tissue produce no deamidation of alanine. The same negative result was found with other amino-acids (glycine, aspartic acid, asparagine, leucine). W. D. H.

**Lactic Acid Formation, Survival Respiration, and Rigor Mortis in Mammalian Muscle.** W. M. FLETCHER (*J. Physiol.*, 1913, **47**, 361—380).—On excision, rabbit's muscle contains but little lactic acid (estimated by the zinc gravimetric method), and this is accounted for by contractions just before or after death, and by the manipulative treatment. A maximum yield is reached after the third hour from excision. The acid production is slower than in pale muscle. The survival output of carbon dioxide at body temperature increases for a short time after excision, and then declines to zero if uninterrupted by evolution of the gas due to bacteria. At room temperature or in red muscles at body temperature, there is no preliminary increase. The yield of carbon dioxide is due to lactic acid displacing the preformed gas from loose combination. There is apparently no independent new formation of carbon dioxide. The post-mortem shortenings of white and red muscles were recorded, but the time relations of the two kinds given by Bierfreund were not confirmed. W. D. H.

**The Origin and Destiny of Cholesterol in the Animal Organism.** XI. The Cholesterol Content of Growing Chickens under Different Diets. J. A. GARDNER and P. E. LANDER (*Proc. Roy. Soc.*, 1914, [*B*], **87**, 229—236).—Batches of chickens were fed on

normal diet, diet freed from cholesterol, and diet with cholesterol added. They were subsequently killed and analysed. The results for the first two weeks of growth show that the cholesterol content depends only on the cholesterol content of the diet, and there is no indication that in the growing animal there is any power to synthesise cholesterol. It has previously been shown that in the egg there is no cholesterol synthesis. W. D. H.

**Cholesterol Contents of the Tissues of Cats under Various Dietetic Conditions, and During Inanition.** JOHN ADDYMAN GARDNER and PERCY EDWARD LANDER (*Biochem. J.*, 1913, 7, 576—587).—The results agree with those obtained by Ellis and Gardner in the rabbit, namely, that cholesterol is a constant constituent of cells, and when these break down, it is utilised in the formation of new cells. The liver breaks down old cells, and their cholesterol passes into the bile; this is re-absorbed, probably as esters, and then utilised in cell construction. Waste is made up from the cholesterol of the food. W. D. H.

**A Fat from the Butterfly.** H. THOMS (*Chem. Zentr.*, 1913, ii, 2052; from *Arb. Pharm. Inst. Univ. Berlin*, 10, 180—181).—The fat was derived from *Myelobia smerintha* Hübn., from which it was obtained in a 22% yield. It is yellowish-white, of similar consistency to butter, and optically inactive. The specimen examined was slightly rancid, and had m. p. 29°; solidifying point, 24°; acid number, 51·8; saponification number, 192·7; iodine number, 53·7; Reichert-Meissl number, 0·74; Polenski number, 0·84; Hehner number, 96·5. The separated fatty acids had m. p. 46°; solidifying point, 42°; saponification number, 194·5, and yielded 56·8% liquid and 33·6% solid acids. The presence of stearic acid and of a liquid acid which yields elaidic acid, m. p. 44—46°, was established. H. W.

**Influence of Cold Storage on the Composition and Nutritive Value of Fish.** CLAYTON S. SMITH (*Biochem. Bull.*, 1913, 3, 54—68).—No change in the chemical composition or nutritive value of fish is noticeable during or after nine months' cold storage.

W. D. H.

**Influence of Prolonged Periods of Cold Storage on the Composition and Nutritive Value of Fish.** WILLIAM A. PERLZWEIG and WILLIAM J. GIES (*Biochem. Bull.*, 1913, 3, 69—71).—After two years' cold storage, the fish undergo no change in chemical composition or nutritive value. This applies to fish which are fresh when placed in storage. W. D. H.

**The Alleged Excretion of Creatine in Carbohydrate Starvation.** GEORGE GRAHAM and E. P. POULTON (*Proc. Roy. Soc.*, 1914, B, 87, 205—220).—In the present experiments on men, a diet free from carbohydrates caused no excretion of creatine. The statement of others that it does so is due to the fact that, under this condition, acetoacetic acid is excreted, and this invalidates the analysis by the

Folin method. The error increases with the amount of acetoacetic acid, and in amounts less than those which may occur in the urine, may rise to more than 50%. The estimation of creatinine is, therefore, too low when acetoacetic acid is present. In the processes involved in the conversion of creatine into creatinine, the acetoacetic acid is removed, and so the estimation of creatine+creatinine is correct. As the creatinine figure is too low, and the creatine+creatinine figure correct, the conclusion is erroneously drawn that creatine has been excreted. It is, therefore, necessary to remove acetoacetic acid before creatinine is estimated, and a method for this purpose is described. Acetone and  $\beta$ -hydroxybutyric acid produce no error.

W. D. H.

**Presence of Tyrosine Crystals in a Urinary Sediment.** P. JUGE (*J. Pharm. chim.*, 1913, [vii], 8, 559—561).—Two specimens of urine from the same patient, one taken immediately after his arrival from Vichy, and the other ten days later, were examined. The first was of dark yellow colour and of normal composition, although there was a slight deficiency of urea, and traces of protein and reducing sugars were present. The slight sediment consisted of uric acid, calcium oxalate, epithelial cells, and very occasional leucocytes and granular hyaline cylinders. The second specimen showed an increase of all soluble constituents, with the exception of urea, which remained constant. The reducing sugar amounted to 1.81 grams per litre (1.99 grams in twenty-four hours), but protein was only present in traces. The sediment was abundant and heavy and consisted of crystals of tyrosine (yellow, silky needles separate or partly or wholly united into spherical aggregates), calcium oxalate, epithelial cells, and very occasional leucocytes. Tyrosine is rarely found in urine, and when it does occur is usually accompanied by leucine. Its occurrence is associated with liver diseases among many other varieties of pathological conditions.

T. A. H.

**Intermediate Reduction Processes in Physiological Break-down.** F. KNOOP and RICHARD OESER (*Zeitsch. physiol. Chem.*, 1914, 89, 141—148).—Unsaturated acids can be converted into saturated acids in the animal body;  $\cdot\text{CO}$  and  $\cdot\text{CH}(\text{OH})\cdot$  groups can be reduced to methylene groups. The presence of carbonyl groups or double unions in the removed part of an acid molecule remote from the carboxyl has no influence; but there appear to be reduction processes which are more easily brought about in the neighbourhood of the carboxyl groups.

W. D. H.

**Theory of Diabetes. II. Glycide and Acetol in the Normal and Phloridzinised Animal.** J. R. GREER, E. J. WITZEMANN, and R. T. WOODYATT (*J. Biol. Chem.*, 1914, 16, 455—464).—Glycide,  $\text{CH}_2 \begin{smallmatrix} | \\ \text{O} \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ , was prepared in pure form and given to dogs; it is very toxic, doses of 0.3 to 0.4 gram per kilo. of body weight causing narcosis and twitchings; larger doses kill. The ring is no doubt opened in the body with difficulty.

Acetol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ , is relatively non-toxic; doses of 2 grams per kilo. do not kill, but even moderate doses cause hæmaturia and hæmoglobinuria. In phloridzinised dogs, given by the mouth or under the skin, it causes no output of extra sugar, and some unchanged acetol may appear in the urine. There is an apparent rise also of acetone substances. The conclusion is drawn that, in the body, it dissociates into acetaldehyde and hydroxymethylene, but it is not an intermediate between substances of the formula  $\text{C}_6\text{H}_{12}\text{O}_6$  and those of the formula  $\text{C}_3\text{H}_6\text{O}_3$ . W. D. H.

**The Lactic Acid of the Muscles in Diabetes Mellitus, and the Glycolytic Power of Muscles.** J. FORSCHBACH (*Biochem. Zeitsch.*, 1913, **58**, 339—342).—In dogs with severe diabetes, twenty days after the extirpation of the pancreas there was found in the muscles a diminution both of lactic acid and of lactacidogen, the substance from which the lactic acid is formed. For the investigation of the latter, Embden's method was employed. S. B. S.

**The Mechanism of Certain Forms of Hyperglycæmia Produced Experimentally in Rabbits.** IVAR BANG (*Biochem. Zeitsch.*, 1913, **58**, 236—256).—In view of the fact demonstrated by the author and others, that psychic excitation of the animal produces hyperglycæmia, it is necessary to repeat various experiments in which excess of sugar in the blood is produced, under conditions which exclude this excitation. The influence of various narcotics on hyperglycæmia was, therefore, investigated, with the object of finding a product which, whilst sufficiently active to exclude psychic excitation, by itself produces no hyperglycæmia. It was found that, by a combination of urethane with ether, complete narcosis could be produced, in which hyperglycæmia was only produced after a long period; this differs, therefore, from the psychic hyperglycæmia, of which the onset is rapid. Under ether-urethane narcosis, neither the operative procedure of exposing the carotid artery, nor the removal of blood produced hyperglycæmia. Venesection, by itself, does not appear, therefore, to cause hyperglycæmia; the results of previous authors, who ascribe hyperglycæmia to this effect, are due to psychic excitation. *Piqûre* produced, in animals narcotised with urethane and ether, only a slight hyperglycæmia, and, in two out of three experiments, no glycosuria. In the absence of ether (urethane narcosis only), the glycosuric effect was marked in both experiments performed. Narcosis also suppresses diuretin hyperglycæmia and glycosuria, which may also, therefore, be ascribed to psychic effect of the pain produced by the injection. The ether-urethane narcosis is a light one. Deep narcosis, on the other hand, appears to intensify various effects. The author gives, in outline, a general theory as to the methods by means of which hyperglycæmia can be produced. S. B. S.

**The Sugar of Pentosuria.** ERNST ZERNER and RUDOLFINE WALTUCH (*Biochem. Zeitsch.*, 1913, **58**, 410—414).—The authors review the recent literature on this question and recapitulate some

of their own results. They draw the conclusion that there are two kinds of pentosuria, namely, those due to the presence of *dl*-arabino-*se*, and those due to a sugar of the *d*-xylose group. S. B. S.

**Disturbances of Carbohydrate Metabolism in Experimental Diphtheria.** FELIX ROSENTHAL (*Arch. expt. Path. Pharm.*, 1914, 75, 99—122).—After diphtheria poisoning in animals, carbohydrate metabolism at first is unaltered; this is followed by a stage of disappearance of the hepatic glycogen without hyperglycemia, then by a stage of diminished glycogen fixation, and finally by paralysis of carbohydrate formation, with rapid disappearance of the blood sugar. The liver changes appear to be secondary to those in the suprarenal bodies. W. D. H.

**Pellagra. I. The Influence of the Milling of Maize on the Chemical Composition and the Nutritive Value of Maize Meal.** CASIMIR FUNK (*J. Physiol.*, 1913, 47, 389—392).—In maize as in rice, the vitamins are chiefly in the outer layers. In different countries the mode of preparation of maize meal varies, and the manifestations of pellagra vary from mild to severe forms. Milling also deprives the grains of much salt, protein, fat, and lipoids. The present mode of milling should be abandoned, and the whole grain used. W. D. H.

**The Secretion of Gastric Juice during Parathyroid Tetany.** ROBERT W. KEETON (*Amer. J. Physiol.*, 1914, 33, 25—49).—After parathyroidectomy in cats, the quantity, acidity, and digestive power of the gastric juice are reduced. During active tetany no relation between the secretion and the symptoms has been traced. When tetany is replaced by depression, the secretion improves; improvement also occurs when calcium salts are injected. W. D. H.

**The Influence of Parathyroid Tetany on the Liver and Pancreas.** O. O. STOLAND (*Amer. J. Physiol.*, 1914, 33, 283—299).—During parathyroid tetany in dogs, no change in sugar tolerance is observed, the blood fibrin is increased, the amino-acids and ammonia of the urine are unchanged, and the secretion of bile and pancreatic juice is lessened; the last condition appears to be secondary to the condition of the digestive tract. There is no other hepatic deficiency. W. D. H.

**The [Physiological] Action of Nitrous Oxide at High Pressures.** JOHANNES BOCK (*Arch. expt. Path. Pharm.*, 1913, 75, 43—52).—The lowest fatal pressure of nitrous oxide for rats is that of 3 atmospheres. The time it takes to kill varies from eight to twenty-two minutes. The cause of death is paralysis of the respiratory centre. W. D. H.

**The Effects of Nitrogen Peroxide on the Constituents of Flour in Relation to the Commercial Practise of Bleaching Flour with that Reagent.** BENJAMIN MOORE and J. T. WILSON (*J. Hygiene*, 1914, 13, 438—466).—Bleaching by nitrogen peroxide is

not a more rapid achievement of a slowly occurring natural process; the natural whitening of flour is due to oxidation of the pigment carotene; bleaching by nitrogen peroxide is due to a formation of additive compounds with the pigment. Nitrogen peroxide alters both fats and proteins by nitrating them; although the changes in the commercial process are small, it cannot be assumed that their continued ingestion over years is immaterial to health. The process of bleaching is condemned on ethical and economic grounds also.

W. D. H.

**Astringent Action of Aluminium Salts.** CARLO BARINETTI (*Chem. Zentr.*, 1913, ii, 1934—1935; from *Arch. Farm. speriment.*, 1913, **16**, 210—240).—Aluminium salts give precipitates with organic colloids (blood serum, white of egg, muscle extract, gelatin, tissue), and precipitation attains a maximum when colloid and aluminium salt are present in a definite proportion. With excess of either reagent, coagulation is a reversible process. If the coagulum remains for several hours in contact with an excess of the aluminium salt, the reaction is no longer reversible. Amounts of aluminium salts which are insufficient to cause coagulation bring about profound changes in the physical condition, which can be followed by determination of viscosity and density; these changes are also those which subsequently lead to precipitation of the colloid. Precipitation is probably not due to the Al-ion, but to hydrolytically formed aluminium hydroxide. The therapeutic action of aluminium salts is generally attributable to the precipitation of colloids, and the usual medicinal solution, containing 2—4% of potassium aluminium sulphate, represents exactly the concentration which is found necessary to yield a precipitate with blood serum.

The same relationships are observed with aluminium sulphate and aluminium chloride, but reaction occurs in a smaller interval of time. Addition of potassium sulphate to potassium aluminium sulphate weakens the reaction of the latter by diminishing the ionisation. Experiments with blood in vitro show that aluminium salts greatly prevent coagulation; at greater concentration, coagulation of blood occurs, which corresponds with the coagulation in the experiments with serum. At extreme concentration of aluminium salts, the coagulum is again dissolved. The increase in the resistance of the red corpuscles, and the lowering of the extensibility of the tissues, which takes place in contact with aluminium salts, are due to the fixation of the latter by the gelatinous cell proteins. The astringent action of aluminium salts is the result of physico-chemical modifications of the intracellular colloids and of the colloids of the histological elements, whereby the resistance of the tissues is increased and the velocity of resorption of toxic products diminished.

Intravenous injection of sodium aluminium sulphate causes non-coagulability of the blood; a direct action on the heart causes paralysis of the latter. The toxicity increases with increasing concentration of the injected solution.

H. W.



**The Influence of Caffeine on the Excretion of Creatine and Creatinine.** WILLIAM SALANT and J. B. RIEGER (*Amer. J. Physiol.* 1914, **33**, 186—203. Compare A., 1913, i, 547).—The effect of caffeine in rabbits and dogs on the excretion of creatine and creatinine is variable, and depends largely on the diet; the difference is attributed to differences in the amount and rate of transformation of glycogen. Stimulation of the nervous system or muscles, per se, does not affect creatine-creatinine metabolism, nor the excretion of nitrogen. The effect of a substance on protein metabolism is not a safe guide for drawing inferences regarding its toxicity. W. D. H.

**The Influence of Dextrose and of Sodium, Potassium, Calcium, and Magnesium Ions on the Excitability, Contractility and Fatigue of Motor Nerves and Skeletal Muscle.** ROBERT BENDA (*Zeitsch. Biol.*, 1913, **63**, 11—77).—The influence of dextrose and sucrose diminishes the fatiguability of the muscle-nerve complex (frog), especially if the muscle is poorly nourished. If, however, the fatigue is intense, as when the sodium ions are diminished, sugar has little or no effect; although treatment with a fluid containing less sodium ions than normal leads to small contractions of the muscle, its excitability rises; the two functions are therefore different. Other salts were investigated, direct and indirect stimulation of the muscle being employed; potassium ions, as a rule, depress excitability and contractility, but numerous exceptions are noted. Experiments with calcium and magnesium ions bring out the difference between muscle and nerve fatigue.

W. D. H.

**Influence of Phytin on the Separation of Nitrogen Compounds in Normal Individuals.** FRANCESCO VENTURI and VLADIMIRO MASSELLA (*Chem. Zentr.*, 1913, ii, 1935; from *Arch. Farm. sperim.*, 1913, **16**, 97—118).—Daily administration of 1·5—2 grams of phytin diminishes the output of carbamide. Uric acid and ammonia elimination remain practically unchanged, whilst extractive nitrogen (creatinine, hippuric acid, xanthine bases) are greatly diminished. At the same time, loss of nitrogen in the faeces is lessened, so that the nitrogen balance in the phytin periods is four to five times as great as in the normal periods. H. W.

**Pyrobromon, a New Organic Bromo-compound.** GIULIO NARDELLI (*Chem. Zentr.*, 1913, ii, 1935; from *Arch. Farm. sperim.*, 1913, **16**, 169—177).—*Pyrobromon*,  $C_{13}H_{18}ON_3Br$ , white needles, m. p.  $190^{\circ}$ , is a bromo-compound of pyrazolone. It has a faintly acid taste. Determinations of rubazonic acid,  $C_{20}H_{17}O_2N_5$ , and of bromine in urine show that the elimination of pyrobromon speedily commences (five minutes after intravenous, twenty minutes after subcutaneous, and thirty-five minutes after oral administration), and is comparatively rapidly complete (after twenty-four hours). The toxic doses are 0·12—0·15 gram by intravenous, 0·50—0·60 gram by subcutaneous, and 1·10—1·20 gram by oral administra-

tion, whilst the lethal doses are 0.20, 0.80, and 1.40 gram respectively. Doses up to 1.0 gram are readily tolerated by man, whilst larger quantities occasion intestinal disturbance; 0.5 gram (subcutaneously) led to a slight reduction in the blood pressure in a rabbit, but a similar effect could not be observed in man, whilst action on the kidneys and respiratory system was not evident. The nervous system of healthy persons is not affected, but a therapeutic action is noticed with epileptic subjects. The temperature is lowered in fever.

H. W.

**Lipoproteins. The Action of Lipoproteins in vivo.** G. IZAR and C. PATANÉ (*Biochem. Zeitsch.*, 1913, 58, 195—201).—Emulsions of compounds of various proteins with palmitic, stearic, and other fatty acids, when injected into sparrows and rabbits in sufficient doses, cause the death of the animals. The symptoms are similar to those produced by the injection of aqueous emulsions, heated for one hour at 50°, of methyl-alcoholic extracts of testes, pancreas, and thyroid. Exophthalmos is not, however, produced. The symptoms produced by sub-toxic doses (paresis, convulsions, etc.) are only very transient. Injection of small doses of the lipoproteins causes a diminution of the complement of the blood. Sub-lethal doses of the lipoproteins do not render the animals resistant to immediate subsequent lethal doses, and in this respect they differ from certain organic extracts. The toxicity of the latter is increased on heating the aqueous emulsions to 50° for one hour. This phenomenon is observed only to a very small extent with the lipoprotein emulsions.

S. B. S.

**The Action of Strophanthin on the Oxygen Consumption of the Frog's Heart.** GERTRUD GOTTSCHALK (*Arch. expt. Path. Pharm.*, 1913, 75, 33—42).—The principal action of strophanthin on the oxygen consumption of the frog's heart is never stimulating; the lowering action is probably indirectly the result of inhibition of the mechanical function.

W. D. H.

**Copper Balance on Seven Experimental Subjects to Determine the Effect of Eating Coppered Vegetables.** CARL L. A. SCHMIDT (*J. Amer. Chem. Soc.*, 1914, 36, 132—136).—An account is given of an experiment in which seven men were put on a constant diet, which included vegetables coloured with copper. The amount of copper excreted was estimated in each case. After making the necessary allowance for copper normally ingested in foods, the results indicated clearly that part of the copper had been retained in the system. It is probable that copper so retained would be but slowly eliminated.

E. G.

**The Action of Poisons which Affect Body-temperature on Animals which have no Heat Regulation. I. Sodium Salicylate, Antipyrin. Quinine, Morphine.** R. ISENSCHMID (*Arch. expt. Path. Pharm.*, 1913, 75, 10—32).—In rabbits in which central heat regulation was excluded, sodium salicylate in small

doses causes a rise of temperature, which is independent of motor stimulation. Antipyrine in the paralysed animals causes no alteration in the utilisation of energy; and in those not paralysed, a small increase in heat development is due to motor unrest. Quinine in moderate doses produces a fall of heat production; in large doses, this effect may be masked by the result of motor stimulation. Morphine, in the smallest doses, depresses heat development; in paralysed animals, this is not so marked, and is produced by the result of depression of mobility.

W. D. H.

**Synergism of Poisons. III. The Antagonistic Influence of Solubility of Narcotics.** HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1913, 75, 53—74).—Numerous narcotics throw others out of aqueous solutions; in strong solutions, in the case of those which are slightly soluble, separation in the form of drops may occur; in dilute solutions, the smaller amount in solution may be detected by the capillarimeter or stalagmometer. In organic solvents, many pairs of narcotics may undergo increase of solubility, which can be explained as a shifting of the partition coefficients.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**The Degradation of *d*-Glucosamine by Bacteria.** KURT MEYER (*Biochem. Zeitsch.*, 1913, 58, 415—416).—The author has already shown (this vol., i, 117) that *d*-glucosamine is degraded by certain bacteria. Investigations have now been extended to the acetyl derivative to ascertain whether an intact amino-group is necessary for this action. It was found that acetylglucosamine is acted on by the following bacilli: *B. paratyphus*, *B. coli* and Friedländer's bacillus, but is left intact by *B. typhus*, *B. paratyphus* A., and Flexner's dysentery organism. S. B. S.

**Chemical Composition of the Cells of *Azotobacter chroococcum*.** W. L. OMELIANSKY and N. O. SIEBER (*Zeitsch. physiol. Chem.*, 1913, 88, 445—459).—Cultivations were made on agar containing the usual mineral salts with 2% dextrin. After about six days' incubation at 30°, a characteristic dark brown growth was obtained, and this, after being scraped off and dried rapidly at 30°, was used for the investigation. The air-dried material was found to contain 6.63% water, 4.16% ash, and 12.92% protein. The nature of the nitrogen-free substance was not determined, but it would appear to belong to the polysaccharides. Among the products of hydrolysis, lysine is present in greater proportion than arginine, and only minute traces of histidine are formed. H. B. H.

**Influence of Certain Colloids on Microbiological Processes.** N. L. SÖHNGEN (*Chem. Weekblad*, 1914, 11, 42—59).—Nitrification processes are accelerated by the presence of colloidal ferric, aluminium, and silicon oxides, and humus. The presence of the two former hinders the amylum fermentation by *B. ochraceus*, that of the two latter promotes it. Negative colloids accelerate the decomposition of urea, but positive colloids have little influence. Animal charcoal and peat facilitate the oxidation of alcohol by acetic bacteria. The alcoholic fermentation is hindered by alkali humates, promoted by biocolloids such as peat, filter-paper, animal charcoal, and vegetable mould, but unaffected by ferric, aluminium, and silicon oxides, and humic acid. Colloids have little influence on denitrification processes. The oxidation of petroleum by bacteria is facilitated by the presence of animal charcoal, colloidal ferric oxide, and silica. A. J. W.

**Effect of Carbon Disulphide and Toluene on Nitrification.** P. L. GAINES (*Centr. Bakt. Par.*, 1914, ii, 39, 584—595).—Nitrification is not affected by 0.1 c.c. of toluene in 100 grams of soil. A large amount of toluene generally has an inhibitory effect for a short time. When, however, the period of incubation is extended, the injurious effect ceases when amounts of toluene up to 1 c.c. per 100 grams are employed. Carbon disulphide, at the rate of less than about 1 c.c. to 100 grams of soil, has no appreciable effect. More than 1 c.c. generally retards nitrification for a time; with even as much as 5 c.c., the retarding effect is soon overcome.

Soils treated with chemical substances in such amounts as inhibit nitrification for twenty weeks may recover without re-inoculation.

The conclusion is drawn that toluene or carbon disulphide applied to fields will not materially affect nitrification if applied at the rate of 0.1 c.c. per 100 grams of soil. N. H. J. M.

**Some Factors Influencing Ammonification and Nitrification in Soils.** J. E. GREAVES (*Centr. Bakt. Par.*, 1913, ii, 39, 542—560).—Arsenic is sometimes found in virgin soils, whilst many cultivated soils contain considerable amounts; it has also been found in sub-soils down to three feet. The arsenic of "insoluble" insecticides is not completely insoluble; the greatest amount is soluble when Paris green has been used and the least with lead arsenate. The trisulphide seems to become more soluble after remaining in soils. Ammonification and nitrification are not decreased by the presence of 100 per million of sodium arsenate in soils rich in calcium and iron; smaller amounts may have a considerable stimulating action. Zinc arsenite, lead arsenate, and arsenic trisulphide stimulate ammonification, and are only toxic when comparatively large amounts are present. The first two salts only reduce ammonification and nitrification one-half when the soil contains 1.12 grams of arsenic per kilogram.

All the arsenic compounds, and especially lead arsenate, stimulate nitrification, which is, however, checked by large amounts of

Paris green and arsenic trisulphide. The only substance which is likely to be injurious to soil bacteria in practice is Paris green, and the quantity added would have to be large.

The beneficial action of arsenic on ammonification, and especially nitrification, is attributed, partly to stimulation, and partly to its influence on injurious species. N. H. J. M.

**The Influence of Arsenic on the Biological Transformation of Nitrogen in Soils.** J. E. GREAVES (*Biochem. Bull.*, 1913, 3, 2—16).—One part per 100,000 of sodium arsenate applied to a soil rich in calcium and iron does not materially decrease the ammonifying or nitrifying powers of that soil; smaller amounts may stimulate them. Similar details are given in respect to other arsenic compounds; Paris green is the most toxic; the toxicity of lead arsenate is least, and this is the safest insecticide. W. D. H.

**Enzymatic Formation of Polysaccharides by Yeast Preparations.** ARTHUR HARDEN and WILLIAM JOHN YOUNG (*Biochem. J.*, 1913, 7, 630—636).—Dextrorotatory polysaccharides of the nature of glycogen are shown to be produced during the alcoholic fermentation of dextrose and lævulose by Lebedev's maceration extract of dried yeast. The difference recorded by Euler and Johansson (*A.*, 1912, ii, 377) between the sugar removed and that equivalent to the carbon dioxide evolved is attributed to the formation of these compounds; it does not mean, as supposed by Euler, that the hexose requires to undergo some change which renders it directly fermentable, and that the difference represents the amount which is in this intermediate condition. It is well known that living yeast forms glycogen when brought into excess of sugar solution (Pavy and Bywaters, *A.*, 1908, ii, 56). E. F. A.

**Pyruvic Acid, a Product of the Life of Yeast.** A. FERNBACH and M. SCHOEN (*Compt. rend.*, 1913, 157, 1478—1480).—By fermentation of sugar in the presence of calcium carbonate, followed by concentration of the liquid in a vacuum and precipitation with alcohol, a white powder is obtained, which, on decomposition in concentrated solution with sulphuric acid and extraction with ether, finally yields a syrup, after removal of the ether, from which succinic acid crystallises. The residual concentrated solution of acids furnishes all the reactions of a ketonic acid, having the characteristics of pyruvic acid, and yields a *p*-nitrophenylhydrazone identical with that of pyruvic acid. On distilling the syrup at 70—90°/20 mm., an oily liquid having the properties of pyruvic acid passes over. W. G.

**Chemical Composition and Formation of Enzymes. IX. Formation of Invertase.** HANS EULER and HARALD CRAMÉR (*Zeitsch. physiol. Chem.*, 1913, 88, 430—444).—The amount of invertase in yeast is increased by previous treatment, either with sucrose or with the products of its hydrolysis. Treatment of the yeast with mannitol or with sodium formate or lactate has no such effect.

Mannose has the same favourable effect as sucrose, and it is apparently the process of fermentation as such, and not the substrate or the products of the reaction, which influences the formation of new invertase. Enzyme formation is closely correlated with the formation of fresh protoplasm.

E. F. A.

**The Volatile Bases Produced in the Autolysis of Yeast.** NICOLAUS IVANOV (*Biochem. Zeitsch.*, 1913, 58, 217—224).—Evidence is brought forward which tends to show that trimethylamine is a product of the autolysis of yeast.

S. B. S.

**Inversion of Sucrose by Water in the Presence of Moulds.** L. VAUVEL (*Ann. Fulsif.*, 1913, 6, 661—662).—To ascertain the extent to which sucrose is inverted by the action of moulds, two solutions containing 630 grams of sucrose per litre were kept for about four months in corked flasks, one flask remaining in the laboratory, whilst the other was placed in a cellar. Moulds were introduced into the solutions, and, after the lapse of the time mentioned, the first flask was found to contain sucrose, 399·8, invert sugar, 167·0, and dextrose (excess), 2·5 grams per litre, whilst the solution kept in the cellar contained sucrose, 326·7, invert sugar, 258·1, and dextrose (excess), 5·4 grams per litre. A portion of the sugar, in each case, was destroyed by the moulds or their secretions, lævulose being attacked to a greater extent than the dextrose. The solutions became acid in reaction.

W. P. S.

**Cleavage of Benzoylalanine and Acetyl glycine by Mould Enzymes.** ARTHUR W. DOX and W. EUGENE RUTH (*Biochem. Bull.*, 1913, 3, 23—25).—Benzoylalanine and, to a greater extent, acetyl glycine are hydrolysed by an enzyme present in lower fungi. The enzymic cleavage of substituted amino-acids is not limited to compounds analogous to hippuric acid.

W. D. H.

**Autolysis of Mould Cultures. II. Influence of Exhaustion of the Medium on the Rate of Autolysis of *Aspergillus Niger*.** ARTHUR W. DOX (*J. Biol. Chem.*, 1914, 16, 479—484).—Autolysis of cultures of *Aspergillus niger* is due chiefly to exhaustion of carbohydrates from the culture medium. The rate of autolysis is increased by removing the autolytic products and replacing by distilled water. Replacement of the medium at regular intervals by a solution of sucrose reduces the rate of autolysis to less than half that of the undisturbed culture, and to less than one-third in cultures where replacement by water is carried out. Autolysis is attended by a loss in weight of the mycelium amounting to about 50% in thirteen weeks.

W. D. H.

**Zinc and "Sterigmatocystis Nigra" [*Aspergillus niger*].** HENRI COUPIN (*Compt. rend.*, 1913, 157, 1475—1476. Compare A., 1903, ii, 446).—A reply to Javillier (compare A., 1908, ii, 124, 317; 1909, ii, 173), and an expression of agreement with the results of Lepierre (compare A., 1913, i, 1423).

W. G.

**Zinc and Aspergillus.** The Experiments of Coupin and Javillier. CHARLES LEPIERRE (*Compt. rend.*, 1914, 158, 67—70. Compare A., 1913, i, 1423).—A reply to Javillier (compare A., 1908, ii, 124, 317), in which the author confirms Coupin's results (compare A., 1903, ii, 446) and the conclusions he drew as to the uselessness of zinc for the culture of *Aspergillus niger*. W. G.

**Action of Anodic and Cathodic Solutions on Germination.** HENRI MICHEELS (*Bull. Acad. roy. Belg.*, 1913, 831—887. Compare A., 1910, ii, 883).—Further experiments have been made on the germination of wheat grains in the anodic and cathodic compartments of an electrolytic cell containing sodium or potassium chloride in 0.001 or 0.01 molar concentration. In order to ascertain the influence of the electrical treatment, a comparison was made of the percentage number of germinations, of the mean length of the first leaf, of the mean length of the roots, and of the mean increase in weight. Tables are given showing the ratios of these quantities for grains which have been submitted to cathodic and anodic treatment respectively. In both series of solutions the maximum difference is exhibited in the case of root growth, and this is most marked in the case of the experiments with solutions of sodium chloride.

The conclusion is drawn that the effect on the germination in a given solution is approximately proportional to the quantity of electricity which has been passed through the solution in which the germinating seeds are immersed, and it is claimed that the difference between the cathodic and anodic effects cannot be accounted for on the basis of the alkali and acid which are formed as a result of the secondary decomposition. In particular it may be noted that the relatively feeble development of the roots in the anodic liquor is attributed to the coagulation of the colloidal solution which they contain under the influence of the cations which can readily pass through the membrane of the root cells.

H. M. D.

**Synthesis of Amides at the Expense of Ammonia Absorbed by the Roots.** D. PRIANISCHNIKOV (*Rev. Gén. Bot.*, 1913, 25, 5—13).—Barley, maize, and *Cucurbita Pepo*, which are not injured by dilute solutions of ammonium salts, absorb ammonia readily, and produce asparagine (or glutamine) without special precautions being taken. With other plants, such as peas and vetches, the presence of ammonium salts retards the decomposition of proteins and the accumulation of asparagine, whilst the absorption of ammonia proceeds with difficulty, if at all. In presence of calcium carbonate, these plants absorb ammonia vigorously, and produce asparagine in considerable amounts.

A third group of plants, which includes lupines, shows fundamental disturbances in presence of ammonium salts, which cannot be remedied by the presence of calcium carbonate. N. H. J. M.



**Passage of an Anthocyanin Pigment Extracted from the Red Autumnal Leaves into the Yellow Pigment Contained in the Green Leaves of the same Plant.** RAOUL COMBES (*Compt. rend.*, 1913, 157, 1454—1457). Compare this vol. i, 121).—The red anthocyanin pigment extracted from red vine leaves can be oxidised in alcoholic solution by hydrogen peroxide to a yellow pigment identical in every respect with that extracted from the green leaves of the same plant. W. G.

**The Passage of Dyes into the Plant Cell.** RAPHAEL ED. LIESEGANG (*Biochem. Zeitsch.*, 1913, 58, 213—216).—A criticism of Ruhland's hypothesis of permeability (A., 1913, ii, 848). The author considers the process is one of diffusion rather than of ultra-filtration. S. B. S.

**The Anthocyanins. Artificial Anthocyanin.** M. CVET (FswETT) (*Biochem. Zeitsch.*, 1913, 58, 225—235).—In apples and other products, alcohol-soluble substances exist, probably related to the tannins, which in the presence of mineral acids and formaldehyde or acetaldehyde are converted into a pigment similar to anthocyanin. The artificial pigment is similar to the natural one, both in its spectral and chemical properties. It undergoes the same colour changes with acids and alkalis, and is decolorised by sodium hydrogen sulphite and phenylhydrazine. These results are not entirely in accord with the recent work of Willstätter (A., 1913, i, 1371). S. B. S.

**Formation of Chlorophyll in Plants. III.** N. A. MONTEVERDE and V. N. LUBIMENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 1007—1028. Compare A., 1912, ii, 800).—The authors have devised an improved apparatus for carrying out the spectro-colorimetric estimation of chlorophyll, xanthophyll, and carotene previously described (compare Lubimenko, *Trans. St. Petersburg Soc. Naturalists*, 1910, 41). With this apparatus, which is described in detail, only a very small volume of liquid is required. By means of alcoholic solutions containing respectively 1 gram and 0.2 gram of xanthophyll per 1000 litres, it is found that the mean of a number of separate estimations is 1.2% too high, the maximum and minimum results showing errors of 5% and 3%. Measurements with a chlorophyll solution exhibit a similar degree of accuracy.

The amounts of the three pigments per kilo. of fresh leaves have been determined with *Thuja orientalis*, *Viburnum Tinus* (young leaves), *Luffa gigantea*, *Albizia Julibrissin*, *Ruta graveolens*, *Ailanthus glandulosa*, *Clematis Vitalba*, *Hyssopus officinalis*, *Rubus caesius*, and *Arundinaria japonica*. The amount of chlorophyll increases in the above order from 0.8114 gram to 2.9 grams; the order is slightly changed in the case of xanthophyll and carotene, the amounts of which are 0.1317—0.4065 gram and 0.0208—0.1081 gram respectively; thus the green colour of leaves is conditioned, not merely by the greater colouring power of the chlorophyll, but also by its predominating proportion, the yellow pigments in the

chloroplasts being masked. From the separate experimental numbers the values have been calculated for leaves of each of the above plants of the ratios: (1) chlorophyll : both yellow pigments; in one case this is about 4 and in another about 7, the remaining values lying between 5 and 6; (2) chlorophyll : xanthophyll, which varies from 5 to 8; (3) chlorophyll : carrotene, for which most of the values are between 25 and 30, the extremes being 20 and 40; (4) xanthophyll : carrotene, which is mostly about 4, the limits being 3 and 6. Duplicate estimations of the amount of chlorophyll per kilo. of green and of brown leaves from the same specimen of *Thuja* gave the results: 0.9434 and 0.9708 (green) and 0.5746 and 0.5714 (brown). As previous experiments show, there is no intimate chemical connexion between the chlorophyll and the yellow pigments, each of which, after its formation, acts independently, and may consequently undergo quantitative change apart from the others. It is, therefore, quite possible that, under the influence of external or internal conditions, the quantity of yellow pigments may change, and so cause alteration of the above ratios.

Further investigations have been made on the influence of various constituents of the ash of plants on the extent to which the leaves turn green, this being measured by the proportion of chlorophyll formed. Two series of experiments were made, the first with etiolated *Luffa* seedlings, which were freed as far as possible from adherent mineral matter by thorough washing in tap-water and then in distilled water; the effects of different salts were then compared with the result of control tests, in which distilled water was employed. All the potassium salts used—dihydrogen phosphate, nitrate, chloride, and permanganate—cause marked increases in the amount of chlorophyll formed, whilst magnesium sulphate produces a slight increase, and calcium or magnesium nitrate a considerable decrease; sodium nitrate gives a small decrease, and sodium dihydrogen phosphate a large increase. The second series of experiments, carried out with etiolated wheat seedlings, gave totally different results. In this case, magnesium sulphate or potassium permanganate or dihydrogen phosphate had virtually no effect on the amount of chlorophyll formed, and potassium nitrate had but a slight positive influence. T. H. P.

**Willow Bark.** III. G. POVARNIN, K. KRASIN and I. POVARNIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1799—1810. Compare A., 1913, i, 576).—Examination of two specimens of willow bark extract shows that both the products of their decomposition and also their non-tannide constituents contain gallic acid and catechol, the non-tannides containing also phenol and an ethereal oil, which readily undergoes bromination, and is changed by the action of hydrochloric acid. One of the extracts includes a substance which gives the characteristic reaction for alicyclic compounds, but was not identified. The tanning substance of willow extract is probably a mixture of tannide, calcium tannate, and a derivative of some nitrogen ring. The tannide gives acetic, butyric, and several non-identified aliphatic and other acids on decomposition, whilst

aldehydes are formed when it is distilled in a current of carbon dioxide. In order to determine the nucleus of the tannides without subjecting them to hydrogenation, reduction by means of aluminium in an atmosphere of light petroleum may be employed, although this procedure does not exclude the possibility of secondary coupling reactions taking place. Platinised asbestos and hydrogen produce marked hydrogenation, but the reaction proceeds at a low temperature.

T. H. P.

**Willow Bark.** IV. G. POVARNIN and V. TOLKUNOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1811—1822).—Further investigations have been made with the bark of different varieties of willow with a view to their classification. A scheme has been evolved which is based on the colour of the supernatant liquid above the precipitate formed with ammoniacal copper sulphate solution (compare A., 1913, i, 576), and on the dyeing properties of the extract. The latter was determined with the standard yellow (*y*), red (*r*), and blue (*b*) glasses of the Lovibond tintometer, the ratio,  $(y-b)/(r-b)$ , being used in the classification. These properties and the proportions of tannides and non-tannides present in extracts prepared under definite conditions have been determined for twenty-two varieties of willow.

T. H. P.

**Action of Antiseptics in Increasing the Growth of Crops in Soil.** EDWARD JOHN RUSSELL and WALTER BUDDIN (*J. Soc. Chem. Ind.*, 1913, **32**, 1136—1142).—Whilst the general effects of different antiseptics is the same, resulting in increased numbers of bacteria and increased production of ammonia, the amounts of the various antiseptics required to produce these results vary considerably. As regards volatile antiseptics, the amounts required were found to be as follows: toluene and carbon disulphide, 0.09%, benzene, less than 0.16%, cyclohexane, 0.17%, chloroform, 0.23%, ethyl ether, 0.74%, hexane, 0.86%, methyl alcohol, 3.2%, and ethyl alcohol, 4.6%, of soil.

The action of non-volatile antiseptics is more complex. In the case of cresol, for instance, although the initial effect is the same as that produced by toluene, etc., the later effects are different in several ways; the number of bacteria increase enormously (in one case to 106 millions per gram) and the flora is very simple as compared with that obtained with volatile antiseptics. The high numbers are not maintained, but fall rapidly. The increase in ammonia is much less than with toluene. Phenol gives similar, and quinol somewhat similar results (with only 0.05%). The latter substance, as well as cresol, seems to be utilised by the surviving bacteria as food. *p*-Benzoquinone behaves similarly, but is less potent.

Formaldehyde is normal in its initial behaviour, killing the protozoa, and reducing the number of bacteria; this is followed by a marked rise in ammonia, but no increase in bacterial numbers. Pyridine has to be applied at the rate of 0.8%, smaller amounts being readily assimilated by the bacteria.

The results obtained with various antiseptics on tomatoes, grown

in soils containing disease organisms, showed that formaldehyde and pyridine are the most effective; next, cresol, phenol, calcium sulphide, carbon disulphide, toluene, benzene, and petroleum; whilst the least effective of the substances tried were the higher homologues of benzene and naphthalene, and some of its derivatives. None of these antiseptics is, however, as effective as steam.

Owing to the different conditions in the laboratory and the culture experiments, the order of effectiveness of the different antiseptics is not quite the same. In the laboratory, the possibility of re-infection was excluded, and an organism once killed could not reappear; in the vegetation experiments such rigid exclusion was, of course, impracticable. N. H. J. M.

**The Catalytic Action of Iron in the Development of Barley.** J. WOLFF (*Compt. rend.*, 1913, 157, 1476—1478. Compare this vol. i, 125).—Iron, in quantities so small as to make it impossible to detect and estimate the amount with certitude, exerts a markedly favourable catalytic influence on the growth of barley. W. G.

**Action of Manganese and Aluminium on the Growth of Plants.** TH. PFEIFFER and E. BLANCK (*Landw. Versuchs-Stat.*, 1913, 83, 257—281. Compare A., 1912, ii, 476).—Sand culture experiments, in which oats, grown in pots holding 17 kilos. of sand, received different amounts of manganese carbonate and sulphate and aluminium sulphate, in addition to the usual salts supplying potassium, calcium, phosphoric acid, and nitrogen. It was found that manganese salts slightly increased the yield of dry matter; to obtain the best results, very considerable amounts of manganese are necessary, especially when applied in a sparingly soluble form, so that it is very doubtful whether the employment of manganese in practice could be remunerative.

Very small amounts of aluminium sulphate, in conjunction with small amounts of manganese sulphate, seem to have a slightly stimulating action; the results, however, varied a good deal. When larger amounts of aluminium salt are employed, the yield is more quickly reduced than by corresponding amounts of manganese salt.

When the produce is increased by applications of manganese salts, the plants give off less water, which is possibly connected with the deposition of manganese in the leaves. It is suggested that the favourable effect of manganese may be connected with the retention of water. N. H. J. M.

**Plasmas after Sugar Dialysis.** M. PIETTRE and A. VILA (*Compt. rend.*, 1913, 157, 1542—1545. Compare A., 1913, i, 661).—An examination of the proteins contained in the plasma solution after removal of the fibrinogen by dialysis against a sugar solution and then against water. The liquid resulting from the dialysis is treated with 2—3 volumes of acetone. The proteins are precipitated, filtered, and washed with 50% acetone, and finally with ether. The proteins so obtained can be separated, by suitable treatment with water, into two groups, one of which is soluble in water, and

the other not. This insoluble fraction can be further sub-divided into two fractions, one consisting of true globulins, soluble in 7% sodium chloride solution, and the other insoluble. The group, soluble in water, is obtained as a white, hygroscopic powder on precipitation with acetone, and its aqueous solution does not give the biuret action, and is precipitated neither by acids nor alkalis, but is entirely coagulated by heat.

W. G.

**The Effects of Enzymes and Other Substances on the Growth of Burley Tobacco.** J. DU P. OOSTHUIZEN and O. M. SHEDD (*J. Biol. Chem.*, 1914, 16, 439—453).—In two months the addition of various enzymes improves the growth of some of the tobacco plants used. Pepsin and emulsin and also caseinogen caused the best results. The effect is not proportional to the nitrogen added. Pepsin, however, in combination with caseinogen and trypsin failed to produce any increase of growth. A large number of other substances were tried; most gave negative results, some produced bad effects. Iron and manganese peptonates, potassium cyanide, hydrocyanic acid, and iron and manganese lactate gave positive results, and in the order named.

W. D. H.

**Influence of Soils and the Amount of Water on the Changes in the Forms of Nitrogen.** F. MÜNTER and W. P. ROBSON (*Centr. Bakt. Par.*, 1913, ii, 39, 419—440).—With low percentages of water the decomposition of horn meal is much more rapid in sandy soil than in loam and clay soils, whilst when considerable amounts of water are present there is no great difference. The ammonia produced from horn meal disappears rapidly in presence of high amounts of water; when, however, the percentage of water is low, the ammonia remains a considerable time, the maximum being reached earlier the lighter the soil. In sandy soil (water 6%), the maximum was 36·7% in three weeks; in loam water (8%), 41·3% in six weeks; and in clay (water 8%), 13·4% in twelve weeks. With the highest amount of water (18—24%), the sandy and loam soils contained no ammonia in the sixth week, and in the clay soil none in the third week.

The nitrification of ammonium sulphate in soils deficient in water is greatest in sandy soils, whilst in presence of sufficient water nitrification is more vigorous in heavy soils. Nitrification of horn meal was most satisfactory in sandy soil; in loam and clay soils the best results were obtained with medium amounts of water. Liberation of free nitrogen only occurred to any extent in presence of the largest amounts of water; with ammonium sulphate the greatest loss (19·8%) was in loamy soil, and with horn meal 32·7% in clay soil. Additions of sucrose caused a more rapid disappearance of ammonium sulphate without a corresponding production of nitrates.

N. H. J. M.

## Organic Chemistry.

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**Origin of Ozokerite.** MARCUSSEN and H. SCHLÜTER (*Chem. Zeit.*, 1914, 38, 73—74).—The simultaneous occurrence of ozokerite and petroleum is pointed out and the rival theories that the former is produced from the latter and that formation occurs in the reverse order are critically discussed. According to the authors, neither explanation is satisfactory, and the theory is advanced that both products are simultaneously formed from the decayed complex organic constituents of plant and animal remains (compare Engler, A., 1912, i, 525). Fats and waxes contain a mixture of solid and liquid fatty acids, the former of which readily yield solid paraffins by loss of water and carbon dioxide, whilst liquid oleic acid only gives liquid paraffins under the most varied experimental conditions. The oil, containing solid paraffins, is forced by earth- or gas-pressure through the overlying strata and thus undergoes a filtration and partial separation into its components, the more liquid portions passing more readily through the strata and leaving thus a solid residue. The theory is supported by observations of the different samples of ozokerite obtained from various classes of rock and from actual experience during boring, and is in accord with the experiments of Koss (A., 1911, i, 761) on the distribution of optically active substances in ozokerite.

The occurrence of amorphous ozokerite is explained in the following manner: the crude oil contains both crystalline and amorphous paraffins. The former have a lower molecular weight and m. p. than the latter. When an oil rich in paraffins undergoes filtration in the earth, the crystalline paraffins become more or less completely liquid and are therefore carried forward by the oil more rapidly than the less soluble, amorphous paraffins, which, therefore, alone have an opportunity to separate. The dark impurities in ozokerite are to be regarded as oxidation and polymerisation products of the hydrocarbons which are partly acquired from the oil, partly formed subsequently. In support of this theory the authors have observed the formation of dark waxy products (pipe wax) in the pipes which are used in Boryslav for conveyance of the crude oil. In m. p., index of refraction, density, molecular weight, and precipitation value, this substance shows a close analogy to ceresin, and can only be distinguished from ozokerite by its greater oil content.

H. W.

**Preparation of Allyl Haloids.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 268340).—Allyl haloids (chloride, bromide, or iodide) are obtained from allyl esters (formate, acetate, etc.) by mixing the latter with the corresponding concentrated halogen acid, saturating the mixture with the hydrogen haloid, and heating in an autoclave, or in an open vessel with the addition of a catalyst (for example, zinc haloids).

J. C. C.

**A General Method for the Conversion of Fatty Acids into their Lower Homologues.** P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1914, 16, 475—478. Compare A., 1912, i, 936; 1913, i, 587).—The fatty acids are readily converted into their  $\alpha$ -hydroxy-derivatives by passage through their  $\alpha$ -bromo-derivatives (compare Le Sueur, T., 1904, 85, 827; 1905, 87, 1888). These can then be readily oxidised in acetone solution by a warm solution of potassium permanganate in the same solvent, giving the potassium salt of the fatty acid with one carbon atom less. The potassium salt is precipitated along with the manganese dioxide, and can be extracted from this with alcohol. The yield is 80—85%, and avoids the preparation of the aldehyde (compare Le Sueur, *loc. cit.*). The authors have applied this method to the preparation of lignoceric, margaric, and pentadecic acids. W. G.

**History of the Discovery of Formic Acid.** F. D. CHATTAWAY (*Chem. News*, 1914, 109, 61—63).—Historical.

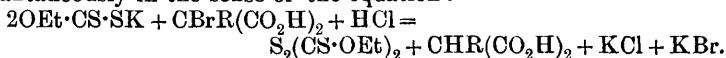
**Action of Persulphates on Acetates.** M. A. GORDON (*J. Physical Chem.*, 1914, 18, 55—66).—If a solution containing sodium persulphate and acetic acid or sodium acetate is heated, a mixture of gases is given off consisting of carbon dioxide and one or more hydrocarbons (methane, ethane, olefines). The amount of carbon dioxide and the composition of the hydrocarbon mixture varies with the conditions of the experiment. Simultaneously with the oxidation of the acetic acid, this appears to be catalytically decomposed by the persulphate in accordance with the equation  $\text{CH}_3 \cdot \text{CO}_2\text{H} = \text{CH}_4 + \text{CO}_2$ . The catalysed reaction is favoured by high concentration of the acetic acid, low acidity, and low concentration of persulphate. Those conditions which are favourable to the decomposition of persulphate give rise to increased oxidation. Such factors are high concentration of persulphate, high temperature, moderate acidity, and the addition of manganous sulphate or platinum foil to the solution. H. M. D.

**New Method of Preparing the Diacetate of Glycerol  $\alpha$ -Monochlorohydrin.** JEAN NIVIÈRE (*Bull. Soc. chim.*, 1914, [iv], 15, 82—83. Compare A., 1913, i, 697; also Aceña, A., 1905, i, 7).—The diacetate of glycerol  $\alpha$ -monochlorohydrin, b. p. 113—114°/9 mm., is obtained in 75% yield when a mixture of  $\alpha$ -monochlorohydrin and acetic anhydride is boiled for three hours under reflux. Acetic anhydride and acetic acid are removed by distillation under diminished pressure; the residue is warmed with water to destroy any remaining acetic anhydride and to dissolve any unchanged  $\alpha$ -monochlorohydrin, and the product obtained is distilled under diminished pressure. The yield may be further improved by a second treatment with acetic anhydride after distillation of the acetic acid formed in the first operation, whereby, also, the addition of water is rendered unnecessary. H. W.

**Some New Esters of Oleic Acid.** N. SULZBERGER (*Zeitsch. angew. Chem.*, 1914, 27, 40).—*Menthyl oleate*,  $\text{C}_{28}\text{H}_{52}\text{O}_2$ , b. p. about 240°/4 mm., *phenyl oleate*, b. p. about 230°/7 mm., and *m-tolyl oleate*, b. p. about 240°/5 mm., are obtained as colourless, oily liquids, which can be

distilled without decomposition in a vacuum, by the action of a slight excess of the respective alcohol or phenol on the chloride of oleic acid. The latter, b. p. about  $200^{\circ}/11$  mm.,  $196^{\circ}/9$  mm., is prepared by Krafft and Tritschler's method (A., 1901, i, 116) or by heating oleic acid on the water-bath with thionyl chloride in slight excess. H. W.

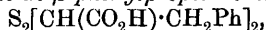
**Organic Thio-acids. V. Action of Potassium Xanthate on Bromomalononic Acids.** EINAR BILLMANN and E. HÖST MADSEN (*Annalen*, 1914, 402, 331—342. Compare A., 1906, i, 625, 626).—In neutral or faintly alkaline aqueous solution the reaction between potassium xanthate and potassium bromomalonate, bromoethylmalonate, bromoisopropylmalonate, or bromobenzylmalonate proceeds more or less rapidly according to the equation:  $\text{OEt}\cdot\text{CS}\cdot\text{SK} + \text{CBrR}(\text{CO}_2\text{K})_2 = \text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CR}(\text{CO}_2\text{K})_2 + \text{KBr}$ , so that 78—99% of the theoretical yield is obtained in twenty-four hours; in acid solution, however, the reaction proceeds quantitatively and almost instantaneously in the sense of the equation:



The xanthomalononic acids obtained by the first reaction are very unstable, readily losing carbon dioxide and forming xantho-fatty acids at temperatures very little above the ordinary.

Aqueous sodium bromobenzylmalonate is reduced to sodium benzylmalonate by sodium hydrosulphide in slight excess.

*$\alpha$ -Xantho- $\beta$ -phenylpropionic acid*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{S}\cdot\text{CS}\cdot\text{OEt})\cdot\text{CO}_2\text{H}$ , m. p.  $89$ — $90^{\circ}$ , colourless crystals, obtained by the decomposition of xanthobenzylmalonic acid, is converted into  *$\alpha$ -thiol- $\beta$ -phenylpropionic acid*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{SH})\cdot\text{CO}_2\text{H}$ , m. p.  $46^{\circ}$ , b. p.  $184$ — $187^{\circ}/11$ — $12$  mm., colourless crystals, by alcohol and concentrated aqueous ammonia at the ordinary temperature; the latter acid, in acid solution, is oxidised by iodine to  *$\alpha$ -disulphido-di- $\beta$ -phenylpropionic acid*,



m. p.  $105$ — $107^{\circ}$ .

A convenient method is described for the preparation of bromomalononic acid by the hydrolysis of ethyl bromomalonate by aqueous sodium hydroxide at  $5$ — $10^{\circ}$ . C. S.

**Transformations of Ethyl  $\alpha$ -Cyano- $\alpha$ -isopropylbutyrate and Ethylisopropylmalonamic Acid.** EMIL FISCHER, ALICE ROHDE, and FRITZ BRAUNS (*Annalen*, 1914, 402, 364—382).—Recent researches on Walden's inversion have shown that change of configuration or racemisation may occur during ordinary substitution of a group attached to the asymmetric carbon atom. Two of the fundamental consequences of the theory of the asymmetric carbon atom, therefore, have been re-examined under conditions in which a group attached to the asymmetric carbon atom is changed without being actually detached from the carbon atom. The first consequence, that optical activity must disappear when two of the unlike groups attached to the asymmetric carbon atom are made like, is tested by treating *d*-ethylisopropylmalonamic acid in aqueous ether with nitrous fumes, whereby ethylisopropylmalonic acid is produced, which proves to be quite



inactive optically. The second consequence, that reversal of the rotation must occur when two of the groups attached to the asymmetric carbon atom exchange places, is tested as follows. An active ethylisopropylmalonic acid is converted successively into its methyl ester and methyl hydrogen ethylisopropylmalonic acid; theoretically, the latter should be converted by ammonia into the optical antipode of the original ethylisopropylmalonic acid; actually, however, the reaction follows a quite different course.

The following new compounds are described: *dl-α-Cyano-α-isopropylbutyric acid*,  $\text{CN}\cdot\text{C}(\text{Et})\text{Pr}^{\beta}\cdot\text{CO}_2\text{H}$ , has m. p. 83—84°. Its ethyl ester is converted by concentrated sulphuric acid on the water-bath into *dl-ethylisopropylmalonic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{Et})\text{Pr}^{\beta}\cdot\text{CO}_2\text{H}$ , m. p. 116—118° (decomp., corr.), and its *ethyl* ester, m. p. 88° (corr.), colourless prisms; the *methyl* ester, obtained by means of diazomethane, has m. p. 74°. An aqueous solution of *dl-ethylisopropylmalonic acid* is converted by nitrous fumes at 40° into ethylisopropylmalonic acid, of which the *ethyl hydrogen* ester has b. p. 152° (corr.)/19 mm. and  $D_4^{22}$  1.0349, and the *methyl hydrogen* ester has m. p. 43°. *α-iso*Propylbutyramide is obtained by heating *dl-ethylisopropylmalonic acid* at 118° and finally at 130°.

The resolution of *dl-ethylisopropylmalonic acid* is effected by quinine in aqueous alcohol, in which the quinine salt of the *d*-acid is the less soluble; the *l*-acid is purified by means of its morphine salt. *d-Ethylisopropylmalonic acid* crystallises in stout needles, has m. p. or decomp. 116° and  $[\alpha]_D^{22} + 14.59^\circ$  in 10.06% alcoholic solution, and yields with diazomethane the *methyl* ester, m. p. 51—52° and  $[\alpha]_D^{20} - 1.97^\circ$  in 9.866% alcoholic solution (these constants are certainly too low, because the *d*-acid used for esterification contained about 5% of the *l*-acid). *l-Ethylisopropylmalonic acid*,  $[\alpha]_D^{22} - 14.62^\circ$  in 10.002% alcoholic solution, forms a *methyl* ester, m. p. 54°,  $[\alpha]_D^{18} 2.09^\circ$  in 9.447% alcoholic solution. *Methyl hydrogen d-ethylisopropylmalonate*, m. p. 26°, has  $[\alpha]_D^{22} 1.84^\circ$  in 9.961% alcoholic solution and  $[\alpha]_D^{23} - 3.41^\circ$  in *N*-potassium hydroxide (1.08 mols.), whilst the *methyl hydrogen* ester of the *l*-acid has  $[\alpha]_D - 1.88^\circ$  in 11.47% alcoholic solution and  $[\alpha]_D^{18} 3.72^\circ$  in *N*-potassium hydroxide.

*l-Ethylisopropylmalonic acid* has been heated at 120°/15—20 mm. and the carbon dioxide rapidly removed in the hope of obtaining an active acetamide; the product, however, is found to be *dl-α-iso*propylbutyramide  
C. S.

**The Stereoisomeric Forms of Xanthosuccinic Acid.** BROR HOLMBERG (*Ber.*, 1914, 47, 167—176. Compare this vol., i, 140).—A few years ago the author treated sodium *l*-bromosuccinate with potassium xanthate, but obtained an almost inactive xanthosuccinic acid. Recent experience on the influence of different cations on such reactions has led to the isolation of the active acids in a pure state (compare A., 1913, ii, 942).

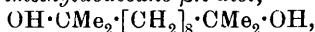
A dilute solution of potassium *l*-bromosuccinate was treated with the equivalent quantity of potassium xanthate and, a day later, with strontium bromide, when a strontium salt crystallised which yielded a mixture of 3% *d*- and 97% *l*-xanthosuccinic acid. From a concen-

trated solution of strontium *l*-bromosuccinate with excess of potassium xanthate and some strontium bromide, however, a mixture of 84% *d*- and 16% *l*-acid was obtained.

Some preliminary experiments showed that the racemic acid is less soluble than the active forms in water or in a mixture of ethyl acetate and benzene, and that, of the acid salts with the active phenylethylamines, those of the acid and base of opposite rotation are the less soluble. These differences were therefore employed in the final purification of the above acids. *d*-Phenylethylamine hydrogen *l*-xanthosuccinate,  $\text{CHMePh}\cdot\text{NH}_2\cdot\text{CO}_2\text{H}\cdot\text{CH}(\text{S}\cdot\text{CS}\cdot\text{OEt})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , formed white crystals, m. p. 117—118°, and *l*-xanthosuccinic acid (*loc. cit.*) was finally obtained in very pale yellow aggregates of small crystals,  $[\alpha]_D^{17} - 101\cdot6^\circ$  in ethyl acetate. *d*-Xanthosuccinic acid has  $[\alpha]_D^{17} + 101\cdot7^\circ$ , in ethyl acetate, +82·8° in absolute alcohol. In aqueous solution  $[\alpha]_D^{17}$  is about  $\pm 72^\circ$ , whereas the acid potassium salt has about half that rotation, and the normal salt only  $\pm 3^\circ$ . The active acids have m. p. 130—131°; the racemic, 148—149°, and the saturated aqueous solutions at 25° contain 24·1 and 8·2 grams per litre respectively.

The racemisation of the acids and their acid and normal salts was studied. When heated alone at 100°, or warmed in aqueous solution, the active acids quickly become inactive, but at the ordinary temperature the change is negligible. Complete neutralisation or the addition of a strong acid hinders racemisation at 35°, but the half-neutralised acids soon become inactive. It may be that the gradual formation of decomposition products in solution influences racemisation, but the kinetics of the change are being studied. J. C. W.

**Action of Magnesium Methyl Iodide on Ethyl Sebacate.** (Mlle.) E. KISLOVSKAJA (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1975—1979).— $\beta\lambda$ -Dimethyl-dodecane- $\beta\lambda$ -diol,



obtained by treatment of ethyl sebacate with magnesium methyl iodide and subsequent decomposition by means of water, forms long, asbestos-like crystals, m. p. 57·5—58°.

$\beta\lambda$ -Dimethyl- $\Delta^{\beta\kappa}$ -dodecadiene,  $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_6\cdot\text{CH}\cdot\text{CMe}_2$ , obtained by heating the above glycol with anhydrous oxalic acid at 140—150°, is a colourless, mobile liquid with an unpleasant odour, b. p. 239·5—240·5° (corr.),  $D_4^{18} 0\cdot7932$ ,  $n_D^{19} 1\cdot4535$ , and has the normal molecular weight in freezing benzene. It combines readily with bromine forming an unstable, oily tetrabromide, which soon loses hydrogen bromide, and it unites with nitrogen tetroxide giving a dark green product. With mercuric acetate solution, it forms a white, curdy precipitate, which gives the hydrocarbon again on distillation with hydrochloric acid. In the air, the hydrocarbon thickens, and on distillation after three months yielded an aldehyde, the semicarbazone of which, m. p. 203°, was prepared. Oxidation of the hydrocarbon by means of permanganate gives mainly sebacic acid and acetone, small quantities of formic and acetic acid obtained being probably due to further oxidation of the acetone. T. H. P.

**Production of Formaldehyde and Acetaldehyde by Oxidation.** L. ROSENTHALER (*Arch. Pharm.*, 1913, 251, 587—595).—The

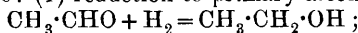
detection of minute amounts of formaldehyde in the leaves of the hornbeam (Curtius and Franzen, A., 1912, ii, 797) cannot be accepted as evidence of Baeyer's theory of the assimilation of carbon dioxide by plants until it has been proved that the aldehyde cannot have been produced by any other process. The author shows that many substances which occur in plants yield formaldehyde by oxidation. The substance, dissolved or suspended in dilute sulphuric acid, is treated with potassium permanganate in slight excess, the excess is destroyed by oxalic acid, the liquid is distilled, and the distillate is tested for formaldehyde by the colour reactions of Denigès, Marquis, Hehner-Leonard, Hehner, and Schryver (Lewin's nitroprusside test for acetaldehyde has also been applied). The substances examined are alcohols, aldehydes, ketones, acids, carbohydrates, phenolic ethers, glucosides, and alkaloids. The results show that formaldehyde is produced by the oxidation of substances containing methoxy-, methylenedioxy-, or methylimino-groups, of most carbohydrates, and of tri- and poly-hydric aliphatic alcohols. Acetaldehyde is obtained by the oxidation of substances containing an ethoxy- or ethylimino-group, and also of rhamnose (the last reaction may serve to distinguish rhamnose, and possibly other methylpentoses, from pentoses). In the case of glycerol, dextrose, sucrose, and rhamnose, sufficient formaldehyde or acetaldehyde is obtained for the identification of the aldehyde in the form of its *p*-nitrophenylhydrazone, or in the case of formaldehyde by Curtius and Franzen's method.

C. S.

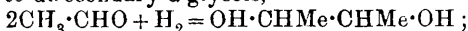
**Preparation of Aldehydes and Ketones.** FABRIQUES DE PRODUITS CHIMIE ORGANIQUE DE LAIRE (D.R.-P. 268786).—Aldehydes or ketones are obtained when hexamethylenetetramine (or a mixture of 6 parts of formaldehyde and 4 parts of ammonia) is boiled in alcoholic solution with a monohalogen compound. The reaction takes place with the intermediate formation of an additive compound, and the conversion of the halogen compounds is represented thus:  $R \cdot CH_2X \rightarrow R \cdot CHO$ ;  $CR_2HX \rightarrow CR_2O$  (where X = halogen). In this manner ethyl iodide yields acetaldehyde, benzyl chloride gives benzaldehyde,  $\alpha$ -chloroethylbenzene yields acetophenone, and mention is made of a large number of aldehydes that may be prepared by this general method.

J. C. C.

**Reduction of Aldehydes to  $\alpha$ -Glycols.** R. CIUSA and A. MILANI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 681—685).—When treated with magnesium amalgam, aldehydes undergo change mainly in the three directions: (1) reduction to primary alcohols,



(2) reduction to disecundary  $\alpha$ -glycols,



(3) condensation to aldols and subsequent reduction of the latter to  $\beta$ -glycols,  $OH \cdot CHMe \cdot CH_2 \cdot CHO + H_2 = OH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot OH$ . These three reactions proceed with different velocities, which determine the relative proportions of the various products. Aliphatic aldehydes undergo aldol condensation with the greatest ease in either acid or alkaline solution, and hence yield principally  $\beta$ -glycols.

Thus, acetaldehyde yields a large proportion of  $\beta\delta$ -butylene glycol, together with smaller amounts of ethyl alcohol, aldol, and  $\beta\gamma$ -butylene glycol (4%) (compare Moureu, *Compt. rend.*, 1902, 134, 472).

Propaldehyde gives mainly  $\delta$ -methyl- $\gamma$ -amylene glycol, and also  $\gamma\delta$ -hexylene glycol,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_3$  (5–6%), which is a colourless, oily liquid, b. p. 233–234°, and is converted into dipropionyl by the action of bromine water and sunlight, and into diethylglyoxime by hydroxylamine.

Benzaldehyde yields hydrobenzoin and isohydrobenzoin.

T. H. P.

**Comparative Value of Catalysts in the Preparation of Ketones.** J. B. SENDERENS (*Bull. Soc. chim.*, 1914, [iv], 15, 84–89).—Mainly polemical. The author points out the superiority of the oxides of thorium, zirconium, and uranium in the catalytic preparation of ketones from acids, and claims priority in their use (compare Senderens, A., 1909, i, 216, 627; 1910, i, 11, 179, 318, 489; 1912, i, 406, 537; 1913, i, 342; Mailhe, A., 1909, i, 452, 692; 1910, i, 807; 1913, i, 828, 954; Sabatier and Mailhe, A., 1913, i, 700).

H. W.

**Syntheses with isoButyrone.** MURAT and AMOUREUX (*J. Pharm. Chim.*, 1914, [vii], 9, 114–118\*).—The authors have obtained a series of tertiary alcohols by the action of Grignard's reagents on isobutyron. The yields are generally not so good as in the case of butyrone (A., 1912, i, 527), and the alcohols are readily dehydrated, so that phenylurethanes could not be obtained.

Di-isopropyl ketone has b. p. 124–125°,  $D_0^0$  0.8413,  $D_0^{17}$  0.8250  $n_D$  1.417.

Di-isopropylisobutylcarbinol,  $\text{C}_4\text{H}_9\cdot\text{CPr}_2^\beta\cdot\text{OH}$ , b. p. 102–105°/40 mm.,  $D_0^{16}$  0.8737,  $n_D$  1.448, is obtained in poor yield by condensing di-isopropyl ketone with magnesium isobutyl chloride.

Di-isopropylisoamylcarbinol, b. p. 137–140°/65 mm.,  $D_0^{16}$  0.8607,  $D_0^0$  0.8718,  $n_D$  1.455, is obtained in 60% yield as a colourless syrup. Dehydration over oxide of thorium at about 350° converts it into an olefine which appears to consist of the two isomerides,  $\beta\zeta$ -dimethyl- $\gamma$ -isopropyl- $\Delta^7$ -heptene,  $\text{C}_5\text{H}_{10}\cdot\text{CPr}_2^\beta$ , and  $\beta\zeta$ -dimethyl- $\gamma$ -isopropyl- $\Delta^\beta$ -heptene,  $\text{C}_5\text{H}_{11}\cdot\text{Pr}^\beta\cdot\text{C}\cdot\text{CMe}_2$ , b. p. 188–190°/772 mm.,  $D_0^{20}$  0.7775,  $n_D$  1.444, which, when hydrogenated over nickel at 200–250°, yields  $\beta\delta$ -dimethyl- $\gamma$ -isopropylheptane, b. p. 186–188°/ordinary pressure,  $D_0^{20}$  0.7655,  $n_D$  1.432.

Phenyl-diisopropylcarbinol, a viscous liquid of pale yellow colour, b. p. 155–158°/60 mm.,  $D_0^{12}$  0.9602,  $D_0^0$  0.9755,  $n_D$  1.531, is obtained in good yield by the acid of magnesium phenyl bromide. Catalytic dehydration by oxide of thorium converts it into  $\gamma$ -phenyl- $\beta\delta$ -dimethyl- $\Delta^\beta$ -pentene,  $\text{CPh}\cdot\text{Pr}^\beta\cdot\text{CMe}_2$ , b. p. 225–228°/760 mm.,  $D_0^{20}$  0.9094,  $n_D$  1.532, which on catalytic reduction over nickel at 250–300° yields  $\gamma$ -phenyl- $\beta\delta$ -dimethylpentane, b. p. 220–225°,  $D_0^{10}$  0.8822,  $n_D$  1.512.

The yield of benzyl-diisopropylcarbinol, a brown, viscous liquid, b. p. 161–164°/35 mm.,  $D_0^{15}$  0.981,  $n_D$  1.538, from isobutyron and magnesium benzyl chloride, is considerably limited by the formation of

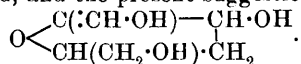
\* and *Bull. Soc. chim.*, 1914, [iv], 15, 159–162.

dibenzyl. On catalytic dehydration by oxide of thorium, it yields an *olefine*, b. p. 252—255°/ordinary pressure,  $D_0^{14}$  0.9110,  $n_D$  1.542.

Magesium cyclohexyl chloride reacts readily with isobutyronone, but on decomposition with water the complex is partly decomposed with formation of cyclohexene. cycloHexyldiisopropylcarbinol, b. p. 125°/12 mm., 138°/25 mm.,  $D_0^{19}$  0.9153,  $n_D$  1.474, is therefore obtained in poor yield. On dehydration it yields an *olefine*, b. p. 225—228°/760 mm.,  $D_0^{19}$  0.8782,  $n_D$  1.482, which probably consists of a mixture of the isomerides  $C_6H_{11} \cdot CPr^{\beta} : CMe_2$  and  $C_6H_{10} : CPr_2^{\beta}$ . H. W.

**New Reduction Products of Dextrose. Glucal and Hydroglucal.** EMIL FISCHER (*Ber.*, 1914, 47, 196—210. Compare A., 1913, i, 445).—A more complete account, and an extension, of the work described in the earlier communication.

Glucal absorbs two atoms of hydrogen in presence of platinum, yielding a crystalline compound,  $C_6H_{12}O_4$ . The same substance is obtained by reducing triacetylglucal (acetoglucal) and hydrolysing the product. From a study of these compounds, the formula  $C_6H_{10}O_4$ , as against  $C_6H_8O_3$ , is assigned to glucal. On reduction, glucal loses its aldehydic and unsaturated characters. It seems possible, therefore, that glucal contains an oxymethylene group, and the pine-splinter reaction further suggests a furan ring. The provisional formula is now considerably modified, and the present suggestion is



In whatever way the results are interpreted, the reduction of aceto-bromoglucose to triacetylglucal is most remarkable.

Triacetylglucal crystallises best from a mixture of alcohol with a little light petroleum, but the process has to be repeated many times before an optically pure product is obtained. It has m. p. 55°,  $[\alpha]_D^{22}$  -15.76°; it may be distilled, reduces Fehling's solution, and absorbs two atoms of bromine. When boiled with water, it is partly hydrolysed, one molecule of acetic acid being set free. The product, ?*diacetylglucal*,  $C_{10}H_{14}O_6$ , was distilled and obtained as a bitter, amorphous substance, which quickly restores the colour to Schiff's reagent and gives a deep violet coloration with cold, fuming hydrochloric acid. It could not be obtained optically pure and may be a mixture. Complete hydrolysis to glucal was effected by leaving a solution with a little more than the theoretical quantity of baryta water in an incubator.

*Triacetylhydroglucal*,  $C_6H_9O_4Ac_3$ , was prepared by catalytic reduction, quickly distilled under 0.5 mm., bath 160—165°, and obtained as a vitreous mass with indefinite constants,  $[\alpha]_D^{17}$  about +34—35°. It is indifferent towards Fehling's solution, acids, alkalis, and bromine. Hydroglucal was prepared by direct reduction, but the best results were obtained by hydrolysing triacetylhydroglucal by means of baryta. *Hydroglucal* forms colourless, hexagonal prisms or plates, m. p. 86—87°,  $[\alpha]_D^{20}$  +16.31°, and distils under 1 mm., bath 195—205°. It is very hygroscopic, has a slight sweet taste, and does not combine with water, even when heated with concentrated hydrochloric acid. When heated with hydriodic acid and phosphonium iodide, it is reduced to a

colourless oil, b. p. 90—95° (bath)/0.4 mm., 128—131°/12 mm., 160° (corr.)/33 mm. The product has the constitution and properties of a di-iodohexane, but has not been identified. Glucal and hydroglucal were both directly acetylated to their parent triacetyl derivatives.

Acetobromolactose was reduced to *acetolactal*,  $C_{24}H_{32}O_{15}$ , a colourless, amorphous mass of leaflets, and probably a hexa-acetyl compound.

J. C. W.

**Biochemical Synthesis of  $\alpha$ -Methylgalactoside.** H. HÉRISSEY and A. AUBRY (*Compt. rend.*, 1914, 158, 204—206\*).—The authors have synthesised  $\alpha$ -methylgalactoside by the action of air-dried bottom yeast, macerated with water, on a solution of galactose in dilute methyl alcohol. The action was slow, owing to the small amount of the necessary enzyme in the yeast. The product was obtained in the form of colourless crystals, having physical properties in close agreement with those given by Fischer (compare A., 1895, i, 437) for the substance prepared by purely chemical methods.

W. G.

**The Inversion of Sucrose.** EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1914, 38, 145—146).—A paper calling attention to the importance of the recent work of Sneath (A., 1913, ii, 1044) in which the catalytic effect of the undissociated acid molecule on the inversion of sucrose is discussed.

T. S. P.

**Applications of the Electronic Conception of Valence. I. Reactions among Certain Classes of Compounds Containing Nitrogen. II. The Beckmann Rearrangement.** LAUDER WILLIAM JONES (*Amer. Chem. J.*, 1913, 50, 414—443).—The processes of oxidation and reduction may be regarded as an exchange of electrons between atoms, a loss of negative electrons corresponding with oxidation, and a gain of negative electrons with reduction. As Fry (A., 1912, ii, 546) has pointed out, a quadrivalent carbon atom would thus show five stages in the series of oxidation and reduction according as to whether its valencies are all positive, all negative, or some positive and others negative. Similarly, a trivalent nitrogen atom presents four stages, corresponding with its states of oxidation in ammonia, hydroxylamine, hyponitrous acid, and nitrous acid, whilst a quinquevalent nitrogen atom presents six stages.

A consideration of the transformations characteristic of primary amines,  $R \cdot CH_2 \cdot NH_2$ , aldimides,  $R \cdot CH : NH$ , nitriles,  $R \cdot C : N$ , nitrile oxides,  $R \cdot C : N : O$ , and related compounds suggested that the electronic hypothesis might be used to elucidate the relations between these compounds and to indicate a mechanism in terms of which their transformations might be represented more precisely than by the ordinary structural formulæ. A discussion is therefore given on these lines of the relations (1) between primary amines and their products of hydrolysis; (2) between aldimides,  $\beta$ -alkylhydroxylamines, and aldehyde ammonias; (3) between nitriles, aldoximes, and amides; (4) between nitrile oxides, isonitroparaffins, and hydroxamic acids, and (5) between hydroxamic acids, carbimides, and carbamic acids.

It is stated that the various reactions generally regarded as examples of the Beckmann rearrangement consist in every case of processes of

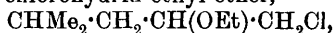
\*and *J. Pharm. Chim.*, 1914, [vii], 9, 225—230.

intramolecular oxidation and reduction; and the bearing of this on the mechanism of the rearrangement is discussed in the light of the electronic hypothesis. E. G.

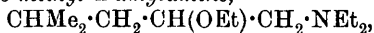
**The Preparation of Hydramine Ethers and Hydramines and a New Way to the Choline Group.** J. HOUBEN and K. FÜHRER (*Ber.*, 1914, 47, 75—82).—The interaction of  $\alpha\beta$ -dichloroethyl ether and organomagnesium compounds to produce substances of the type  $\text{OEt}\cdot\text{CHR}\cdot\text{CH}_2\text{Cl}$ , as already described by the authors (*A.*, 1908, i, 73), can serve as a first step to the synthesis of several important groups of compounds because the remaining chlorine atom can be replaced in various manners. Alkali hydroxides remove the chlorine with formation of an unsaturated ether. The action of ammonia and primary amines is complicated by the usual formation of secondary and tertiary bases respectively by the further action of the halogen compound on the primary product. With dialkylamines the chemical change proceeds smoothly with formation of substances of the general formula  $\text{OEt}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NR}_2$ , in which the ethoxy-group can be converted into hydroxyl by the action of concentrated hydrobromic acid.

When butylene  $\alpha\beta$ -chlorohydrin ethyl ether,  $\text{OEt}\cdot\text{CHEt}\cdot\text{CH}_2\text{Cl}$ , was heated with a bimolecular proportion of diethylamine for twenty-four hours at  $135^\circ$ , followed by two hours at  $160^\circ$ , the major portion was converted into *diethyl- $\beta$ -ethoxy-n-butylamine*,  $\text{OEt}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{NEt}_2$ , a mobile liquid, b. p.  $179\text{—}181^\circ$ , of strong basic odour; *hydrochloride*, hygroscopic.

If *isohexylene- $\alpha\beta$ -chlorohydrin ethyl ether*,



is heated with diethylamine, first at  $100^\circ$  and then at  $130^\circ$ , the product is *diethyl- $\beta$ -ethoxy- $\delta$ -methyl-n-amylamine*,



a colourless, basic liquid, b. p.  $86\text{—}89^\circ/9\text{ mm.}$ ,  $196\text{—}206^\circ/\text{ord. pressure}$ , of characteristic odour.

*isoHeptylene chlorohydrin ethyl ether* reacted very incompletely with diethylamine at  $135^\circ$ , producing a small quantity of *diethyl- $\beta$ -ethoxy- $\epsilon$ -methyl-n-hexylamine*, b. p.  $108^\circ/9\text{ mm.}$

The interaction of phenylethylene chlorohydrin ethyl ether and diethylamine at  $128^\circ$  gave rise to *diethyl- $\beta$ -ethoxy- $\beta$ -phenylethylamine*,  $\text{OEt}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NEt}_2$ , a liquid, b. p.  $124\text{—}125^\circ/10\text{ mm.}$ , of basic odour, accompanied by a little acetophenone.

From the reaction product of phenylethylene chlorohydrin ethyl ether and ammonia, obtained by prolonged heating of the mixture in alcoholic solution at  $90^\circ$  and  $120^\circ$ , there could be separated by distillation  *$\beta$ -ethoxyphenylethylamine*,  $\text{OEt}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2$ , a strong base, b. p.  $228\text{—}230^\circ/\text{ord. pressure}$ ,  $125^\circ/20\text{ mm.}$ , of characteristic odour, and *di- $\beta$ -ethoxyphenylethylamine*,  $\text{NH}(\text{CH}_2\cdot\text{CHPh}\cdot\text{OEt})_2$ , a base of feeble odour, b. p.  $210\text{—}213^\circ/10\text{ mm.}$

In a similar manner, the interaction of phenylpropylene chlorohydrin ethyl ether and diethylamine in alcoholic solution at  $120^\circ$  produced  *$\beta$ -ethoxy- $\gamma$ -phenyl-n-propylamine*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\cdot\text{NH}_2$ , b. p.  $139\cdot5\text{—}140\cdot5^\circ/14\text{ mm.}$ , of basic odour, together with *di- $\beta$ -ethoxy- $\gamma$ -phenyl-*

*n*-propylamine,  $\text{NH}[\text{CH}_2\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\text{Ph}]_2$ , b. p. 235—236°/13 mm., the latter substance preponderating.

When diethyl- $\beta$ -ethoxybutylamine is heated with hydrobromic acid (D 149) under such conditions that the ethyl bromide produced can pass away, over 80% of the theoretical quantity of ethyl bromide can be collected in the course of five hours, and the reaction flask contains diethyl- $\beta$ -hydroxy-*n*-butylamine,  $\text{OH}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{NEt}_2$ , a colourless liquid, b. p. 63—64°/13 mm., of strong odour. It can be acetylated and its salts are easily soluble in water; *hydrochloride*, hygroscopic. The quaternary ammonium hydroxides derivable from this base will be homologues of choline.

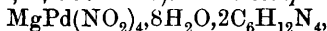
D. F. T.

**Physico-chemical Researches on Urotropine [Hexamethylenetetramine]** regarding the Constitution of the Base. C. Russo (*Gazzetta*, 1914, 44, i, 16—26).—Conductivity measurements in solutions of hexamethylenetetramine and hydrochloric, sulphuric and nitric acids show the formation of monoacid salts and their hydrolytic decomposition, but afford no indication of the formation of diacid salts. The reaction which occurs is probably represented by the formula:  $\text{C}_6\text{H}_{13}\text{N}_4^+ + \text{H}^+ + \text{H}_2\text{O} = \text{C}_5\text{H}_{14}\text{N}_4^{++} + \text{CH}_2\text{O}$ . Conductivity measurements and also measurements of the change of rotatory power of dextrose show that hexamethylenetetramine is a little more strongly basic than aniline, and this agrees with the cyclic formulæ which have been proposed rather than with the formula of Lösekann. R. V. S.

**Cobaltous Tetraborate and Hexamethylenetetramine.** G. Rossi (*Gazzetta*, 1913, 43, ii, 669—671).—Cobaltous tetraborate, although it exists in solution, cannot be prepared in the solid state. When, however, a solution of cobaltous acetate and hexamethylene-tetramine is treated with a solution of sodium tetraborate, a red, amorphous substance,  $(\text{CoB}_4\text{O}_7)_3\cdot\text{C}_6\text{H}_{12}\text{N}_4\cdot 2\text{H}_2\text{O}$ , is obtained.

R. V. S.

**Some Palladionitrites of Bivalent Metals Fixed by means of Organic Bases.** G. SCAGLIARINI and G. B. ROSSI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 506—508).—The compound,



is a straw-yellow, crystalline substance which is obtained by the gradual addition of a cold solution of palladium chloride and sodium nitrite, slightly acidified with hydrochloric acid, to a cold, saturated solution of magnesium nitrite and hexamethylenetetramine, obtained by adding the requisite quantity of sodium nitrite and hexamethylenetetramine to a solution of magnesium acetate.

The compound,  $\text{MnPd}(\text{NO}_2)_4\cdot 8\text{H}_2\text{O}\cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ , forms yellow crystals.

The compound,  $\text{NiPd}(\text{NO}_2)_4\cdot 8\text{H}_2\text{O}\cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ , forms emerald-green crystals.

The compound,  $\text{CoPd}(\text{NO}_2)_4\cdot 8\text{H}_2\text{O}\cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ , forms pink crystals, which rapidly alter in air, so that the preparation is best carried out in an atmosphere of hydrogen. The substance is isomorphous with the corresponding magnesium and manganese compounds, and forms solid solutions with them.

R. V. S.



**Study of Some New Alkylhydroxylamines.** CHARLES H. HECKER (*Amer. Chem. J.*, 1913, 50, 444—466).—This work was undertaken with the object of discovering methods for readily obtaining good yields of alkylhydroxylamines.  $\alpha\beta$ -Dialkylhydroxylamines have been prepared by Jones' method (A., 1907, i, 897), which consists in the hydrolysis of a hydroxyalkylurethane ether (carbethoxy- $\alpha\beta$ -dialkylhydroxylamine).

By the action of ethyl iodide on carbethoxy- $\alpha$ -ethylhydroxylamine (hydroxyurethane ethyl ether) (Jones, A., 1898, i, 174) in presence of sodium ethoxide, carbethoxy- $\alpha\beta$ -diethylhydroxylamine (hydroxy-ethylurethane ethyl ether),  $\text{CO}_2\text{Et}\cdot\text{NEt}\cdot\text{OEt}$ , b. p.  $72-74^\circ/12$  mm., is obtained, which, when heated with potassium hydroxide solution in a sealed tube at  $100^\circ$ , is converted into  $\alpha\beta$ -diethylhydroxylamine.

Carbethoxy- $\alpha$ -ethyl- $\beta$ -propylhydroxylamine,  $\text{CO}_2\text{Et}\cdot\text{NPr}^\alpha\cdot\text{OEt}$ , has b. p.  $189^\circ/740$  mm.; on hydrolysis it yields  $\alpha$ -ethyl- $\beta$ -propylhydroxylamine,  $\text{NHPr}^\alpha\cdot\text{OEt}$ , b. p.  $83.8-84^\circ$ ,  $D_{25}^{25}$  0.8033,  $n_D^{25}$  1.39426, which is a colourless liquid with an ammoniacal odour and a sweet, pungent taste; the hydrochloride has m. p.  $72.5-73^\circ$ .

Carbethoxy- $\alpha$ -ethyl- $\beta$ -isopropylhydroxylamine has b. p.  $182^\circ/748$  mm. and  $84-87^\circ/15$  mm.  $\alpha$ -Ethyl- $\beta$ -isopropylhydroxylamine, b. p.  $78^\circ$ ,  $D_{25}^{25}$  0.8132, has an odour like that of ethylamine; its platinichloride forms small, lemon-yellow crystals.

By the action of propyl iodide on the potassium salt of hydroxyurethane there are produced carbethoxy- $\alpha$ -propylhydroxylamine,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{OPr}^\alpha$ , b. p.  $109-111^\circ/15$  mm., and carbethoxy- $\alpha\beta$ -dipropylhydroxylamine,  $\text{CO}_2\text{Et}\cdot\text{NPr}^\alpha\cdot\text{OPr}^\alpha$ , b. p.  $107.5-108^\circ/20$  mm.  $\alpha$ -Propylhydroxylamine,  $\text{NH}_2\cdot\text{OPr}^\alpha$ , b. p.  $86.6-87^\circ$ ,  $D_{25}^{25}$  0.8687, obtained by the hydrolysis of carbethoxy- $\alpha$ -propylhydroxylamine, is a colourless liquid with a sweet, ammoniacal odour; its hydrochloride, m. p.  $140-141^\circ$ , and platinichloride are described.  $\alpha\beta$ -Dipropylhydroxylamine, b. p.  $85-86^\circ$ ,  $D_{25}^{25}$  0.8141, obtained by the hydrolysis of carbethoxy- $\alpha\beta$ -dipropylhydroxylamine, yields a hydrochloride, m. p.  $146.6^\circ$ , and a platinichloride.

Carbethoxy- $\beta$ -ethyl- $\alpha$ -propylhydroxylamine,  $\text{CO}_2\text{Et}\cdot\text{NEt}\cdot\text{OPr}^\alpha$ , has b. p.  $191^\circ/750$  mm. and  $92.5^\circ/20$  mm., and on hydrolysis furnishes  $\beta$ -ethyl- $\alpha$ -propylhydroxylamine, which gives a hydrochloride, m. p.  $96.2^\circ$ , and a platinichloride.

Carbethoxy- $\alpha$ -isopropylhydroxylamine, b. p.  $102-103^\circ/12$  mm., is almost odourless; carbethoxy- $\alpha\beta$ -diisopropylhydroxylamine has b. p.  $101-101.5^\circ/15$  mm.  $\alpha$ -iso-Propylhydroxylamine, b. p.  $72.2^\circ$  (uncorr.),  $D_{25}^{25}$  0.8459, has a pungent, disagreeable odour; its hydrochloride has m. p.  $84.8^\circ$ .  $\alpha\beta$ -Diisopropylhydroxylamine, b. p.  $76.6-77^\circ$ ,  $D_{25}^{25}$  0.8525, yields a hydrochloride, m. p.  $74.8^\circ$ .

Carbethoxy- $\beta$ -ethyl- $\alpha$ -isopropylhydroxylamine has b. p.  $181-182^\circ$ , and on hydrolysis furnishes  $\beta$ -ethyl- $\alpha$ -isopropylhydroxylamine, b. p.  $82^\circ$ ,  $D_{25}^{25}$  0.8730; the hydrochloride and platinichloride of the latter are described.

The carbethoxy-alkyl- and -dialkylhydroxylamines are colourless oils with characteristic odours, and do not reduce silver nitrate or Fehling's solution. The  $\alpha$ -alkylhydroxylamines and the  $\alpha\beta$ -dialkylhydroxylamines containing two identical groups are readily soluble in

water, whilst the mixed  $\alpha\beta$ -dialkylhydroxylamines are not very soluble. Aqueous solutions of the  $\alpha$ -alkylhydroxylamines exert an energetic reducing action, but the  $\alpha\beta$ -dialkylhydroxylamines are much less active in this respect. E. G.

**Glycocyamidine.** ERNST SCHMIDT (*Arch. Pharm.*, 1913, 251, 557—562).—The conversion of glycoeyamine into glycoeyamidine by hydrochloric acid is much more difficult than that of creatine into creatinine (Körndorfer, A., 1905, i, 29). A nearly quantitative conversion can be effected by heating glycoeyamine, just covered with concentrated sulphuric acid, in a steam-bath for twenty-four hours; the solution is diluted with water, freed from sulphuric acid by aqueous barium hydroxide, and finally barium carbonate, and evaporated to dryness, the residue of glycoeyamidine is dissolved in boiling alcohol and a little water, and crystallised therefrom by spontaneous evaporation. The *aureichloride*,  $C_3H_5ON_3 \cdot HAuCl_4$ , m. p.  $158^\circ$ , has been prepared. C. S.

**Synthesis of  $\psi$ -Leucine.** F. KNOOP and GEORG LANDMANN (*Zeitsch. physiol. Chem.*, 1914, 89, 157—159).—This substance,  $\psi$ -butylaminoacetic acid, has been synthesised from trimethylpyruvic acid, which yields an *oxime*,  $C_6H_{11}O_3N \cdot H_2O$ , m. p.  $85$ — $86^\circ$  (anhydrous  $121^\circ$ , decomp.). When the oxime is reduced by boiling with zinc dust and 50% acetic acid, or with aluminium amalgam in 50% alcohol,  $\psi$ -leucine,  $C_6H_{13}O_2N$ , is obtained; it forms hard, laminar crystals, which begin to sublime at  $250^\circ$ . The *naphthalenesulphonyl* derivative,  $C_{16}H_{19}O_4NS$ , forms long, acicular prisms, m. p.  $200$ — $203^\circ$ . The *p-toluenesulphonyl* derivative,  $C_{18}H_{19}O_4NS$ , crystallises in short, rectangular prisms, m. p.  $226^\circ$ . The *nitrate* forms needles, m. p. about  $151^\circ$ . R. V. S.

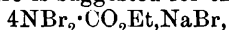
**The Action of Chlorine on Ethyl Carbamate.** The Isolation of Ethyl Chlorocarbamate and its Behaviour towards Amines and Acid Amides. RASIK LAL DATTA and SATYARANJAN DAS GUPTA (*J. Amer. Chem. Soc.*, 1914, 36, 386—390).—Although Schmidt (*J. pr. Chem.*, 1881, [ii], 24, 120) failed to obtain ethyl chlorocarbamate by the action of chlorine on ethyl carbamate at  $90$ — $100^\circ$ , this substance can be obtained if the reagents are brought together in well-cooled aqueous solution.

A current of chlorine is passed into a dilute aqueous solution of ethyl carbamate, when a yellow oil separates, which from its behaviour towards potassium iodide must be *ethyl chlorocarbamate*,  $NHCl \cdot CO_2Et$ . It is a pale yellow, rather viscous oil,  $n_D^{30}$  1.44235, b. p. near  $99^\circ$  (decomp.). When kept either alone or under water it gradually decomposes. It has a pungent odour resembling the chlorocarbamides, and painfully affects the skin, causing a violet-black coloration or even a scar.

Ethyl chlorocarbamate is an energetic chlorinating agent, but less vigorous than dichlorocarbamide. With benzylamine it produces benzyl-chloroamine or -dichloroamine according to the relative amount

of the reagents, whilst with benzamide the product is benzoyl-chloroamide.

An alternative structure is suggested for the substance,



described by Hantzsch (A., 1894, i, 363).

D. F. T.

**The Hydrolysis of Salts.** NILRATAN DHAR (*Zeitsch. anorg. Chem.*, 1914, 85, 198—205).—The electrical conductivity of solutions of carbamide nitrate and oxalate has been determined at 30°. Both salts are hydrolysed to a considerable extent, even in the presence of an excess of the corresponding acid.

C. H. D.

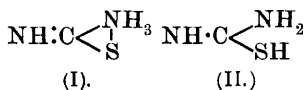
**Action of Bromine and Alkali Hydroxide on Carbamide and Guanidine Derivatives.** II. V. VON CORDIER (*Monatsh.*, 1914, 35, 9—45. Compare A., 1912, i, 684).—The author has extended his work and obtained results which, for the main part, confirm those previously described. Decomposition has generally been effected with sodium hypobromite, occasionally with potassium hypobromite. Reaction generally takes place at the ordinary temperature, but in certain cases slight cooling is necessary to moderate the violence. In many cases, reaction occurs with extreme slowness.

The most important new results may be summarised as follows:

In the case of derivatives of thiocarbamide, either no nitrogen or only one atom is evolved. The first behaviour is shown by all derivatives containing univalent radicles as substituents, which have been hitherto assumed to be constituted according to the symmetrical formula. As previously observed, the influence of the sulphur atom is restricted to the portion of the molecule in which it is contained. The second mode of reaction (elimination of 1 atom of nitrogen), which had been previously observed only in the case of methylenethiocarbamide, occurs when bivalent radicles are contained as substituents in the thiocarbamide molecule. As an alternative to the hypothesis of a restrictive action of the sulphur atom, it is possible that the constitution of the thiocarbamide molecule may be the deciding factor, and that derivatives of it are not produced from the symmetrical form; those compounds which do not yield nitrogen are constituted according to the formula (I) of Werner (T., 1912, 101, 2180), whilst those giving 1 atom of nitrogen are derived from the *iso*-form of thiocarbamide (II) (compare Storch, A., 1891, 548).

Selenocarbamide evolves a certain amount of nitrogen, which, however, does not attain the quantity calculated for one atom.

A regularity in the evolution of nitrogen from alkyl derivatives of carbamide or guanidine could not be observed. This influence of alkyl groups is also apparent in the case of substances which contain, in addition, other substituents (acetylmethylcarbamide, nitrosomethylcarbamide, creatine) and is probably exercised in additive compounds when the added component contains an alkyl (methyl) group; thus guanidinesarcosine hydrochloride in contrast to glycine guanidine



(I.)

(II.)

carbonate, reacts with hypobromite solution as an ordinary additive compound, that is, it immediately gives the normal amount of nitrogen and no more, which is probably due to the methyl group of the sarcosine.

Contrary to the opinion expressed in the previous publication, no general conclusions can be drawn from the results which have been obtained up to the present with halogen derivatives (bromo- and chloro-guanidine).

As far as can be judged, the nitroso-group (nitrosoguanidine, nitroso-methylcarbamide) appears to behave in the same manner as the nitro-group, that is, it does not appear to hinder the evolution of nitrogen and, itself, yields free nitrogen; on the other hand, the oximino-group (violuric acid) has apparently no influence on the evolution of nitrogen.

In the compounds of carbamide with metallic oxides (carbamide mercuric oxide,  $\text{CO}(\text{NH}_2)_2 \cdot 3\text{HgO}$ ), the latter substances do not inhibit the evolution of nitrogen.

Nitrogen is only very slowly evolved by the action of hypobromite solutions on melamine, and the amount corresponds but poorly with that calculated for one atom. The author is therefore led to the conclusion that melamine does not contain a free amino-group, and thus regards the formula  $\text{NH}:\text{C} \begin{smallmatrix} \text{NH}\cdot\text{C}(\text{NH}) \\ \text{NH}\cdot\text{C}(\text{NH}) \end{smallmatrix} \text{NH}$  as the most probable.

H. W.

**Ethyl Diazoacetate and Thiocyanic Acid.** BROR HOLMBERG (*Ber.*, 1914, 47, 165—166).—The speed of the reaction between the thiocyanate ion and ethyl diazoacetate has been measured by the method employed in the study of the influence of the sulphate and nitrate ions (A., 1908, i, 387). The thiocyanate ion is approximately as active as the iodine ion. On a preparative scale, 20 grams of ethyl thiocyanacetate were obtained by gradually acidifying a mixture of 150 grams of potassium thiocyanate in 200 c.c. of water and 34 grams of ethyl diazoacetate, the decomposition of the latter almost exclusively following the course:  $\text{N}_2\text{CH}\cdot\text{CO}_2\text{Et} + \text{H} + \text{SCN} = \text{NC}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{N}_2$ .

J. C. W.

**Physico-chemical Investigations of Some Complex Cuprous Salts.** NILRATAN DHAR (*Zeitsch. anorg. Chem.*, 1914, 85, 44—48).—Cuprous thiocyanate dissolves in solutions of alkali thiocyanates, but is re-precipitated on dilution. The conductivity of solutions of ammonium or potassium thiocyanate is lessened by the addition of cuprous thiocyanate, indicating the formation of a complex ion,  $\text{Cu}(\text{CNS})_n$ .

C. H. D.

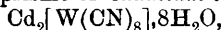
**Reactions in Non-Aqueous Solutions. VI. In Acetonitrile.** ALEX. NAUMANN [with ADAM SCHIER] (*Ber.*, 1914, 47, 247—256. Compare A., 1910, ii, 211).—Qualitative and quantitative measurements of the solubilities in anhydrous acetonitrile of a large number of different salts, and also of the halogens have been made. The

following efflorescent compounds with acetonitrile of crystallisation were obtained:  $\text{CuCl}_2 \cdot 2\text{MeCN}$ ,  $\text{CuCl}_2 \cdot \text{MeCN}$ ,  $\text{CuBr}_2 \cdot \text{MeCN}$ ,  $\text{CuI}_2 \cdot 2\text{MeCN}$ ,  $\text{CaCl}_2 \cdot \text{MeCN}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot \text{MeCN}$ ,  $\text{ZnCl}_2 \cdot 2\text{MeCN}$ ,  $\text{CoCl}_2 \cdot 3\text{MeCN}$ . The reactions of the haloid salts of copper, cobalt, iron (ferrie), bismuth, zinc and tin (stannous) with various reagents in acetonitrile solution were also studied qualitatively, and a number of abnormal reactions observed. T. S. P.

**Univalent Compounds of Nickel.** III. I. BELLUCCI and R. CORELLI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 485—489. Compare A., 1913, ii, 604; i, 839).—By effecting the reduction of a solution of nickelocyanide (yellow) with potassium amalgam in an atmosphere of hydrogen and adding to the red solution an excess of alcohol, the atmosphere of hydrogen being maintained, the authors have isolated the red cyano-salt, and find it has the formula  $\text{K}_2\text{Ni}(\text{CN})_3$ , so that it contains univalent nickel. When its solution is acidified, an orange-yellow precipitate is formed, which is *nickel monocyanide*,  $\text{NiCN}$ . It is very readily oxidised, forming nickelic cyanide,  $\text{Ni}(\text{CN})_2$ . R. V. S.

**Tungsten Cyanides.** ARTHUR ROSENHEIM and EITEL DEHN (*Ber.*, 1914, 47, 392—400).—Several years ago, Rosenheim described a molybdenum cyanide,  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ , in which the molybdenum acted towards oxidising agents as a quinquevalent metal, although, according to the formula, it should be quadrivalent (compare A., 1910, i, 101, 232). The authors have now prepared corresponding compounds of tungsten, which show a similar behaviour.

A solution of Marignac's compound,  $\text{H}_8[\text{Si}(\text{W}_2\text{O}_7)_6] \cdot 28\text{H}_2\text{O}$ , in concentrated hydrochloric acid is reduced electrolytically in the apparatus described by Rosenheim and Loebel (A., 1908, ii, 294) until the solution becomes greenish-yellow in colour. The excess of acid is then quickly neutralised with strong alkali hydroxide, a large excess of potassium cyanide added, and the solution concentrated on the water-bath. A similar solution may be obtained by treating the compound  $\text{K}_3\text{W}_2\text{Cl}_9$ , described by Olsson (A., 1913, ii, 328), directly with potassium cyanide. When this solution is treated with a concentrated solution of cadmium sulphate and digested on the water-bath, an impure cadmium salt separates; this is dissolved in concentrated ammonia solution, and the solution saturated with ammonia whilst cooled in a freezing mixture. Long, golden-yellow needles of the *cadmiumtriammine tungsten cyanide*,  $[\text{Cd}(\text{NH}_3)_3]_2[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  separate, in which the tungsten acts as a quinquevalent element towards oxidation with potassium permanganate, although according to the formula it should be quadrivalent. On exposure to the air, or on washing with water, one molecule of ammonia is lost, giving the corresponding *diammine salt*,  $[\text{Cd}(\text{NH}_3)_2]_2[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ . On treatment with 1—2% sulphuric acid, microscopic, yellow prisms of *cadmium tungsten cyanide*,



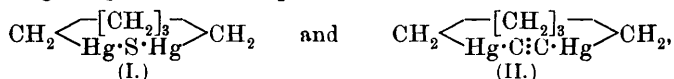
are obtained, from which the *potassium salt*,  $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ , is obtained as light yellow, microscopic prisms by double decomposition

with potassium carbonate. All these salts act in the same way as the triammine salt towards potassium permanganate.

A tentative explanation of the anomalous behaviour is given.

T. S. P.

**Mercury Derivatives of  $\alpha\epsilon$ -Dibromopentane and Multi-membered Ring Systems Derived from Them.** SIEGFRIED HILPERT and GERHARD GRÜTTNER (*Ber.*, 1914, 47, 177—185).—The discovery of the magnesium compounds of the  $\omega\omega'$ -dihalogenoparaffins has opened up the way of preparing simple mercury derivatives of the higher aliphatic hydrocarbons. When an ethereal solution of the magnesium compound of  $\alpha\epsilon$ -dibromopentane (von Braun and Sobecki, A., 1911, i, 701), for example, is treated with powdered mercuric bromide, it is converted, quantitatively, into pentamethylene- $\alpha\epsilon$ -dimercuri-dibromide. The mercury atoms are very firmly attached, but the halogen atoms are reactive; thus the compound can be converted into the iodide, nitrate or hydroxide. Hydrogen sulphide and acetylene form ring compounds, the simplest formulæ for which would be:



although the substances may be polymerides. The replacement of the bromine atoms by a dibasic acid radicle gives rise to ring systems containing oxygen; thus azelaic acid forms a compound with eighteen members in the ring. The bromide also reacts with magnesium phenyl bromide, yielding the remarkable compound, pentamethylene- $\alpha\epsilon$ -dimercuridiphenyl,  $\text{Ph} \cdot \text{Hg} \cdot [\text{CH}_2]_5 \cdot \text{Hg} \cdot \text{Ph}$ , a representative of mixed mercury dialkyls, of which other members will soon be described.

The results obtained by Grignard (A., 1907, i, 687) and by von Braun (*loc. cit.*) in the action of magnesium on  $\alpha\epsilon$ -dibromopentane do not coincide. The latter was able to show in his experiment, that only about 50% of the normal organomagnesium salt had been formed, whereas the former obtained products which corresponded with a high yield of that salt. The reaction with mercuric bromide affords a clue to the actual amount of normal magnesium derivative present. If the reaction is accelerated by using very dry ether and activated magnesium, a 50% yield is obtained, whereas with imperfectly dry ether the reaction is slow but the yield is 90%.

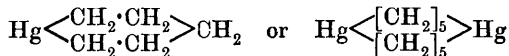
*Pentamethylene- $\alpha\epsilon$ -dimercuri-dibromide*,  $\text{C}_5\text{H}_{10}\text{Hg}_2\text{Br}_2$ , forms white, doubly refractive needles from toluene, m. p.  $150^\circ$ . It is very soluble in pyridine, but when not quite pure is blackened by that base. When boiled with alcoholic potassium iodide it yields the *di-iodide* in slender, white needles, m. p.  $117^\circ$ , whilst hydrogen sulphide precipitates the *sulphide* (I) from a cold pyridine solution, quantitatively, as a snow-white, odourless, insoluble powder. The *hydroxide* was obtained by boiling the bromide with silver oxide in 80% alcohol. It forms very slender, white needles. Sulphuric acid gradually precipitated the *sulphate*,  $\text{C}_5\text{H}_{10}\text{Hg}_2\text{SO}_4$ , from a 50% alcoholic solution of the hydroxide, in microscopic, white needles which suddenly blacken above  $150^\circ$ . The *nitrate* was obtained by treating the bromide with silver nitrate. Its solution in alcohol was used to prepare the *chloride*, white needles,

m. p. 184°, the *oxalate*, *succinate* and *ferrocyanide*, white precipitates, the *azelate*,  $C_{14}H_{24}Hg_2O_4$ , white scales, and the *acetylide* (II), a white precipitate which takes fire on heating.

*Pentamethylene- $\alpha$ -dimercuridiphenyl* was obtained as a colourless, viscous oil with repulsive smell. It only begins to decompose in vacuum at 180°. It quickly decolorises iodine in benzene at 35°, forming the above di-iodide, and on prolonged boiling with the solution, decomposes into mercuric iodide,  $\alpha$ -di-iodopentane, and iodobenzene.

J. C. W.

**Heterocyclic Systems Containing Metals. I. *cyclo*Mercuripentamethylene.** SIEGFRIED HILPERT and GERHARD GRÜTTNER (*Ber.*, 1914, 47, 186—196).—Attempts have been made to prepare simple mercury-carbon ring compounds by the action of sodium amalgam on  $\omega$ '-dihalogenoparaffins. Ethylene and trimethylene bromides did not react, but  $\alpha$ -dibromopentane gave a mixture of a small quantity of a well-defined, crystalline solid, m. p. 120°, a larger amount of a substance, m. p. 41°, but chiefly an oil. They have the same empirical formula,  $C_5H_{10}Hg$ , and are identical in their reactions. Of these, the most characteristic is the behaviour towards bromine or iodine. These agents cause the formation of the pentamethylene- $\alpha$ -dimercury haloids (preceding abstract) and the dihalogenopentanes. Mercuric haloids also produce the same mercury compounds. The results can be interpreted on the basis of either of the annexed formulæ:



The estimation of the molecular weights of mercury compounds in general by ebullioscopic methods gives unsatisfactory results, but the product, m. p. 120°, corresponded roughly with the simple ring, M.W. 270; the substance, m. p. 41°, has four times this molecular weight, and the oil, six times. Certainly, the latter are polymerides, the *cyclomercuripentamethylene* corresponding with the polymethylene-oxygen and -sulphur ring compounds in its readiness to undergo polymerisation.

Thirty grams of  $\alpha$ -dibromopentane, 100 grams of benzene, 3 grams of ethyl acetate, and 900 grams of 1% sodium amalgam were shaken for twenty hours at 75° in a pressure flask, when the solvent layer was washed, evaporated, and the residue extracted with absolute alcohol. The insoluble, wax-like product (23 grams) was extracted with light petroleum and ether, leaving the compound, m. p. 41° (6.5 grams). The extract was allowed to evaporate, when the substance, m. p. 120° (2.5 grams), crystallised and was filtered from the oil.

*cycloMercuripentamethylene* forms hard, white, rhombic, doubly refractive crystals, m. p. 120°, from a mixture of benzene and light petroleum. The solid *polymeride* was purified by crystallisation from much ether and obtained as a white powder, m. p. 41°. The behaviour of these and of the polymeric oil towards bromine, iodine, and mercuric haloids is described. The reaction with iodine at about 35° was followed quantitatively, and theoretical yields of pentamethylenedimercuri-iodide and di-iodopentane were obtained.

J. C. W.

**Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences. I. Anomalous Behaviour of Certain Derivatives of Benzene.** HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1914, **36**, 248—262).—The theory given in previous papers (A., 1911, i, 431; 1912, ii, 713) is applied to explain: (1) the formation of the different disubstituted benzene derivatives when chlorobenzene and nitrobenzene are respectively nitrated and chlorinated; (2) the exchange of halogen for hydroxyl when *o*- and *p*-bromonitrobenzene are treated with potassium hydroxide, whereas the meta-compound is not affected; (3) the action of the halogens on silver benzoate; (4) the elimination of only one molecule of carbon dioxide from the dihydrophthalic acids when oxidised; (5) the elimination of carbon dioxide from *o*- and *p*-hydroxybenzoic acids, but not from the meta-isomeride, when heated with water or aniline; (6) the elimination of carbon dioxide from ethyl chloroformate by heating with pyridine. In the latter case, experimental evidence is given in support of the author's theory, which predicts the formation of an unstable, intermediate compound.

According to the author, theory and various chemical reactions show that ethyl chlorocarbonate is the only correct name for the compound,  $\text{Cl}\cdot\text{CO}_2\text{Et}$ , and not ethyl chloroformate, as it is often called.

T. S. P.

**Positive and Negative Hydrogen, the Electronic Formula of Benzene, and the Nascent State.** HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1914, **36**, 262—272).—Applying the principles given in his previous papers (see preceding abstract), the author considers the evidence for the existence of positive and negative hydrogen and for the electronic formula of benzene, in which the hydrogen atoms are alternatively positive and negative. The nascent state of an element is defined to be "an unstable condition of a substance which manifests an adaptability and a tendency to lose or gain electrons and thereby revert to a more stable condition. If the substance (ion, atom, or compound) lose negative electrons, it acts as a reducing agent. If it combines with negative electrons it acts as an oxidising agent." As a matter of fact, practically all actions classed as "nascent" are of an oxidation or reduction type.

T. S. P.

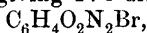
**The Crystallographic Properties of Dichlorobenzene.** FRED. WALLERANT (*Compt. rend.*, 1914, **158**, 385—386).—Dichlorobenzene is trimorphous under atmospheric pressure, and the three states can co-exist at the ordinary temperature, side by side in the same mass. The reversible transformations occur at 25° and 29°, the three forms being biaxial, monoclinic, and having the plane of the optical axes coinciding with the plane of symmetry. The author gives an account of these forms and the changes they undergo.

W. G.

**Dinitro-derivatives of Meta-dihalogenated Benzenes.** W. KÖRNER and CONTARDI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 625—634).—With the dibromodinitrobenzene described below, the whole of the eleven possible isomerides have been prepared. The crystallographic examinations were made by E. Artini.



3:5-Dibromo-1:2-dinitrobenzene,  $C_6H_2Br_2(NO_2)_2$ , prepared by the action of nitric and sulphuric acids on 3:5-dibromo-1-nitrobenzene, forms almost colourless crystals, m. p.  $84.8^\circ$ , and is trimorphous. The  $\alpha$ -modification belongs to the prismatic class of the monoclinic system,  $a:b:c = 1.4301:1:1.1901$ ,  $\beta = 81^\circ 39'$ ,  $D = 2.317$ ; the  $\beta$ -modification to the rhombic system,  $a:b:c = 1.7917:1:0.5667$ ,  $D = 2.279$ ; and the  $\gamma$ -modification to the prismatic class of the monoclinic system,  $a:b:c = 1.7040:1:0.5280$ ,  $\beta = 86^\circ 27'$ ,  $D = 2.274$ . It reacts with alcoholic ammonia, even in the cold, giving 4:6-dibromo-2-nitroaniline,



m. p.  $127^\circ$ .

3:5-Dichloro-1:2-dinitrobenzene,  $C_6H_2Cl_2(NO_2)_2$ , obtained similarly to the preceding compound, forms tetragonal crystals,  $a:c = 1:1.9767$ , m. p.  $95^\circ$ ,  $D = 1.773$ , and is hence neither isomorphous nor isosymmetrical with the corresponding dibromo-derivative.

2:4-Dibromo-1:3-dinitrobenzene,  $C_6H_2Br_2(NO_2)_2$ , obtained by nitrating 2:6-dibromo-1-nitrobenzene, forms well-developed, greenish-yellow, triclinic prisms, m. p.  $82.8^\circ$ , and, on further nitration in presence of sulphuric acid, gives 2:4-dibromo-1:3:5-trinitrobenzene,  $C_6HBr_2(NO_2)_3$ , in greenish-yellow prisms, m. p.  $135^\circ$ . With alcoholic ammonia, the latter compound forms 2:4:6-trinitro-*m*-phenylenediamine as a yellow powder, m. p. above  $200^\circ$  (decomp.), and this is converted by potassium hydroxide into potassium styphnate.

4:6-Dibromo-2:5-dinitroaniline,  $C_6HBr_2(NO_2)_2 \cdot NH_2$ , obtained by the action of bromine on a suspension of 2:5-dinitroaniline in hydrobromic acid, forms orange-yellow needles, m. p.  $143^\circ$ .

3:5-Dibromo-1:4-dinitrobenzene,  $C_6H_2Br_2(NO_2)_2$ , obtained by the spontaneous decomposition, in presence of ice, of the nitrite of the diazo-compound of 2:6-dibromo-4-nitroaniline, forms yellow, striated, monoclinic prisms, m. p.  $130^\circ$ .

3:5-Dichloro-1:4-dinitrobenzene,  $C_6H_2Cl_2(NO_2)_2$ , obtained similarly to the preceding compound from 2:6-dichloro-4-nitroaniline, forms shining, colourless prisms, m. p.  $114^\circ$ .

3:5-Di-iodo-1:4-dinitrobenzene,  $C_6H_2I_2(NO_2)_2$ , prepared similarly to the two preceding compounds, forms monoclinic prisms, m. p.  $155^\circ$ .

3-Chloro-5-bromo-1:4-dinitrobenzene,  $C_6H_2ClBr(NO_2)_2$ , prepared similarly from 2-chloro-6-bromo-4-nitroaniline, forms almost colourless needles or prisms, m. p.  $114.5^\circ$ .

3-Chloro-5-iodo-1:4-dinitrobenzene,  $C_6H_2ClI(NO_2)_2$ , similarly prepared, forms slender, white needles or prisms, m. p.  $100^\circ$ .

3-Bromo-5-iodo-1:4-dinitrobenzene,  $C_6H_2BrI(NO_2)_2$ , similarly prepared, forms monoclinic crystals, m. p.  $140^\circ$ .

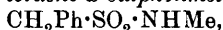
Each of these dihalogenated dinitrobenzenes is converted by alcoholic ammonia into the dihalogenated nitroaniline from which it was prepared.

T. H. P.

Researches on Amines. IV. The Alkylation and Hydrolysis of Aliphatic Sulphonamides. A New Synthesis of Sarcosine. TREAT B. JOHNSON and JOSEPH A. AMBLER (*J. Amer. Chem. Soc.*, 1914, **36**, 372—385).—Toluene- $\omega$ -sulphonamide is especially well adapted to the synthesis of amines by Hinsberg's method (A., 1892, 64) as

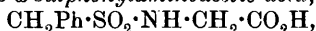
the toluene- $\omega$ -sulphonic acid produced on hydrolysis with hydrochloric acid undergoes complete decomposition into sulphur dioxide and benzyl chloride, thus obviating the necessity of the precipitation of the synthesised base before its hydrochloride can be separated.

Toluene- $\omega$ -sulphonamide,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}_2$ , possesses acidic properties and gives a *sodium* and a *potassium* salt, the latter forming micaceous flakes. Both these salts react with a warm alcoholic solution of methyl iodide, producing *toluene- $\omega$ -sulphonmethylamide*,



colourless needles, m. p.  $109-110^\circ$ , together with *toluene- $\omega$ -sulphondimethylamide*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NMe}_2$ , thin plates, m. p.  $102-103^\circ$ , which are readily separable by potassium hydroxide solution in which the latter is insoluble.

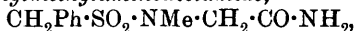
In a similar manner the potassium salt when digested with an alcoholic solution of ethyl bromoacetate undergoes condensation to form *ethyl toluene- $\omega$ -sulphonylaminoacetate*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , a viscous oil which on hydrolysis with the requisite amount of potassium hydroxide is converted into the corresponding *potassium* salt, a colourless powder. Condensation of toluene- $\omega$ -sulphonamide with chloroacetamide in an analogous manner gives rise to the formation of *toluene- $\omega$ -sulphonylaminoacetamide*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , small, granular crystals, m. p.  $157^\circ$ , which on digestion with sodium hydroxide solution gives *toluene- $\omega$ -sulphonylaminoacetic acid*,



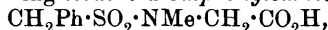
plates, m. p.  $149-150^\circ$ ; this can also be obtained, but in poor yield, by the interaction of toluene- $\omega$ -sulphonyl chloride and glycine in the presence of alkali. This acid when heated with ammonium thiocyanate in acetic anhydride containing a little acetic acid yields 3-*toluene-*

*$\omega$ -sulphonyl-2-thiohydantoin*,  $\begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{NH}-\text{CS} \end{array} > \text{N}\cdot\text{SO}_2\cdot\text{CH}_2\text{Ph}$ , yellow prisms, m. p.  $204^\circ$  (decomp.).

*Toluene- $\omega$ -sulphonylmethylaminoacetamide*,



colourless crystals, m. p.  $206^\circ$ , can be obtained by the action of methyl iodide on toluene- $\omega$ -sulphonylaminoacetamide, as also of chloroacetamide on toluene- $\omega$ -sulphonmethylamide. It is hydrolysed quantitatively by barium hydroxide, giving *toluene- $\omega$ -sulphonylsarcosine*,



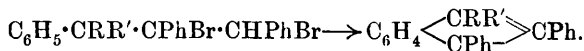
colourless prisms, m. p.  $136^\circ$ , which is slowly hydrolysed further by hydrochloric acid with formation of sarcosine,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , the accompanying benzyl chloride being easily evaporated away over a steam-bath.

*Toluene- $\omega$ -sulphonbenzylamide*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , was prepared analogously to the methyl and ethyl derivatives above by interaction of benzyl chloride and the potassium derivative of toluene- $\omega$ -sulphonamide; it forms colourless needles, m. p.  $145-146^\circ$ , and for its hydrolysis needs to be heated with hydrochloric acid at  $130^\circ$ , when benzylamine is produced.

D. F. T.

**A New Synthesis of Some Indene Derivatives.** ALEX. ORECHOFF (*Ber.*, 1914, 47, 89-95).—In the course of an investigation

on the pinacolin rearrangement, the author has submitted deoxy benzoin pinacone,  $\text{CH}_2\text{Ph}\cdot\text{CPh}(\text{OH})\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\text{Ph}$ , to the action of acetyl chloride with the result that  $\alpha\beta\gamma\delta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -butadiene was found amongst the products. The dibromide of this hydrocarbon when boiled with acetic acid yields 2:3-diphenyl-1-benzylideneindene, and examination indicates that this is but one case of a general method for the formation of an indene ring. The changes are represented by the general formulæ  $\text{C}_6\text{H}_5\cdot\text{CRR}'\cdot\text{CPh}\cdot\text{CHPh}\rightarrow$



[In part with (Miss) R. GRINBERG.]—When deoxybenzoin pinacone is heated with boiling acetyl chloride,  $\alpha\beta\gamma\delta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -butadiene,  $\text{CHPh}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{CHPh}$ , begins to crystallise after one and a-half hours, but the heating should be extended to four to five hours. The hydrocarbon, colourless needles, m. p. 183—184°, on oxidation with chromic acid in acetic acid solution, gives a mixture in which benzaldehyde, benzoic acid, and benzylidenedeoxybenzoin,  $\text{CBzPh}\cdot\text{CHPh}$ , can be detected, thus giving evidence in support of the assumed structure; a small quantity of a colourless substance, m. p. 236—237°, was also obtained.

If a chloroform solution of bromine is gradually introduced into a suspension of the tetraphenylbutadiene in chloroform, the bromine colour persists after the addition of a unimolecular proportion, and evaporation of the solution yields a dibromide,



colourless prisms, m. p. 175—176° (decomp.). When this is heated under reflux with acetic acid, a vigorous evolution of hydrogen bromide ensues, but is ended after half an hour, and the solution, on cooling, deposits golden-yellow needles, m. p. 184—185°, of 2:3-diphenyl-1-

benzylideneindene,  $\text{C}_6\text{H}_4\begin{matrix} \text{C}(\text{CHPh}) \\ \text{CPh} \end{matrix}\text{CPh}$ , the constitution of which is indicated by its oxidation with chromic acid in acetic acid solution to benzoic acid and diphenylindone,  $\text{C}_6\text{H}_4\begin{matrix} \text{CO} \\ \text{CPh} \end{matrix}\text{CPh}$ , which is already known (Heyl and Meyer, A., 1896, i, 146).

$\alpha\beta\gamma$ -Triphenylpropan- $\beta$ -ol was prepared from ethyl benzoate and magnesium benzyl chloride by a slight modification of Klages' method (A., 1904, i, 488) in a yield 60—65% of the theoretical. It very easily parts with the elements of water, for example, when shaken at the ordinary temperature with sulphuric acid, forming  $\alpha\beta\gamma$ -triphenylpropene,  $\text{CHPh}\cdot\text{CPh}\cdot\text{CH}_2\text{Ph}$ , large, colourless needles, m. p. 62—63°. The dibromide was obtained as a yellow, viscous oil by evaporating the chloroform from the solution in which it had formed, and on boiling for half an hour with acetic acid rapidly loses hydrogen bromide with production of 2:3-diphenylindene,  $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_2 \\ \text{CPh} \end{matrix}\text{CPh}$ , colourless needles,

m. p. 177—178°; this substance readily unites with bromine, and slowly gives a deep green solution in sulphuric acid. A solution in warm alcohol containing a little benzaldehyde, on the addition of a few drops of potassium hydroxide solution, gives a gradual deposition of the 2:3-diphenyl-1-benzylideneindene described above. D. F. T.

**Dinitrotolane and Some Tolane Derivatives.** A. WINTHER (*Ber.*, 1914, **47**, 310—311).—The author claims co-operation in Reinhardt's results (this vol., i, 31).  
T. H. P.

**Aromatic Substances Containing Multivalent Iodine.** VIII. L. MASCARELLI and G. BRUSA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 494—498. Compare Mascarelli and Toschi, A., 1912, i, 322; Mascarelli, A., 1913, i, 171).—2:2'-Di-iodo- $\alpha$ : $\alpha'$ -dinaphthyl,  $C_{20}H_{12}I_2$ , can be prepared by diazotising a suspension of the corresponding diaminodinaphthyl, and pouring the product into a solution of potassium iodide; after purification, the substance forms pale yellow, acicular crystals, m. p. 224—225°. If it is treated in chloroform solution at 0° with chlorine, a *dichloro*-derivative,  $C_{20}H_{12}Cl_2I_2$ , m. p. 118—120° (decomp.), is obtained.  
R. V. S.

**Aromatic Substances Containing Multivalent Iodine.** IX. L. MASCARELLI and M. NEGRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 498—500. Compare preceding abstract).—The paper records unsuccessful attempts to obtain 1:1'-diamino- $\beta$ : $\beta'$ -dinaphthyl by reduction of the corresponding dinitro-compound with stannous chloride, colloidal platinum, and other reducing agents.  
R. V. S.

**The Metaquinonoid Question.** IV. O. STARK and L. KLEBAHN (*Ber.*, 1914, **47**, 125—130. Compare A., 1913, i, 361, 849, 1165).—The authors have very frequently failed to obtain the deep yellow, quinonoid tetraphenyl-*m*-xylylene, and, indeed, have not been able to discover a method by which its preparation may be assured. In unsuccessful attempts, yellow benzene solutions were obtained which gave an absorption band rather more towards the violet than in the successful experiments, and deposited a white powder, decomp. 297—303°. This is most probably a *polymeride* of tetraphenyl-*m*-xylylene, and the case is therefore analogous to Thiele's tetraphenyl-*p*-xylylene and xylenes in general, which polymerise readily. The less than unimolecular values obtained in bromoform are probably due to addition of the solvent, after depolymerisation. Halogen acids in the cold simply polymerise the hydrocarbon, and the additive compound with hydrogen chloride (*loc. cit.*, 849) is now cancelled. The action of hydrogen chloride in the boiling, original benzene solution leads to other products which will be studied.

Tetraphenyl-*m*-xylylene glycol was treated with potassium thiocyanate in glacial acetic acid, yielding *tetraphenyl-m-xylylene dithiocyanate*,  $C_{34}H_{24}N_2S_2$ , in white crystals, m. p. 120—121°.

A quantitative yield of *tetraphenyl-m-xylylene*,  $C_{30}H_{26}$ , was obtained by reducing the xylylene dichloride by zinc dust and acetic acid. The hydrocarbon forms stout, colourless crystals, m. p. 110—111°.

J. C. W.

**Preparation of Pure Dimethyl-*o*-toluidine.** J. VON BRAUN and E. AUST (*Ber.*, 1914, **47**, 260—262).—The authors' previous investigations (A., 1912, i, 968; 1913, i, 1327, 1330) have shown that excess of formaldehyde readily attacks methyl-*o*-toluidine and the

dimethyl derivatives of aniline, and of *m*- and *p*-toluidines, which all occur as impurities in the product obtained on methylating imperfectly purified *o*-toluidine. The latter gives, even by prolonged treatment with the aldehyde, only a very small proportion of the corresponding dimethylaminomethylbenzyl alcohol and practically no diphenylmethane derivative. A yield of 88% of pure dimethyl-*o*-toluidine was obtained from a mixture of the amine with the four above bases by treatment with formaldehyde, distillation of the resultant product under a pressure of 10 mm., and redistillation at ordinary pressure of the fraction boiling below 100°. The pure ortho-amine was also readily obtained from commercial samples.

The constants of pure dimethyl-*o*-toluidine are:  $D_4^{20^\circ}$  0.9252—0.9261 and  $n_D^{20}$  1.5153—1.5155 (compare Brühl, A., 1895, ii, 194; Kahlbaum, A., 1898, ii, 556), and those of the purest dimethyl-*p*-toluidine, prepared from *p*-tolyltrimethylammonium iodide by way of the ammonium base, are: b. p. 211—211.5°,  $n_D^{20}$  1.53664,  $D_4^{20^\circ}$  0.9379 (compare Brühl, *loc. cit.*; Kahlbaum, *loc. cit.*).

The preparation of pure 4-dimethylamino-5-methylbenzyl alcohol requires the employment of dimethyl-*o*-toluidine previously purified by treatment with formaldehyde, since in presence of only 3% of the para-base, nearly 20% of the isomeric 2-dimethylamino-5-methylbenzyl alcohol would be obtained.

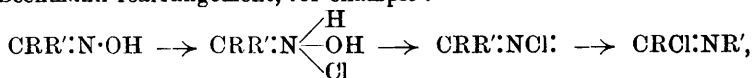
T. H. P.

**The Molecular Rearrangement of Triarylmethylhydroxylamines and the "Beckmann" Rearrangement of Ketoximes.** JULIUS STIEGLITZ and PAUL NICHOLAS LEECH (*J. Amer. Chem. Soc.*, 1914, 36, 272—301).—A preliminary account of some of the results embodied in this work has already been published (A., 1913, i, 852).

The possible courses of the Beckmann rearrangement are discussed from the point of view of the electron conception of valency (Falk and Nelson, A., 1911, ii, 104; Falk, *ibid.*, 711), combined with the general explanation of Stieglitz that the intermediate formation of the grouping :NPh plays an important part in such changes in nitrogen compounds (compare A., 1903, i, 235; 1913, ii, 398; etc.).

Triphenylmethylhydroxylamine,  $CPh_3 \cdot NH \cdot OH$ , m. p. 130—135°, was obtained by the interaction of triphenylmethyl chloride and hydroxylamine in benzene alcoholic solution. When heated for approximately a half hour with phosphorus pentachloride in ethereal solution, an almost quantitative conversion into benzophenoneanil hydrochloride,  $CPh_3 \cdot NPh \cdot HCl$ , m. p. 187—189°, was effected. With other agents which are employed to induce the rearrangement of oximes, the change proceeded in a different manner with formation of triphenylcarbinol and hydroxylamine. Phosphoric oxide, however, when warmed with triphenylmethylhydroxylamine hydrochloride caused rearrangement into benzophenoneanil as in the former case, possibly due to a primary dehydration of  $CPh_3 \cdot NH \cdot OH \cdot HCl$  into :N $\cdot$  $CPh_3 \cdot HCl$ , which would be exceedingly unstable and pass readily into  $CPh_2 \cdot NPh \cdot HCl$ . The *benzoyl* derivative (structure undetermined), m. p. 155°, of triphenylmethylhydroxylamine, when heated with soda-lime at 160—165°, also yielded benzophenoneanil.

These results suggest the possibility of an analogous course for the Beckmann rearrangement, for example :



the last type of substance undergoing subsequent hydrolysis in the commonly accepted manner with the formation of an amide. The main distinction of this explanation from that of Hantzsch (A., 1892, 338) lies in the assumption of the free valencies at the nitrogen atom; these render the case comparable with that of the univalent nitrogen already assumed by Stieglitz in other rearrangements (see above).

These views are to a certain extent confirmed by the behaviour of *triphenylmethylmethylhydroxylamine*,  $\text{CPh}_3\cdot\text{NMe}\cdot\text{OH}$  (colourless crystals, m. p.  $113^\circ$ , obtained by the interaction of triphenylmethyl chloride and methylhydroxylamine hydrochloride in the presence of sodium methoxide), with phosphorus pentachloride; these give very little alteration under the conditions which are effective with the mono-substituted hydroxylamine above, but under prolonged treatment a product is obtained consisting mainly of triphenylmethyl chloride and methylhydroxylamine, accompanied by a little acetomethyl-anilide.

*p*-Chlorotriphenylmethylhydroxylamine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CPh}_2\cdot\text{NH}\cdot\text{OH}$ , colourless crystals, m. p.  $117^\circ$ , obtained from *p*-chlorotriphenylmethyl chloride and hydroxylamine hydrochloride in methyl-alcoholic solution containing sodium methoxide, undergoes rearrangement when treated with phosphorus pentachloride as easily as does triphenylmethylhydroxylamine itself, yielding *p*-chlorobenzophenoneanil and benzophenone-*p*-chloroanil in an approximate proportion of 2 : 1.

The *condensation* product of triphenylmethylhydroxylamine and benzaldehyde, namely,  $\text{CPh}_3\cdot\text{N} \begin{array}{l} \text{O} \\ \diagup \\ \text{CHPh} \end{array}$ , forms colourless crystals, m. p.  $114^\circ$ . D. F. T.

**Preparation of a Substituted Diaminodiphenylcarbamide.** FARBERWERKE VORM. MEISTER, LÜCIUS & BRUNING (D.R.-P. 268658).—When a slow stream of carbonyl chloride is led through a solution of 2 : 6-dichloro-*p*-phenylenediamine below  $20^\circ$  in the presence of sodium acetate, *tetrachlorodiaminodiphenylcarbamide* is produced. J. C. C.

**Peat Tar. I. The Phenols of Peat Coke Tar.** E. BÖRNSTEIN and FERDINAND BERNSTEIN (*Zeitsch. angew. Chem.*, 1914, 27, 71—72).—The author has isolated the following phenols in the fractionation of peat coke tar : Phenol, *o*-, *p*- and *m*-cresols, 1 : 2 : 3- and 1 : 2 : 4-xyleneols, catechol resulting from guaiacol, homocatechol resulting from creosol, and pyrogallol. T. S. P.

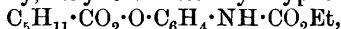
**Acyl Derivatives of *o*-Aminophenol.** J. H. RANSOM and R. E. NELSON (*J. Amer. Chem. Soc.*, 1914, 36, 390—393).—An extension of an earlier investigation (Ransom, A., 1900, i, 218) in which it was found that when two groups  $-\text{CO}_2\text{R}$  and  $-\text{CO}_2\text{R}'$  are introduced into

*o*-aminophenol, the lighter group is found finally to be attached to nitrogen whatever the order in which the groups are introduced. The rearrangement which occurs here is also found to occur when two acyl groups are introduced, whilst if one of the groups is of the type  $\text{-CO}_2\text{R}$  whilst the other is an acyl radicle, the former will be found attached to the nitrogen atom.

When *o*-aminophenol is treated in ethereal suspension with a bimolecular quantity of *iso*amyl chloroformate, *iso*amyl *o*-hydroxyphenylcarbamate, colourless needles, m. p.  $68.5\text{--}69.5^\circ$ , is obtained; the same substance was also obtained by the reduction of *o*-nitrophenyl *iso*amyl carbonate, in which case rearrangement must have occurred. If, however, the reaction mixture from the reduction of the carbonate is immediately thrown into a concentrated solution of potassium hydroxide, a different substance giving a *hydrochloride*, m. p.  $134^\circ$ , can be obtained; this is stable when dry, but on warming with water is converted into *iso*amyl *o*-hydroxyphenylcarbamate, and as a consequence must be regarded as of the isomeric *o*-aminophenyl *iso*amyl carbonate.

The action of benzoyl chloride on an alkaline solution of *iso*amyl hydroxyphenylcarbamate gave *iso*amyl benzoyloxyphenylcarbamate, colourless needles, m. p.  $65.5^\circ$ , the same substance also being produced by the action of *iso*amyl chloroformate on benzoyl-*o*-aminophenol, the chemical change in this case being accompanied by intramolecular rearrangement.

In a similar manner the interaction of ethyl hydroxyphenylcarbamate and *iso*amyl chloroformate, as also of ethyl chloroformate and *iso*amyl hydroxyphenylcarbamate, gave a substance, b. p.  $185\text{--}200^\circ/15\text{ mm.}$ , m. p.  $65\text{--}66^\circ$ , namely, ethyl *o*-carbisoamyloxyphenylcarbamate,



which is formed in the case of the latter pair of reagents by the rearrangement of the primarily produced  $\text{CO}_2\text{Et}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11}$ .

D. F. T.

**Trinitro-*m*-anisidine, 3 : 5-Dichloro-4-bromonitrobenzene, and Chlorination of *p*-Nitroaniline.** BERNHARD FLÜRSCHHEIM (*Ber.*, 1914, 47, 426).—A claim for priority over Reverdin and Widmer (this vol., i, 166) and Körner and Contardi (*A.*, 1913, i, 963) in the preparation of trinitro-*m*-anisidine (*Zeitsch. ges. Schiess- & Sprengstoffwesen*, 1913, 8, 185) and of 3 : 5-dichloro-4-bromonitrobenzene (*A.*, 1905, i, 614), and the chlorination of *p*-nitroaniline in hot dilute hydrochloric acid (*T.*, 1908, 93, 1773).

C. S.

**Action of Grignard's Reagent on Alkyloxy Groups.** H. SIMONIS and P. REMMERT (*Ber.*, 1914, 47, 269—271).—Although, in general, alkyloxy groups are indifferent to Grignard's reagent, yet the iodoanisoles, for instance, are capable of forming normal organomagnesium compounds without appreciable secondary reactions occurring. Further, in the Grignard reaction, anisole is often advantageously employed as a solvent when it is necessary to work at a higher temperature than is allowed by ether or benzene. The view that, in this case, the anisole acts merely as an indifferent solvent, is accurate

only when the temperature does not greatly exceed that of boiling water. When, however, the boiling point of anisole is attained, this solvent reacts as follows:  $\text{Ph}\cdot\text{OMe} + \text{MgMeI} = \text{Ph}\cdot\text{OMgI} + \text{C}_2\text{H}_6$ , considerable quantities of phenol being formed according to the equation  $\text{Ph}\cdot\text{OMgI} + \text{H}_2\text{O} = \text{Ph}\cdot\text{OH} + \text{MgI}\cdot\text{OH}$ . A similar result follows when phenetole is used in place of anisole. When dimethoxybenzenes are employed, ethane is vigorously evolved, but as the formation of the solid  $\text{C}_6\text{H}_4(\text{OMgI})_2$  proceeds, a tendency to decomposition appears.

T. H. P.

**A General Method for the Reduction of the Carbonyl Group in Aldehydes and Ketones to the Methylene Group. II.** ERIK CLEMMENSEN (*Ber.*, 1914, **47**, 51—63. Compare A., 1913, i, 733).—The method already applied by the author to the reduction of ketones and aldehydes is shown to be generally useful except for such substances as are decomposed by hydrochloric acid. It promises to be of especial value for the preparation of homologues of the various phenols from hydroxy-ketones, and although its value for the reduction of hydroxy-aldehydes is diminished by the sensitiveness of many of these towards hydrochloric acid, the methyl substituted phenols obtainable are of a high degree of purity.

In the reduction of the ketones mentioned below, the general procedure was to take 100 grams of amalgamated zinc (produced by placing ordinary granulated zinc in a 5% solution of mercuric chloride for a few hours) with 25 grams of the ketone, and to add 300—500 c.c. of hydrochloric acid obtained by mixing concentrated acid with an equal or double volume of water. A vigorous evolution of hydrogen was maintained for several hours by warming on a water-bath with the occasional addition of small quantities of more concentrated acid. The reduction was then complete, and the yield generally excellent.

In this manner *p*-hydroxyacetophenone gave rise to *p*-ethylphenol, b. p. 217—217.5°/750 mm., m. p. 45—46°; *acetate*, b. p. 226—227°/750 mm., has an odour like anise. The free phenol gives a blue coloration with ferric chloride.

*p*-Hydroxypropiophenone in a similar manner undergoes reduction to *p*-propylphenol, a colourless, crystalline solid, m. p. 21—22°, b. p. 228°/748 mm.; *acetate*, with a feeble odour resembling anise, b. p. 245—246°/745 mm.

*m*-Acetyl-*o*-cresol on reduction yields 2-methyl-4-ethylphenol, a strongly refractive liquid, b. p. 224.5°/740 mm., with a feeble phenolic odour; it gives the general reactions of the phenols.

*o*-Acetylresorcinol gives 4-ethylresorcinol, colourless leaflets (by sublimation) or stout prisms (by recrystallisation from chloroform), m. p. 97°; this substance shows the fluorescein reaction with phthalic anhydride, and gives a deep red colour on warming with chloroform and a little sodium hydroxide; the coloration with ferric chloride is deep blue, changing slowly to a green.

Acetylquinol is reduced to ethylquinol,  $\text{C}_6\text{H}_3\text{Et}(\text{OH})_2$ , which crystallises in rosettes or sublimes, giving needles, m. p. 112° (compare Bayrac, A., 1895, i, 412). This is easily oxidisable to ethyl *p*-benzoquinone.



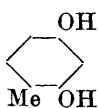
The reduction of *m*-acetylcatechol gives rise to *m*-ethylcatechol as a crystalline mass, m. p. 37—39°; this gives a transient green coloration with ferric chloride, the subsequent addition of sodium carbonate causing a red colour.

*o*-Acetylpyrogallol becomes reduced to *o*-ethylpyrogallol, silvery plates from chloroform, m. p. 106°. The ferric chloride coloration is an evanescent, deep blue, and the subsequent addition of sodium carbonate solution produces a violet colour. An alkaline solution of the substance does not darken so rapidly as one of pyrogallol.

4-Acetyl-6-ethylpyrogallol, obtained by the action of acetyl chloride on the last product, forms colourless prisms or fine needles, m. p. 141°. It is reducible to 4:6-diethylpyrogallol, silky needles, m. p. 80°, of which the aqueous solution reduces silver nitrate. The reddish-violet coloration with ferric chloride soon disappears, and the addition of a little sodium carbonate solution then gives a permanent violet colour, which changes to reddish-brown with more carbonate.

The structures assumed for the substances used above are those commonly accepted, but in some cases these possibly require further confirmation.

Of the hydroxyaldehydes investigated, salicylaldehyde, *m*-hydroxybenzaldehyde, and *p*-hydroxybenzaldehyde are reducible to *o*-cresol, b. p. 189.3°/750 mm., *m*-cresol, b. p. 201.5°/750 mm., and *p*-cresol, b. p. 201°/750 mm., respectively. The various descriptions of these substances are to be attributed to lack of purity in the specimens examined. *o*-Cresol has a pleasant carbolic odour, and gives with one drop of ferric chloride solution a deep violet-blue colour, which within a minute changes through green to a dirty yellow; the colour reaction is not obtained with excess of ferric chloride. *m*-Cresol has a faint odour resembling that of leather, and the reddish-violet coloration with ferric chloride fades more slowly and is still perceptible after a week. *p*-Cresol has as an odour very like that of *p*-ethylphenol, and the pure blue coloration obtained with ferric chloride disappears in less than one day. The ortho- and para-isomerides remain uncoloured in the air even after six months, but in this time *m*-cresol becomes yellow.



The reduction of resorcydaldehyde gives rise to cresorcinol (4-methylresorcinol, annexed formula), m. p. 83—84°. The discrepancy between this m. p. and the 102—104° recorded in the literature may be due to error in the latter, or to the commonly accepted structure of resorcylic acid being incorrect.

*p*-Thymotaldehyde on reduction gives *p*-methylthymol, rhombohedra, m. p. 70°, b. p. 250—250.5°/745 mm., with a pleasant odour, quite distinct from that of thymol.

D. F. T.

**Influence of Acetylation of Phenolic Groups on the Velocity of Nitration, and Measurement of the Latter in the Case of Ethereal Solutions of Phenols.** ALFONS KLEMENC (*Monatsh.*, 1914, 35, 85—117. Compare A., 1912, i, 695).—The author shows in a number of cases that acetylation of the phenolic group destroys its powerful directive action on the position taken up by fresh substituents, and that an advantageous process is thus frequently provided

for preparing isomeric substitution products from phenols and phenol-carboxylic acids. Attempts to measure the velocity of nitration of phenols dissolved in ether or glacial acetic acid are also recorded.

*Acetylquinol monomethyl ether*, b. p. 134—135°/18 mm., 147—148°/33 mm., 243°/751 mm., is obtained by the action of acetic anhydride and a little concentrated sulphuric acid on quinol monomethyl ether. When dissolved in acetic acid and treated with nitric acid (D 1·52), it gives *3-nitroacetylquinol monomethyl ether*, colourless needles, m. p. 106°, from which, on cautious saponification with potassium hydroxide, *3-nitroquinol monomethyl ether*, pale yellow needles, m. p. 97—99°, is obtained; this acts as a delicate indicator. Direct nitration of quinol monomethyl ether yields 2-nitroquinol monomethyl ether (Weselsky and Benedikt, A., 1881, 1139).

Vanillic acid can be nitrated by 8% nitric acid at 48° during twenty-four hours, a mixture of 5-nitrovanillic acid, m. p. 215°, and 3:5-dinitroguaiacol being produced. When acetylvanillic acid is nitrated by fuming nitric acid (D 1·52) at 0° and the product subsequently saponified by potassium hydroxide and then acidified, 2-nitrovanillic acid, decomposing at 246°, is obtained (compare Tiemann and Matsumoto, A., 1876, ii, 524; Pschorr and Sumuleanu, A., 1900, i, 178). The composition of the acid is proved by converting it by means of diazomethane into methyl 2-nitroveratrate, m. p. 126°, which on saponification yields 2-nitroveratric acid, m. p. 201—202°.

*iso*Vanillic acid is readily nitrated by 8% aqueous nitric acid at 48°, giving 2:6-dinitro*iso*vanillic acid (compare Matthiessen and Foster, *Jahresber.*, 1867, 520; Wegscheider and Klemenc, A., 1910, i, 671). Acetyl*iso*vanillic acid yields with nitric acid (D 1·52) a substance which on successive treatment with potassium hydroxide and acid gives 5-nitro*iso*vanillic acid, needles, m. p. 174° (compare Matsumoto, A., 1878, 502). This compound has, apparently without ground, been described in the literature as 6-nitro*iso*vanillic acid; its constitution follows from its conversion by diazomethane into methyl 5-nitroveratrate. In this instance of nitration, only one nitro-derivative is formed.

Guaiacolcarboxylic (2-hydroxy-3-methoxybenzoic) acid, m. p. 151°, is somewhat volatile at 100°, so that the water of crystallisation cannot be easily estimated directly. It cannot be accurately titrated with phenolphthalein as indicator. It is readily esterified by methyl alcohol and hydrogen chloride; it is not completely methylated by diazomethane nor acetylated by acetic anhydride or acetyl chloride. When nitrated with 8% aqueous nitric acid at 48° or by nitric acid (D 1·53) in glacial acetic acid suspension, it yields 5-nitroguaiacolcarboxylic acid, needles, m. p. 227° (decomp.), the orange-coloured *potassium* and sparingly soluble *ammonium* salt of which are also described. When boiled with aniline, the acid yields 4-nitroguaiacol, m. p. 99—100°. *Methyl acetylguaiacolcarboxylate*, m. p. 62—63°, b. p. 193°/34 mm., is somewhat resistant to nitration, but is converted by protracted contact with fuming nitric acid (D 1·52), at first at -10° to -20°, subsequently at 0°, into a product from which an *acid*, leaflets, m. p. 195° (decomp.), is obtained in the usual manner. The constitution of this acid has not been definitely ascertained, but, in all probability, it is 4:6-dinitroguaiacolcarboxylic acid.

The nitration of methyl 2-hydroxy-5-methoxybenzoate has previously been described (Klemenc, A., 1913, i, 49). The proof that the nitro-group enters in the position 3 is now given by conversion of the product by boiling with aniline into 2-nitroquinol monomethyl ether, m. p. 80°. *Methyl 2-acetoxy-5-methoxybenzoate*, b. p. 180—181°/114 mm., is nitrated by fuming nitric acid (D 1.52), and, after treatment in the usual manner, yields a mixture of 4-nitro-2-hydroxy-5-methoxybenzoic acid, m. p. 191—192°, and 6-nitro-2-hydroxy-5-methoxybenzoic acid, m. p. 221° (decomp.). The acids are very incompletely esterified by methyl alcohol and hydrogen chloride. Since the material was insufficient for a direct determination of the velocity of esterification, the author has relied on the treatment of the two acids under identical conditions with methyl alcohol and hydrogen chloride, and the determination of the percentage of  $-OCH_3$  in the crude products, and has, in this manner, been able to assign probable formulæ. By extraction of the above crude products with ammonia, *methyl 6-nitro-2-hydroxy-5-methoxybenzoate*, m. p. 125—126°, and *methyl 4-nitro-2-hydroxy-5-methoxybenzoate*, yellow leaflets, m. p. 103°, have been obtained. *Methyl 6-nitro-2:5-dimethoxybenzoate*, a yellow, microcrystalline substance, m. p. 117—118°, is obtained by the action of diazomethane on 6-nitro-2-hydroxy-5-methoxybenzoic acid; when saponified with potassium hydroxide it yields an impure 6-nitro-2:5-dimethoxybenzoic acid, partial elimination of a methoxy-group appearing to occur.

Measurements of the velocity of nitration of phenol and guaiacol have been made in ethereal solution at 25°. The course of the reaction is followed by estimation of the unused nitric acid, either by addition of aliquot portions of the liquid after definite intervals to a solution of potassium iodide and potassium iodate to which sodium thiosulphate in known excess has been previously added, and subsequent titration of the residual thiosulphate with iodine, or by adding aliquot portions of solution to an excess of potassium hydroxide and estimation of unchanged nitrate by reduction with Devarda's alloy. The latter method, however, can only be used in certain cases, since ammonia is sometimes obtained in appreciable quantity by the action of the alloy on the nitro-compound.

In the presence of a small excess of nitric acid, phenol and guaiacol are either not nitrated or only acted on extremely slowly. With excess of phenol, on the other hand, nitration occurs readily, and follows approximately the law for a bimolecular reaction.

Anisole and acetylphenol are only slowly nitrated in ethereal solution, even at considerable concentration. In glacial acetic acid solution, the former is readily nitrated, whereas the latter is but little affected. The reaction, however, does not take a simple course.

During the nitration of acetylphenol, the solution, after some time, becomes distinctly green, and contains nitrous acid. With anisole, the acetic-nitric acid solution becomes deep violet and effervescence occurs (evolution of nitric oxide). Nitration only occurs in the coloured solution; after some time, the colour disappears, whereon nitration ceases. Probably the colour is due to an additive compound of anisole and nitric or nitrous acid, which is decomposed by water.

H. W.

**Bromoquinolsulphonic Acids and Their Conversion into Bromo-*p*-benzoquinonesulphonic Acids.** A. SEYEWETZ and J. PARIS (*Bull. Soc. chim.*, 1914, [iv], 15, 121—125. Compare A., 1911, i, 360; 1912, i, 492, 723).—Bromoquinol on sulphonation with fuming sulphuric acid (containing 15% sulphur trioxide) at a temperature not exceeding 50°, and subsequent treatment of the reaction product with a concentrated solution of sodium sulphate, yields *sodium bromoquinolsulphonate*,  $C_6H_2Br(OH)_2 \cdot SO_3Na$ , white needles, which reduces cold silver nitrate solution and acts as a photographic developer in the presence of alkalis. Oxidation with sodium dichromate and sulphuric acid at a temperature not exceeding 20° converts it into *sodium bromo-*p*-benzoquinonesulphonate*, yellow needles. The aqueous solution has oxidising properties and decomposes slowly at the ordinary temperature, rapidly when heated.

Sodium *p*-benzoquinone-2-sulphonate is converted by a saturated aqueous solution of hydrobromic acid at temperatures below 30° into *sodium 6-bromoquinol-2-sulphonate*,  $C_6H_2Br(OH)_2 \cdot SO_3Na$ , white needles. The aqueous solution has reducing power which seems to be slightly less than that of the isomeride described above. At a temperature exceeding 30°, 2:6-dibromoquinol is produced. On oxidation under the conditions adopted for the isomeride, sodium 6-bromoquinol-2-sulphonate is transformed into *sodium bromo-*p*-benzoquinonesulphonate*,  $C_6H_2BrO_2 \cdot SO_3Na$ , golden-yellow needles, soluble in water, giving solutions which decompose rapidly when heated, slowly in the cold, and liberate iodine from potassium iodide in the presence of acids.

H. W.

**Double Salts of Mercuric Chloride with Aromatic Tellurides.** KARL LEDERER (*Ber.*, 1914, 47, 277—279).—Aliphatic sulphides form well crystallised double salts with mercuric chloride, but analogous compounds of aliphatic selenides or tellurides are unknown.

Aromatic sulphides or selenides do not appear to give double salts with mercuric, platinic, or auric chloride, but aromatic tellurides form well crystallised, stable double salts with mercuric chloride, and also yield precipitates, which were not investigated, with platinic chloride. Phenyl telluride and auric chloride give a double salt, which rapidly blackens even when protected from the action of light and air.

The following double salts were obtained by shaking ethereal solutions of the tellurides with aqueous mercuric chloride.

Mercuric chloride and phenyl telluride give  $TePh_2, HgCl_2$ , which forms needles, sintering at 155°, m. p. 158° (rapidly from alcohol) or m. p. 160—161° (from acetic acid). The crystals formed slowly from alcoholic solution contain  $5Et \cdot OH$ , sinter at 115°, and resinify at 130°.

Mercuric chloride and *o*-tolyl telluride give  $Te(C_6H_4Me)_2, HgCl_2$ , sintering at 209°, m. p. 212°.

Mercuric chloride and *p*-tolyl telluride give  $Te(C_6H_4Me)_2, HgCl_2$ , which forms crystals containing  $6Et \cdot OH$ , m. p. 135—136°, or  $3CH_3 \cdot CO_2H$ , sintering at 128°, m. p. 132—133°.

The chlorine present in these double compounds was estimated by the lime method, that of Carius failing completely. T. H. P.

**The Displacement of the Ethoxy-group by Radicles. A Synthesis of Ethers and of Hydrocarbons.** A. E. TSCHITSCHIBABIN and S. A. JELGASIN (*Ber.*, 1914, 47, 48—50).—In the preparation of  $\alpha$ -naphthaldehyde from ethyl orthoformate and magnesium  $\alpha$ -naphthyl bromide by the well-known process (Tschitschibabin, A., 1904, i, 221), indications have been obtained of a further stage in the reaction with formation of di- $\alpha$ -naphthylcarbinol. This has led to an extension of the investigation of the reaction between ethyl orthoformate and organomagnesium compounds, and the results of preliminary experiments point to the possibility of the successive replacement of all the three ethoxy-groups with the formation of aldehyde-acetals, ethers and hydrocarbons respectively, according to the equations:  $\text{H}\cdot\text{C}(\text{OEt})_3 + \text{R}\cdot\text{Mg}\cdot\text{Hal} = \text{CHR}(\text{OEt})_2 + \text{MgHal}\cdot\text{OEt}$ ,  $\text{CHR}(\text{OEt})_2 + \text{RMgHal} = \text{CHR}_2\cdot\text{OEt} + \text{MgHal}\cdot\text{OEt}$ , and  $\text{CHR}_2\cdot\text{OEt} + \text{R}\cdot\text{Mg}\cdot\text{Hal} = \text{CHR}_3 + \text{MgHal}\cdot\text{OEt}$ .

Thus magnesium phenyl bromide acts fairly readily on a boiling ethereal solution of benzaldehyde-acetal, but the reaction develops much less heat than does the formation of the acetal from ethyl orthoformate. To induce the interaction of benzhydryl ethyl ether with magnesium phenyl bromide, a higher temperature is necessary, and triphenylmethane can be obtained as the chief product by distilling off the ether, during which process the third ethoxy-group becomes replaced by phenyl. D. F. T.

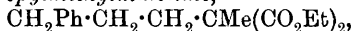
**Syntheses in the Fatty Aromatic Series. XII.** J. von BRAUN and G. KIRSCHBAUM (*Ber.*, 1914, 47, 262—269. Compare A., 1913, i, 772).—It has been shown previously (von Braun, Grabowski and Kirschbaum, A., 1913, i, 612) that substitution by a methyl group at the carbon atom adjacent either to the carbinol group of phenylpropyl alcohol or to the aldehyde group of phenylpropaldehyde is of greater influence on the odour than substitution at the carbon atom next to the phenyl group. In order to ascertain if this is a general rule, and, especially, whether the  $\beta$ -position of the methyl to hydroxyl or its  $\beta$ -position to the benzene nucleus is the determining factor, the investigations have been extended to the two next higher homologous alcohols and aldehydes.

With  $\epsilon$ -phenyl- $\beta$ -methylamyl and  $\epsilon$ -phenyl- $\beta\delta$ -dimethylamyl alcohols, it is found that the complex,  $\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , is as readily converted by the "nitro" method into  $\cdot\text{CHMe}\cdot\text{CHO}$  as is the unbranched grouping,  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ . The odours of these new alcohols and aldehydes differ somewhat from those of the non-methylated compounds, but they are so weakened that accurate comparison is scarcely possible. Further study in this direction should hence be confined to compounds with the alcoholic or aldehydic group in the  $\beta$ - or  $\gamma$ -position, since with such compounds any regularities in odour are more clearly expressed.

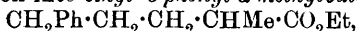
*Ethyl  $\beta$ -phenylethylmethylmalonate*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CMe}(\text{CO}_2\text{Et})_2$ , prepared from methyl iodide and ethyl  $\gamma$ -phenylethylmalonate (com-

pare Fischer and Schmitz, A., 1906, i, 584), is a colourless liquid, b. p.  $192^{\circ}/20$  mm., and the corresponding acid,  $C_{12}H_{14}O_4$ , m. p.  $160^{\circ}$ , is slowly converted on heating at  $165^{\circ}$  into  $\gamma$ -phenyl- $\alpha$ -methylbutyric acid,  $CH_2Ph \cdot CH_2 \cdot CHMe \cdot CO_2H$ , b. p.  $180^{\circ}/19$  mm., the ethyl ester of which, b. p.  $143-144^{\circ}/17$  mm., yields  $\delta$ -phenyl- $\beta$ -methylbutyl alcohol,  $C_{11}H_{16}O$ , b. p.  $145-148^{\circ}/18$  mm.,  $D_4^{20}$  0.9719, on reduction.

*Ethyl  $\gamma$ -phenylpropylmethylmalonate,*



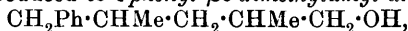
b. p.  $194^{\circ}/15$  mm., prepared by methylation of the corresponding phenylpropylmalonate (von Braun and Kruber, A., 1912, i, 265), is converted on hydrolysis with aqueous-alcoholic potassium hydroxide (2 mols.) principally into the oily ethyl hydrogen  $\gamma$ -phenylpropylmethylmalonate,  $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot CMe(CO_2H) \cdot CO_2Et$ , which is converted on distillation into ethyl  $\delta$ -phenyl- $\alpha$ -methylvalerate,



b. p.  $158^{\circ}/17$  mm.;  $\delta$ -phenyl- $\alpha$ -methylvaleric acid,  $C_{12}H_{16}O_3$ , is an oil, b. p.  $190^{\circ}/19$  mm. Although partial hydrolysis of a malonic ester is in general very difficult, the above ethyl hydrogen malonate exhibits marked stability and is only with difficulty attacked further by the hydrolysing agent. Where the malonic ester transformation is to lead to the formation of an alcohol, this partial hydrolysis allows of the diminution of the number of operations by two, the distilled product of hydrolysis being directly reduced and the preparation of the di- and mono-carboxylic acids omitted.

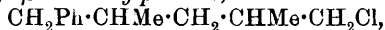
$\epsilon$ -Phenyl- $\beta$ -methylamyl alcohol,  $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot OH$ , prepared in this way, has b. p.  $159-160^{\circ}/20$  mm.,  $D_4^{20}$  0.9642.  $\alpha$ -Chloro- $\epsilon$ -phenyl- $\beta$ -methylpentane,  $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2Cl$ , has b. p.  $140-142^{\circ}/18$  mm. The corresponding iodo-compound,  $C_{12}H_{17}I$ , b. p.  $160-166^{\circ}/20$  mm., reacts readily with silver nitrite, giving in about equimolecular proportions, (1) the nitrite, b. p.  $130^{\circ}/18$  mm., which is readily hydrolysed to the alcohol, and (2)  $\alpha$ -nitro- $\epsilon$ -phenyl- $\beta$ -methylpentane,  $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot NO_2$ , a yellow liquid, b. p.  $172-180^{\circ}$ . When this nitro-derivative is reduced with stannous chloride and the oily oxime boiled with 15% sulphuric acid solution, on passing water vapour through the liquid,  $\delta$ -phenyl- $\alpha$ -methylvaleraldehyde,  $C_{12}H_{16}O$ , distils as a colourless liquid, b. p.  $148-152^{\circ}/21$  mm., giving only oily derivatives with the usual reagents.

*Ethyl  $\gamma$ -phenylisobutylmalonate,*  $CH_2Ph \cdot CHMe \cdot CH_2 \cdot CH(CO_2Et)_2$ , prepared from  $\gamma$ -phenylisobutyl bromide (A., 1913, i, 612), has b. p.  $189^{\circ}/11$  mm., and on methylation yields ethyl  $\gamma$ -phenylisobutylmethylmalonate,  $CH_2Ph \cdot CHMe \cdot CH_2 \cdot CMe(CO_2Et)_2$ , b. p.  $192-194^{\circ}/13$  mm., which undergoes semi-hydrolysis less readily than the lower homologues. The corresponding acid and also  $\delta$ -phenyl- $\alpha$ - $\gamma$ -dimethylvaleric acid,  $CH_2Ph \cdot CHMe \cdot CH_2 \cdot CHMe \cdot CO_2H$ , b. p.  $282-284^{\circ}$ , do not crystallise, and the ethyl ester of the latter,  $C_{15}H_{22}O_2$ , b. p.  $154^{\circ}/25$  mm., can be reduced to  $\epsilon$ -phenyl- $\beta\delta$ -dimethylamyl alcohol,



b. p.  $156-158^{\circ}/17$  mm.,  $D_4^{20}$  0.9549.

$\alpha$ -Chloro- $\epsilon$ -phenyl- $\beta\delta$ -dimethylpentane,



b. p.  $146-148^{\circ}/20$  mm.; the corresponding iodo-compound,  $C_{13}H_{19}I$ ,

b. p. 163—166°/20 mm.; the *nitro*-compound,  $C_{13}H_{19}O_2N$ , b. p. 176—181°/20 mm., and  $\delta$  *phenyl- $\alpha$ -dimethylvaleraldehyde*,  
 $CH_2Ph \cdot CHMe \cdot CH_2 \cdot CHMe \cdot CHO$ ,

b. p. 151—156°/20 mm., which forms only oily derivatives with the ordinary reagents for aldehydes, were also prepared. T. H. P.

### The Splitting of Benzhydrols by the Action of Bromine.

GUSTAVUS J. ESSELEN, jun., and LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1914, **36**, 308—324).—In following up an observation that benzaldehyde was produced in the action of bromine on *p*-aminobenzhydrol and 3:5-dibromo-4-aminobenzhydrol in chloroform solution (A., 1911, i, 725), the authors have found that this action of bromine on *p*-aminobenzhydrol derivatives is a general one, the molecule of the latter undergoing fission with formation of an aldehyde and a bromo-substituted aniline. The following series of changes is suggested as representing the course of the action:  $OH \cdot CHPh \cdot C_6H_4 \cdot NR_2 \rightarrow OH \cdot CHPh \cdot C_6H_4 \cdot NR_2Br \rightarrow CHPhO + C_6H_4Br \cdot NR_2, HBr$ .

4-Amino-3-methylbenzhydrol, prepared by the reduction of 4-amino-3-methylbenzophenone by sodium amalgam in alcoholic solution, forms colourless needles, m. p. 110°; when boiled with acetic acid, it yields a greenish-yellow substance, possibly an anhydride, decomp. near 210°. When treated in chloroform solution with a bimolecular proportion of bromine, it readily reacted, giving benzaldehyde and 3:5-dibromo-*o*-toluidine.

*p*-Nitro-*p*'-methylaminobenzhydrol under similar conditions with a unimolecular proportion of bromine yielded *p*-nitrobenzaldehyde and dibromomethylaniline, m. p. 47° (compare Fries, A., 1904, i, 571). With *p*-dimethylaminobenzhydrol and a bimolecular proportion of bromine, benzaldehyde and *p*-bromodimethylaniline were obtained, but at -80° an amine dibromide was first obtainable as an unstable, yellow oil; the formation of this is a confirmation of the stages suggested above.

3-Bromo-4-dimethylaminobenzophenone, colourless, rhombic plates, m. p. 80°, obtained by direct bromination of *p*-dimethylaminobenzophenone, can be reduced by aluminium amalgam and alcohol to 3-bromo-4-dimethylaminobenzhydrol, a straw-coloured, viscous oil, b. p. near 275°/55—60 mm. (decomp.). This is converted by bromine into benzaldehyde and 2:4-dibromodimethylaniline. At -80°, 3-bromo-4-dimethylaminobenzhydrol behaved towards bromine in a manner similar to *p*-dimethylaminobenzhydrol, producing a very unstable, red, solid substance.

*p*-Nitro-*p*'-dimethylaminobenzhydrol and *pp*'-tetramethyldiaminobenzhydrol were converted by bromine into *p*-bromodimethylamine, mixed with *p*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde respectively. *p*-Nitro-*p*'-diethylaminobenzhydrol was similarly affected.

2-Amino-5-methylbenzhydrol, colourless, feathery crystals or rhombohedra, m. p. 107°, which was obtained by the reduction of 6-amino-3-methylbenzophenone (Chattaway and Lewis, T., 1904, **85**, 594) with sodium amalgam and alcohol, was converted by bromine into 3:5-dibromo-*p*-toluidine and benzaldehyde.

*m*-Aminobenzophenone was reduced to *m*-aminobenzhydrol, colourless rhombohedra, m. p. 78°, by sodium amalgam and alcohol. This benzhydrol compound, as well as unsubstituted benzhydrol itself, does not suffer fission under the action of bromine, although in the former case a yellow oil of uncertain nature was obtained.

Chlorine and iodine appear to affect *p*-dimethylaminobenzhydrol in the same way as bromine, but the change produced is less satisfactory, being complicated by the formation of additional products. The use of chloroform as solvent is not essential, as alcohol or ether is equally successful, the latter, indeed, possessing the advantage of immediately separating the products, the aldehyde remaining in solution whilst the hydrobromide of the aromatic amine derivative is deposited.

D. F. T.

**Reduction of Triphenylcarbinol.** A. GARCÍA BANÚS (*Anal. Fis. Quim.*, 1913, 11, 599—601).—Triphenylcarbinol (1 gram) is dissolved in 10 c.c. of boiling glacial acetic acid with 0.5 gram of trioxymethylene, and 2.5 c.c. of concentrated sulphuric acid added at 45—50 c.c. In a few minutes, 1 gram of triphenylmethane, of m. p. 89—90°, or on recrystallisation 90—92°, separates.

Boiling for four hours with acetic acid and trioxymethylene without sulphuric acid also gives a good yield, but the action is accelerated by the addition of three or four drops of sulphuric acid.

G. D. L.

**Preparation of Optically Active  $\alpha$ :2:6-Dihydroxyphenylpropanolamines.** FARBENFABRIK VORM. FRIEDR. BAYER & Co. (D.R.P. 269327).—Amino- $\alpha$ :2:6-dihydroxyphenylpropyl alcohol can be resolved into its optically active constituents by means of *d*- or *l*-tartaric acid. The *dAdB* salt has m. p. 86°, the *dAlB* salt, m. p. 86°, the *lAdB* salt, m. p. 85—87°, and the *lAlB* salt, m. p. 92°. The *d*-base has m. p. 217° and  $\alpha_D$  33.75°, whilst the *l*-base has m. p. 218° and  $\alpha_D$  30°. The action of the latter in raising the blood pressure is two to three times as strong as the racemic base.

J. C. C.

**Halogen Substituted Anthranilic Acids.** EUG. GRANDMOUGIN (*Ber.*, 1914, 47, 384).—The author agrees with Lesser and Weiss (this vol., i, 180) that Dorsch's tri- and tetra-bromoanthranilic acids should be cancelled. The substance obtained by Dorsch was tribromoaniline.

J. C. W.

**Perkin Reaction: Reply to the Criticism of Meyer and Beer.** ARTHUR MICHAEL (*Amer. Chem. J.*, 1913, 50, 411—414).—The work of Meyer and Beer (*A.*, 1913, i, 617) is discussed, and it is stated that their results do not disprove Michael and Hartmann's view that the first phase of the Perkin reaction consists of an interaction between the aldehyde and anhydride (*A.*, 1901, i, 358), but that they afford new facts in confirmation of it.

E. G.

**The Behaviour of *m*-Nitrocinnamic Acid Compared with the ortho- and para-Acids.** FRIEDRICH WOLLRING (*Ber.*, 1914, 47, 108—111).—An account is given of experiments with derivatives of *m*-nitrocinnamic acid which are in many respects identical with those



described by Reich and Koehler (this vol., i, 41), and support the view that the nitro-group in the meta-position does not weaken the attachment of bromine atoms in the side-chain, as is the case in the ortho- and para-series.

$\alpha\beta$ -Dibromo- $\beta$ -*m*-nitrophenylpropionic acid, m. p. 175°, gives a *sodium* salt, with  $2\text{H}_2\text{O}$ , a *calcium* salt, with  $4\text{H}_2\text{O}$ , a methyl ester, m. p. 91—92°, and an ethyl ester, m. p. 86—87°, which is hydrolysed to *m*-nitrocinnamic acid by heating with water at 200° for a few hours. When heated with alcoholic potassium hydroxide (2 mols.) the ester yields  $\alpha$ -bromo-*m*-nitrocinnamic acid and also the *allo*-variety, which is transformed into the stable acid by sublimation in vacuum. The *sodium* and *barium* salts and the *ethyl* ester, long needles, m. p. 74°, of the stable acid, and the methyl ester, m. p. 82—83°, and the *ethyl* ester, an oil, of the labile acid, were isolated. A smaller quantity of alkali yields, in addition, a mixture of these ethyl esters, whilst an excess of alkali yields *m*-nitrophenylpropionic acid, the barium salt of which decomposes on boiling with water into *m*-nitrophenylacetylene. On submitting the sodium salt of the above dibromide to steam distillation, *o*-bromo-*m*-nitroallostyrene was obtained as an oil which is transformed into the stable isomeride, m. p. 78—79°, on distillation in vacuum.

J. C. W.

**The *allo*-Nitrocinnamic Acids.** FRIEDRICH WOLLRING (*Ber.*, 1914, 47, 111—115).—Attempts have been made to convert the stable *m*- and *p*-nitrocinnamic acids into the labile *allo*-modifications by submitting them to the action of ultra-violet light, the method which Stoermer successfully employed in the case of the ortho-isomeride (*A.*, 1912, i, 974). A transformation of about 22% was effected in the case of the meta-compound, but *p*-nitrocinnamic acid was extensively decomposed, and yielded only minute quantities of the labile acid. The latter was prepared, however, by the nitration of *allo*-cinnamic acid.

*m*-Nitrocinnamic acid was dissolved in alcoholic ammonia and exposed for 100 hours to the light of a mercury lamp, in quantities of about 5 grams in 20 c.c. After evaporating a part of the solvent and removing some flocculent products of decomposition by the addition of water, the acid was fractionally precipitated by hydrochloric acid, the last fractions yielding *m*-nitroallocinnamic acid. This forms small needles, m. p. 158°, and is re-converted into the stable acid by illumination in chloroform with a trace of bromine. The *ethyl* ester is an oil. The dibromide,  $\alpha\beta$ -dibromo- $\beta$ -*m*-nitroallophenylpropionic acid, was obtained by dissolving the acid in bromine as a semi-solid mass, which was a mixture of two forms of the derivative, one with m. p. 121°, and the other an oil which was extracted by cold benzene and which changed into the crystalline form after a few weeks. *m*-Aminoallocinnamic acid was prepared by adding a solution of the ammonium salt of the nitro-acid to ferrous sulphate rendered alkaline by baryta, and warming. It forms sparingly soluble, yellow crystals, m. p. 193°, and its *hydrochloride* is considerably esterified merely by boiling with methyl or ethyl alcohol, the *esters* being oils. The acid was diazotised and boiled with water, when *m*-hydroxyallocinnamic acid was

obtained as an oil which yielded  $\beta$ -*m*-hydroxyphenylpropionic acid on reduction with sodium amalgam.

*allo*-Cinnamic acid was nitrated by fuming nitric acid, free from nitrous fumes, at 0—5°, and the solution of the product in ammonia was fractionally precipitated. The first fractions yielded *o*-nitro*allo* cinnamic acid and the later fractions *p*-nitro*allo*cinnamic acid, which forms yellow crystals, m. p. 143°. The crude mixture of isomerides was reduced as above, when excess of ammonia precipitated carbostyryl, due to the *allo*-*o*-amino-acid. *p*-Amino*allo*cinnamic acid was isolated from the filtrate in yellow needles, decomp. 103—104°. The *hydrochloride* crystallises in spikes. J. C. W.

**Some Derivatives of Cinnamic Acid.** H. RUPE, H. STEIGER, and F. FIEDLER (*Ber.*, 1914, 47, 63—75).—*Ethyl*  $\beta$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -methylpropionate,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , was obtained by boiling a mixture of benzophenone, ethyl bromopropionate, and metallic zinc with a mixture of benzene and toluene for an hour with special precautions, and then acidifying with ice-cold dilute sulphuric acid. The ester forms needles or colourless, stout prisms, m. p. 101—102°, and dissolves in sulphuric acid to a deep green colour. It can be hydrolysed by heating for three hours with hydrochloric acid, D 1.19, at 150°, giving  $\beta$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -methylpropionic acid, colourless, microscopic needles, m. p. 182°. The ester was successfully converted into  $\beta$ -phenyl- $\alpha$ -methylcinnamic acid,  $\text{CPh}_2\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , by simultaneous dehydration and hydrolysis induced by treatment with diluted sulphuric acid in boiling acetic acid for three to four hours; the product forms colourless prisms, m. p. 163°, gives a deep green solution in sulphuric acid, and forms salts which are all sparingly soluble. All attempts to obtain the chloride of  $\beta$ -phenyl- $\alpha$ -methylcinnamic acid, for example, by warming with thionyl chloride, resulted only in the formation of 3-phenyl-2-methylindone,  $\text{C}_6\text{H}_4\begin{smallmatrix} \diagup \text{CO} \diagdown \\ \text{CPh} \end{smallmatrix} \text{CMe}$ , reddish-yellow leaflets, m. p. 86—87; semicarbazone, tetragonal platelets, m. p. 200—201°.

*Ethyl*  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methyl-*n*-butyrate,  
 $\text{OH}\cdot\text{CPhMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ ,

a pleasant smelling oil, b. p. 144—145°/13 mm., can be dehydrated by boiling for six hours with 85% formic acid, giving *ethyl*  $\alpha\beta$ -dimethylcinnamate, a pleasant smelling, yellow oil, b. p. 129.5—130°/12 mm., which was accompanied by a small quantity of the free acid and dimethylstyrene. Hydrolysis of this ester by potassium hydroxide yields  $\alpha\beta$ -dimethylcinnamic acid as a mixture of two forms, a solid, needles, m. p. 112—113° (13% of the product), and a viscous, yellow liquid (87%) which distilled with some decomposition at 107—114°/0.1 mm. (compare Daïn, A., 1909, i, 435; Raikow, A., 1888, 369). The solid acid is the more stable and begins to liberate carbon dioxide appreciably at 202°; it is therefore regarded as the *trans*-isomeride, whilst to the liquid acid, which gives appreciable evolution of carbon dioxide at 131°, and for which the decomposition curve is somewhat less regular, is ascribed the *cis*-configuration, but its purity is uncertain. The solid acid gave an ethyl ester, b. p. 130°/12 mm., identical with the parent ester, and a *dibromide*, colourless needles, decomp. at 110°.

Hydrolysis of the parent ester by formic acid gave only the solid isomeride. The *menthyl* ester of the liquid  $\alpha\beta$ -dimethylcinnamic acid was obtained by direct esterification aided by hydrogen chloride, and constituted a colourless oil, b. p.  $198^{\circ}/14$  mm.; the liquid acid also gave a *hydrochloride*, crystallising in needles.

Hydrogenation of either of the preceding isomerides by hydrogen and colloidal palladium or less well by sodium amalgam gave rise to  $\beta$ -phenyl- $\alpha$ -methyl-*n*-butyric acid,  $\text{CHPhMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , colourless needles, m. p.  $130$ — $131.5^{\circ}$ . An attempt to convert the liquid acid into the solid isomeride by the action of sulphuric acid was unsuccessful on account of the formation of an *indone* derivative, m. p. near  $70^{\circ}$ ; *oxime*, m. p. near  $180^{\circ}$ .

*Ethyl  $\beta$ -hydroxy- $\beta$ -p-tolyl- $\alpha$ -methylbutyrate*,  
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{CMe}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ ,

obtained by the interaction of *p*-tolyl methyl ketone, ethyl  $\alpha$ -bromopropionate, and zinc in benzene solution, is a pale yellow liquid, b. p.  $149$ — $150^{\circ}/10$  mm. It is dehydrated by boiling with 85% formic acid for three hours, yielding *ethyl  $\alpha\beta$ -p-trimethylcinnamate*, a yellow liquid, b. p.  $141$ — $141.5^{\circ}/11$  mm., together with a quantity of  $\alpha\beta$ -*p-trimethylcinnamic acid*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , needles from light petroleum or plates from alcohol, m. p.  $163^{\circ}$ , which can also be obtained by hydrolysis of the ester with potassium hydroxide solution. In the synthesis of this acid the corresponding liquid modification was produced in insufficient quantity for investigation. The crystals of  $\alpha\beta$ -*p-trimethylcinnamic acid* belong to the rhombic system

( $a:b:c = 0.786:1:1.223$ ).

Hydrogenation of  $\alpha\beta$ -*p-trimethylcinnamic acid* by hydrogen and colloidal palladium produced  $\beta$ -*p-tolyl- $\alpha$ -methyl-*n*-butyric acid*,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ ,

colourless needles, m. p.  $113$ — $114^{\circ}$ .

D. F. T.

**Abietic Acid and Some of its Salts.** EMIL OSCAR ELLINGSON (*J. Amer. Chem. Soc.*, 1914, 36, 325—335).—Pure abietic acid was obtained from colophony by extraction with alcohol followed by recrystallisation from the same solvent. The acid formed colourless, triangular plates, which always contained traces of a viscid substance, the presence of which is possibly due to some change in the acid itself. The melting point, which is influenced by the rate of heating, is near  $152^{\circ}$  if the temperature is raised by approximately one degree per minute. The wide discrepancies as to the m. p. as recorded by various investigators are considered to indicate the existence of isomerides of different properties.

After fusion, the acid is reddish-brown, and evidence of chemical change is forthcoming; for example, the heat of combustion of the acid after fusion is somewhat less than that of the unfused acid.

Cryoscopic and ebullioscopic experiments in various solvents gave results which were far from concordant, the apparent molecular weight ranging from 200 in boiling pyridine to 500 in freezing benzene.

Sodium and potassium abietates were prepared by direct neutralisation of the acid with the corresponding alkali; the *silver* (white),

copper (pale blue), calcium, barium, strontium, cobalt (lavender), nickel (greenish-yellow), iron (light brown), zinc, chromium (greenish-yellow), aluminium, manganese (pale pink), and cadmium salts were obtained by precipitation of solutions of salts of the respective metals by a solution of the alkali salt of the acid. The stannic salt was instantaneously produced on mixing stannic chloride and cupric abietate in benzene solution, the solution of tin abietate being filtered from the precipitated copper chloride. The abietates of the heavier metals all contained an excess of abietic acid.

D. F. T.

**Preparation of Derivatives of *p*-Aminophenyl Salicylate containing Sulphur.** ISAK ABELIN, EMIL BÜRGI, and MENDEL PERELSTEIN (D.R.-P. 268174).—*p*-Sulphomethylaminophenyl salicylate,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$ , m. p.  $134-136^\circ$  (decomp.), is obtained on acidifying aqueous solutions of its salts of which the sodium salt is prepared by heating an aqueous suspension of *p*-aminophenyl salicylate with 8 to 10 parts of formaldehyde sodium hydrogen sulphite. It crystallises in white needles that are readily soluble in water, which property enables it to be used in therapeutics where the insolubility of phenyl salicylate (salol) is a disadvantage. The potassium salt is prepared in an analogous manner, and has similar properties. An alternative method of preparation is to employ sodium hydroxymethylsulphonate instead of the formaldehyde compound.

J. C. C.

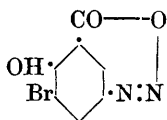
**Pinacol-Pinacolin Rearrangement. Preparation of Benzoylformic [Phenylglyoxylic] Acid and Some of its Derivatives.** S. F. ACREE (*Amer. Chem. J.*, 1913, **50**, 389—395. Compare A., 1903, i, 724; 1904, i, 742; 1905, i, 216).—Phenylglyoxylic acid can be readily obtained in good yield by the interaction of cold dilute solutions of mandelic acid and potassium permanganate. The chloride, b. p.  $125^\circ/9$  mm., can be prepared by warming the acid with thionyl chloride at about  $40^\circ$ , and when treated with alcohol yields the corresponding ethyl ester.

By the action of magnesium phenyl bromide (3 mols.) on ethyl phenylglyoxylate (1 mol.), a product is obtained which on decomposition with cold dilute sulphuric acid yields benzpinacone. When ethyl phenylglyoxylate (1 mol.) is treated with magnesium phenyl bromide (1 mol.) and the product decomposed with water, an excellent yield of ethyl benzilate is obtained. A similar experiment was made with ethyl phenylglyoxylate and magnesium *p*-tolyl bromide with a view to obtaining ethyl phenyl-*p*-tolylglycollate; most of the ethyl phenylglyoxylate was recovered unchanged, but a small quantity of an ester, b. p.  $210-212^\circ/15$  mm., was isolated.

E. G.

**Some New Derivatives of Di- and Tri-hydroxybenzoic Acids.** FRANZ VON HEMMELMAYR (*Monatsh.*, 1914, **35**, 1—8. Compare A., 1911, i, 983; 1912, i, 977).—The hydrochloride of 3-bromo-5-amino- $\beta$ -resorcylic acid is most readily obtained by the reduction of an acid, alcoholic solution of 3-bromo-5-nitro- $\beta$ -resorcylic acid with dilute stannous chloride solution. It forms white needles, which darken and slowly decompose above  $200^\circ$  and are not melted at  $275^\circ$ . When boiled with water, it is partly decomposed with evolution of

carbon dioxide. *3-Bromo-5-amino-β-resorcylic acid*, colourless prisms which decompose slightly without melting at 280°, is prepared by the action of warm water on the chloride. *3-Bromo-5-amino-β-resorcylic acid hydrobromide*, colourless crystals, is obtained by reducing the



nitro-acid by tin and hydrobromic acid. When dissolved in warm, dilute hydrobromic acid and treated with potassium nitrite it yields *bromodiazob-β-resorcylic acid* (annexed formula), dark orange-yellow crystals which explode when heated, and which are converted by

successive treatment with potassium hydroxide and alkaline stannous chloride solution into *3-bromo-β-resorcylic acid*, brown needles, m. p. 202°. The latter is decomposed by boiling water to about the same extent as *β-resorcylic acid*, so that the stabilising influence of the bromine atom in the meta-position to the carboxyl group appears to be neutralised by the proximity of the two hydroxyl groups.

*Aminogentisic acid hydrochloride*, colourless plates, is obtained by the reduction of nitrogentisic acid by stannous chloride and dilute hydrochloric acid. Protracted treatment with water decomposes it completely into *aminogentisic acid*, which decomposes at 204° after previous darkening.

The action of methyl sulphate on hydroxyquinolcarboxylic acid has been investigated by Bargellini and Martegiani (A., 1912, i, 981), who thereby obtained asaronic acid. The author finds, however, that the main product of the action is *hydroxyquinolcarboxylic acid dimethyl ether*, brown needles, m. p. 202° (decomp.). Sodium methoxide and methyl iodide in methyl-alcoholic solution convert this substance, as also hydroxyquinolcarboxylic acid, into the corresponding *methyl ester*, colourless needles, m. p. 95°.

H. W.

**Acetylsalicylic Acid.** HEINRICH VON KRANNICHFELDT (Ber., 1914, 47, 156—159).—Phenol and *p*-hydroxyacetophenone have been isolated as the products of the distillation of acetylsalicylic acid with lime. The acid is therefore established as 2-hydroxy-5-acetylbenzoic acid, as the discoverers, Bialobrzewski and Nencki suggested (A., 1897, i, 531). The occurrence of phenol was traced to the action of lime on the *p*-hydroxyacetophenone, and this unexpected reaction will be applied to other ketones.

When the acid was treated with the required amount of chloroacetic acid and potassium (but not sodium) hydroxide (compare R. Meyer, A., 1913, i, 1344) a small yield of 2-carboxy-4-acetylphenoxyacetic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Ac}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , was obtained. The compound forms yellow scales, m. p. 179°, which give a reddish-brown colour with alcoholic ferric chloride, traces of acetylsalicylic acid producing a violet coloration.

Acetylsalicylic acid was also converted into the *ethyl ester*, white needles, m. p. 70—71°, and by means of methyl sulphate, followed by hydrolysis of the ester by calcium hydroxide, into the *methoxy-derivative*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Ac}\cdot\text{CO}_2\text{H}$ . The latter formed white needles, m. p. 152°, and yielded an *ethyl ester*, pale yellow, prismatic needles, m. p. 41—42°, and by means of diazomethane, the *methyl ester*, in slender, white needles, m. p. 96°.

J. C. W.

**Ketens. XXV. The Action of Acid Chlorides on Diphenylketen.** H. STAUDINGER, O. GÖHRING, and M. SCHÖLLER (*Ber.*, 1914, 47, 40—48. Compare Staudinger, Anthes, and Schneider, A., 1913, i, 1339) —It is found that many acid chlorides condense with diphenylketen at the ethylenic linking. This is of interest because, although acid chlorides have been found capable of condensation at a carbonyl group (Staudinger, A., 1909, i, 1905), no such effect has previously been produced at an ethylenic linking.

The method was to enclose the diphenylketen and acid chloride in separate sealed test glasses, and to allow interaction by breaking these inside a sealed bomb tube containing an atmosphere of carbon dioxide. If no chemical change occurred in twenty-four hours in the cold, the tube was heated in a water-bath or in a bomb furnace.

Diphenylketen and oxalyl chloride react in the cold, giving *diphenylmalonyl chloride*,  $\text{COCl} \cdot \text{CPh}_2 \cdot \text{COCl}$ , colourless crystals, b. p. 51.5—52.5°, b. p. 183—184°/13 mm.; *di-anilide*, colourless crystals, m. p. 187—188°. The chloride when heated with alcohol produced crystalline *methyl diphenylmalonate*, m. p. 94—95°, but its considerable resistance to the action of water was in accord with the usual effect of the phenyl group on the stability of an acid chloride (compare Schmidlin and Hodgson, A., 1908, i, 170). Carbonyl chloride gave with diphenylketen the same product as was obtained with oxalyl chloride, but a temperature of 120—130° was necessary. In an analogous manner, oxalyl bromide gave *diphenylmalonyl bromide*, m. p. 88—90°, and ethyl chloroglyoxylate yielded *ethyl diphenylmalonyl chloride*,  $\text{COCl} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{Et}$ , m. p. 74—75°.

Ethyl chloroformate, which might have been expected to give rise to the same product as ethyl chloroglyoxylate, actually gave rise at 100° to a slow polymerisation yielding a yellow, crystalline *substance*, m. p. 187—188°; this is not identical with the dimeric tetraphenylcyclobutanedione described earlier (Staudinger, A., 1911, i, 306; compare also Staudinger and Kon, A., 1911, i, 876).

Chloroglyoxylanilide and chloroformanilide did not react in the expected manner with formation of diphenylmalonanil; the former gave a somewhat complex change at 100°, diphenylacetyl chloride, oxanilide and diphenylcarbamide being obtained, whilst the latter substance parted smoothly with the elements of hydrogen chloride, producing phenylcarbamide and diphenylacetyl chloride. The

*diphenylmalonanil*,  $\text{CPh}_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NPh}$ , which failed to appear as the product of the interaction of the last two reagents with diphenylketen, was obtainable as colourless crystals, m. p. 125—126°, by heating phenylcarbamide with diphenylketen at 220°, although at 150° the only change observed was the polymerisation of the diphenylketen to tetraphenylcyclobutanedione. Diphenylmalonanil when heated with aniline at 200° becomes converted into the diphenylmalonanilide described above, but is remarkably stable towards mere heating, and decomposes slowly with regeneration of its components at 300°.

Thiocarbonyl chloride failed to react in the cold, and on warming caused resinification. Bromoacetyl bromide, phthalyl chloride, cyanogen iodide, and triphenylmethyl chloride gave a similar result.

Acetyl chloride reacted first at 100°, the products being diphenyl-

acetyl chloride and a resinous mass, the latter being probably formed by the polymerisation of the simple keten which had been primarily produced from the acetyl chloride. Succinyl chloride gave the same products.

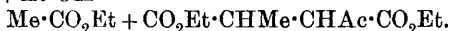
Benzoyl chloride and bromide behaved like ethyl chloroformate, inducing polymerisation to the substance, m. p. 188°.

It has already been shown that the action of phosphorus pentachloride on diphenylketen yields diphenylchloroacetyl chloride; phosphorus trichloride merely gives rise to the dimeride, m. p. 188°, together with resinous substances. Sulphuryl chloride gives similar products to phosphorus pentachloride, whilst thionyl chloride produces chlorodiphenylacetyl chloride together with sulphur dioxide and sulphur. In the case of the last two reagents, it is possible that the molecule of halogen compound first unites at the characteristic keten grouping, the resulting compounds then losing sulphur dioxide and SO respectively, the latter of which resolves itself into sulphur dioxide and sulphur.

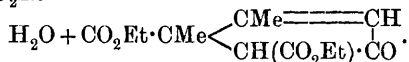
D. F. T.

**Methylation of Ethyl Diacetylsuccinate.** RICHARD WILL-STÄTTER and CHARLES HUGH CLARKE (*Ber.*, 1914, **47**, 291—310).—Ethyl diacetylsuccinate having been used by Knorr, and acetonylacetone by Paal, as the starting point in the synthesis of substituted pyrroles, the authors have attempted to obtain mono- and di-alkyl derivatives of these compounds with a view to the synthesis of tri- and tetra-substituted pyrroles.

Under the ordinary conditions for alkylating ethyl acetoacetate, the methylation of ethyl diacetylsuccinate follows a complicated course. The furan derivative of ethyl carbopyrotritarate and the lactone of ethyl isocarbopyrotritarate are formed, as also are ethyl *O*:*O*-dimethyldiacetylsuccinate and ethyl *C*-methyldiacetylsuccinate, the latter then undergoing change in three directions: (1) By alcoholysis it loses a carboxyl group and yields ethyl  $\alpha$ -acetyl- $\beta$ -methylsuccinate,  $\text{CO}_2\text{Et}\cdot\text{CMeAc}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et} + \text{Et}\cdot\text{OH} =$

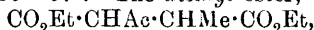


(2) Part undergoes further methylation, hydrolysis yielding *s*-dimethylsuccinic acid. (3) Condensation to a cyclopentenone derivative occurs, thus:  $\text{CO}_2\text{Et}\cdot\text{CMeAc}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et} =$



The compound obtained by Dietzel (A., 1889, 593) along with methylpyrotritaric acid by distilling methylmethronic acid is not a dimethylcyclopentenone, but trimethylfuran, whilst the so-called methylketopentamethylene from methronic acid is dimethylfuran.

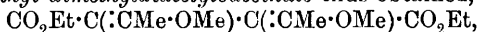
*Ethyl hydrogen  $\alpha$ -acetyl- $\beta$ -methylsuccinate*,  $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , forms prisms, m. p. 66—67°. The *diethyl* ester,



is a colourless, moderately, mobile oil, b. p. 94—95°/0.07 mm.,  $D_4^{17.5}$  1.0620.

Hydrolysis and removal of carbon dioxide from the ethyl dimethylcyclopentenonedicarboxylate yield 2:3-dimethyl- $\Delta^1$ -cyclopenten-5-one,  $\text{CHMe} \begin{cases} \text{CMe} = \text{CH} \\ \text{CH}_2 - \text{CO} \end{cases}$ , a mobile oil, b. p. 67—68°/9 mm.

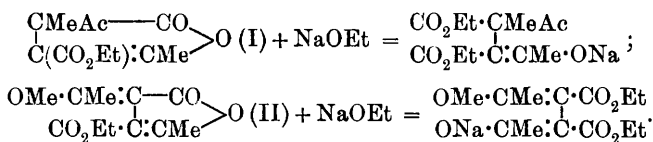
Methylation of the disodium or dipotassium salt of ethyl diacetylsuccinate in ethereal suspension by means of methyl sulphate at the ordinary temperature proceeds readily and exclusively at the oxygen atom. The *ethyl dimethyldiacetylsuccinate* thus obtained,



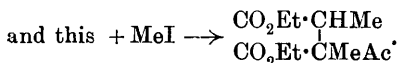
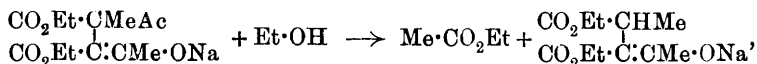
forms *cis*- and *trans*-isomerides: (1) a colourless, viscous oil, b. p. 134.5—136.5°/0.2 mm.,  $D_4^{15}$  1.1214, which does not react with hydroxylamine in acetic acid solution, but unites with bromine in alcohol; (2) rhombohedral, almost cubical crystals, m. p. 106°. The action of methyl sulphate in presence of boiling xylene yields only oxygen-substituted derivatives, mixed with ethyl carbopyrotritarate. The two dimethyldiacetylsuccinic esters may also be obtained by methylating with diazomethane, but the action is very slow.

*Ethyl dipropionylsuccinate*,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{COEt})\cdot\text{CH}(\text{COEt})\cdot\text{CO}_2\text{Et}$ , forms rhomb-shaped plates, m. p. 87°, and gives no reaction with ferric chloride. By dissolution in dilute sodium hydroxide solution and precipitation with ice-cold sulphuric acid, it is converted into an oily enolic form, which is re-converted into the ketonic modification when distilled in a vacuum. With hydroxylamine it gives *ethyl 1-hydroxy-2:5-diethylpyrrole-3:4-dicarboxylate*,  $\text{C}_{14}\text{H}_{21}\text{O}_5\text{N}$ , a viscous oil, b. p. 205—206°/0.05 mm., whilst ammonium acetate converts it into *ethyl 2:5-diethylpyrrole-3:4-dicarboxylate*,  $\text{C}_{14}\text{H}_{21}\text{O}_4\text{N}$ , an oil, b. p. 170°/0.025 mm. Methylation of the disodium compound of ethyl dipropionylsuccinate in ether by means of methyl sulphate yields, besides furan derivative, only the *O:O-dimethyl ether*,  $\text{C}_{16}\text{H}_{26}\text{O}_6$ , as an oil, b. p. 130—135°/0.1 mm.

As regards its behaviour on methylation, ethyl *isocarbopyrotritarate* occupies a position intermediate between ethyl acetoacetate and ethyl diacetylsuccinate. Treatment of its dry sodium salt with methyl sulphate always yields a mixture, in about equal proportions, of the carbon-substituted (formula I, below) and of the *cis*- and *trans*-modifications of the oxygen-substituted methyl derivative (formula II, below). From these, the corresponding mono-alkylated ethyl diacetylsuccinates may be obtained by treatment in the cold with sodium ethoxide, which is simply added to the molecule.



These sodium salts cannot be alkylated in the same way as ethyl acetoacetate, since they readily lose an acetyl group by alcoholysis and pass into homologues of the monoacetylsuccinic ester. Thus, on heating with methyl iodide,





Under milder conditions of methylation, for example, with methyl sulphate in the cold, replacement of the sodium occurs, giving  $\text{CO}_2\text{Et}\cdot\text{CMeAc}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{OMe}$ .

*Ethyl C-methylisocarbopyrotritarate* (formula I, above) is a colourless, slightly viscous oil, b. p.  $142-143^\circ/9$  mm.,  $D_4^{20}$  1.1468.

The *cis*- and *trans*-modifications of *ethyl O-methylisocarbopyrotritarate* (formula II, above) have the properties:  $\alpha$ -form, domed, hexagonal prisms, m. p.  $63^\circ$ ;  $\beta$ -form, quadratic plates, m. p.  $95^\circ$ .

*Ethyl C-ethylisocarbopyrotritarate*,  $\text{C}_{12}\text{H}_{16}\text{O}_5$ , obtained by means of ethyl sulphate, is a colourless oil, b. p.  $143-144^\circ/9$  mm.,  $D_4^{15}$  1.1133.

*Ethyl diacetyl-C-methylsuccinate*,  $\text{C}_{13}\text{H}_{20}\text{O}_6$ , is an oil, b. p.  $150-160^\circ/11$  mm.,  $D_4^{15}$  1.1168, and gives a reddish-violet coloration with ferric chloride. The corresponding *O:O-dimethylsuccinate*,  $\text{C}_{14}\text{H}_{22}\text{O}_6$ , has b. p.  $160-161^\circ/10$  mm.,  $D_4^{15}$  1.1022, and the *O:O-diethylsuccinate*,  $\text{C}_{15}\text{H}_{24}\text{O}_6$ , is a moderately viscous oil, b. p.  $163-164^\circ/14$  mm.

*Ethyl diacetyl-C-ethylsuccinate*,  $\text{C}_{14}\text{H}_{22}\text{O}_6$ , b. p.  $158-163^\circ/10$  mm., gives with methyl sulphate a *O-methyl* derivative, b. p.  $156-157^\circ/9$  mm.

The  $\alpha$ -form of ethyl *O-methylisocarbopyrotritarate*, m. p.  $63^\circ$ , gives, with sodium ethoxide, *ethyl O-methyldiacetylsuccinate*,  $\text{C}_{13}\text{H}_{20}\text{O}_6$ , as a viscous oil, b. p.  $164-165^\circ/13$  mm., which forms a violet coloration with ferric chloride.

Since mono-alkylated ethyl diacetylsuccinates cannot be further substituted at the carbon atom, alkylation of ethyl  $\alpha\beta$ -diacetylbutyrate has been resorted to in order to obtain homologues of acetonylacetone. In this case the alkyl becomes attached to the carbon atom, giving derivatives of dimethylacetonylacetone which Ciamician and Silber obtained from methyl ethyl ketone and converted into tetramethylpyrrole (A., 1912, i, 537). The methylated and more especially the ethylated diacetylbutyric ester, with which conversion into furan derivatives is no longer possible, readily condense to cyclopentenones. Since this ring closure occurs in an alkaline medium, methylation always yields a mixture of ethyl  $\alpha\beta$ -diacetyl- $\alpha$ -methylbutyrate and ethyl 2:3:4-trimethyl- $\Delta^1$ -cyclopenten-5-one-3-carboxylate, which can scarcely be separated by fractionation. If this mixture of esters is subjected to ketonic decomposition in alkaline solution, condensation to 2:3:4-trimethyl- $\Delta^1$ -cyclopenten-5-one advances further, and the latter cannot be separated from the dimethylacetonylacetone. Ketonic decomposition by means of dilute sulphuric acid or hydrobromic and glacial acetic acids results in the loss of the greater part of the diketone, which is converted into tetramethylfuran, this being distinguished from its lower homologues by the greater stability of the furan ring.

2:3:4-Trimethyl- $\Delta^1$ -cyclopenten-5-one,  $\text{CO} \begin{array}{l} \text{CH}=\text{CMe} \\ \text{CHMe}\cdot\text{CHMe} \end{array}$ , is a colourless, mobile oil, b. p.  $78^\circ/11$  mm.,  $D_4^{21}$  0.939, and gives a semicarbazone,  $\text{C}_9\text{H}_{15}\text{ON}_3$ , m. p.  $209^\circ$ .

1:2:3-Trimethylcyclopentan-4-ol,  $\text{OH}\cdot\text{CH} \begin{array}{l} \text{CH}_2-\text{CHMe} \\ \text{CHMe}\cdot\text{CHMe} \end{array}$ , obtained by hydrogenating the ketone in presence of platinum, is a liquid,

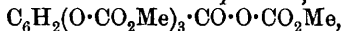
b. p. 68—70°/12 mm., with an odour resembling that of menthol. Its *naphthylurethane*,  $C_8H_{15} \cdot O \cdot CO \cdot NH \cdot C_{10}H_7$ , has m. p. 111—112°.

Ethylation of ethyl  $\alpha\beta$ -diacetylbutyrate by means of ethyl iodide and sodium ethoxide gives a mixture, two-thirds of which consists of cyclic condensation product. Treatment of the mixture with aqueous barium hydroxide yields almost pure 2:4-*dimethyl-3-ethyl- $\Delta^1$ -cyclopenten-5-one*,  $C_9H_{14}O$ , b. p. 88—89°/12 mm., which forms a *semi-carbazone*,  $C_{10}H_{17}ON_3$ , m. p. 158°. T. H. P.

**Methylcarbonato-derivatives of Phloroglucinolcarboxylic Acid and of Phloreitic Acid.** EMIL FISCHER and HERMANN STRAUSS (*Ber.*, 1914, 47, 317—322. Compare A., 1913, i, 731, 976, 1352).—The preparation of trimethylcarbonato-derivative of phloroglucinolcarboxylic acid presents unusual difficulties, since in aqueous alkaline solution only a monomethylcarbonato-derivative is obtained (A., 1910, i, 248), whilst in the presence of dimethylaniline the formation of trimethylcarbonato-compound is accompanied by the production of considerable quantities of a neutral intermediate compound. The nature of the latter has now been examined, and a ready method for converting it into the trimethylcarbonato-derivatives is described.

*Trimethylcarbonatophloroglucinolcarboxylic* [2:4:6-*trimethylcarbonatobenzoic*] acid, m. p. about 123° (decomp.), is obtained in 86% yield when a solution of phloroglucinolcarboxylic acid in benzene is treated with methyl chloroformate in the presence of dimethylaniline; the crude product is treated with potassium hydrogen carbonate in aqueous acetone solution, whereby the intermediate compound is decomposed and the acid is isolated by addition of hydrochloric acid and extraction with ethyl acetate. It can be more readily obtained from monomethylcarbonatophloroglucinolcarboxylic acid.

The above-mentioned intermediate product,



m. p. 81—82°, is contained in considerable quantity in the benzene solution obtained after the action of methyl chloroformate and dimethylaniline, and may be obtained in the crystalline form when this solution is simultaneously shaken with dilute sulphuric acid and much ether. It is scarcely affected by cold aqueous solutions of bases, probably on account of its sparing solubility in water.

2:4:6-*Trimethylcarbonatobenzoic acid* has been obtained in the solid state, m. p. about 53—55°.

Phloreitic acid [ $\beta$ -*p*-hydroxyphenylpropionic acid], obtained from phloridzin by the method of Cremer and Seuffert (A., 1912, i, 885), is transformed by methyl chloroformate in aqueous alkaline solution into  $\beta$ -*p*-methylcarbonatophenylpropionic acid, fine needles or thin plates, m. p. 83—84°. For the similar product obtained from synthetic *p*-hydroxy- $\alpha$ -phenylpropionic acid, Sonn (this vol., i, 184) gives m. p. 86—87°. Phosphorus pentachloride in the presence of chloroform converts it into the corresponding *chloride*, which can be distilled without decomposition under greatly reduced pressure and has b. p. about 120°/0.13 mm. When cooled from -40° to -50° it slowly solidifies to a crystalline mass, m. p. about 10—12°. H. W.

[Resorcinolbenzein and Fluorescein.] F. KEHRMANN (*Ber.*, 1914, 47, 84—87).—A final contribution by the author to the controversy (compare A., 1913, i, 1352) with von Liebig (compare this vol., i, 49; A., 1913, i, 865). D. F. T.

Galloflavin. J. HERZIG and R. WACHSLER (*Monatsh.*, 1914, 35, 77—84).—Previous work on the constitution of galloflavin (Herzig, Erdös, and Ruzicka, A., 1910, i, 676) has been greatly hampered by the poor yields obtained in converting galloflavin tetramethyl ether into isogalloflavin trimethyl ether. An improvement has now been effected by the preparation of isogalloflavin and the conversion of the latter into its trimethyl ether with intermediate formation of the tetramethyl ether, the yields in each of the processes being very good.

When galloflavin is dissolved in 10% aqueous potassium hydroxide, it may be recovered unchanged by immediate addition of acid; after some time, addition of acid causes no precipitate, but a solution is formed which, when warmed, deposits isogalloflavin. The identity of the latter follows from its conversion into isogalloflavin tetramethyl ether, m. p. 232—233°, and transformation of the latter by potassium hydroxide and methyl sulphate into the ether ester,  $C_{12}H_2O_4(OMe)_6$ , m. p. 92—95°. Acetic anhydride and sodium acetate convert isogalloflavin into triacetylisogalloflavin, m. p. 220—223° (decomp.). Acetic acid is lost at the m. p., the carboxyl group, unlike that in isogalloflavin trimethyl ether, being apparently stable. The molten substance, after renewed acetylation, is re-converted into the original compound. The presence of a carboxyl group in triacetylisogalloflavin cannot thus be directly proved, but is rendered probable from the fact that diazomethane converts it into a substance,  $C_{12}H_2O_4(OAc)_3 \cdot OMe$ , m. p. 216—219°.

[With TRENKLE.]—The almost quantitative production of isogalloflavin trimethyl ether from the tetramethyl ether is secured by dissolving the latter in methyl alcohol and cautiously warming with potassium hydroxide and water; the reaction mixture is quickly cooled, poured into concentrated sulphuric acid, and cautiously diluted with water. The method is much less successful when applied to the preparation of isogalloflavin trimethyl ether from galloflavin tetramethyl ether.

Attempts have been made to obtain methyl ethers of still unchanged galloflavin by the rapid methylation of the latter immediately following its solution in potassium hydroxide. In this manner, methyl sulphate yielded a small, smeary precipitate (which gave isogalloflavin tetramethyl ether with diazomethane), isogalloflavin trimethyl ether, a substance which with diazomethane gave isogalloflavin tetramethyl ether, and the ether ester,  $C_{10}H_2O(OMe)_4(CO_2Me)_2$ , together with syrupy, amorphous products which could not be distilled. H. W.

“Paired” Glycuronic Acids. YOSHITA SERA (*Zeitsch. physiol. Chem.*, 1913, 88, 460—464).—When the urine of a rabbit fed with orcinol is treated with lead acetate, filtered, and treated with basic lead acetate, a precipitate is obtained which, after decomposition with hydrogen sulphide, yields a solution which gives with barium carbonate barium orcinolglycuronate,  $Ba(C_{13}H_{17}O_9)_2$ . The

salt has  $[\alpha]_D -73.58^\circ$  (in aqueous solution), and yields orcinol and glycuronic acid when hydrolysed with sulphuric acid. It is not hydrolysed by emulsin, and the author also finds that vanillin-glycuronic acid is also unacted on by emulsin (compare Hildebrandt, *Beitr. chem. Physiol. Path.*, 1906, 7, 438), so that there is no reason to suppose that either of these acids is of the nature of a glucoside.

R. V. S.

**Constitution of Two Nitro-*m*-tolualdehydes.** FRITZ MAYER (*Ber.*, 1914, 47, 406—411).—It has long been known that the nitration of *m*-tolualdehyde yields two products, m. p.  $64^\circ$  and  $44^\circ$ , which have been regarded as 4-nitro-*m*-tolualdehyde and 2-nitro-*m*-tolualdehyde respectively. The author now finds that by oxidation with 1% potassium permanganate, the aldehyde, m. p.  $44^\circ$ , yields 4-nitro-*m*-toluic acid, m. p.  $134^\circ$ , and is, therefore, 4-nitro-*m*-tolualdehyde, whilst the aldehyde, m. p.  $64^\circ$ , yields 2-nitro-*m*-toluic acid, m. p.  $219^\circ$ , and is, therefore, 2-nitro-*m*-tolualdehyde. Consequently it follows that the series of compounds prepared by the author (A., 1912, i, 478) from the supposed 2-nitro-*m*-tolualdehyde (in reality, the 4-nitro-compound) are 6-amino-3-methylbenzaloxime, 6-iodo-3-methylbenzaldehyde, 6-iodo-3-methylbenzylideneaniline, 2:2'-dialdehydo-4:4'-dimethyldiphenyl, and 2:7-dimethylphenanthraquinone; the last substance is identical with Liebermann's 2:7-dimethylphenanthraquinone, m. p.  $224^\circ$  (A., 1911, i, 656).

Starting from 2-nitro-*m*-tolualdehyde, m. p.  $64^\circ$ , the following series of compounds has been prepared by reactions similar to those already recorded (*loc. cit.*): 2-amino-3-methylbenzaloxime, m. p.  $134^\circ$ ; 2-iodo-*m*-tolualdehyde, m. p.  $55$ — $56^\circ$ ; 2:2'-dialdehydo-6:6'-dimethyldiphenyl, m. p.  $118^\circ$ . The unsatisfactory yield in the last reaction is in accord with the author's experience that in Ullmann's reaction with copper powder the yield is bad or good according as the halogen atom is situated between two positive or two negative groups.

6-Iodo-3-methoxybenzaldehyde, m. p.  $114$ — $115^\circ$ , prepared from 6-amino-3-methoxybenzaloxime, is converted through the benzylideneaniline into 2:2'-dialdehydo-4:4'-dimethoxydiphenyl, m. p.  $123$ — $124^\circ$ , which reacts with boiling aqueous alcoholic potassium cyanide to form 2:7-dimethoxyphenanthraquinone, m. p.  $214$ — $215^\circ$ , dark red powder.

C. S.

**Alkylation of the cyclopentanones and Rupture of the Cyclic Chain of 1:3-Tetra-alkyl Derivatives by Sodamide.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1914, 158, 298—304).—The direct alkylation of cyclopentanone in ethereal solution by means of sodamide and methyl iodide gives but a very small yield of methylcyclopentan-2-one, the major portion being converted into condensation products (compare Godchet and Taboury, A., 1913, i, 873). 1-Methylcyclopentan-2-one, prepared from ethyl cyclopentanonecarboxylate, can, however, be readily, successively methylated by the action of sodamide followed by methyl iodide in ethereal solution. By this method the authors have prepared 1:3-dimethylcyclopentan-2-one, b. p.  $145$ — $146^\circ$  (corr.),  $D_4^{20}$  0.8898,  $n_D^{20}$  1.4321.

1 : 1 : 3-Trimethylcyclopentan-2-one, b. p. 151—152° (corr.),  $D_4^{20}$  0.8781,  $n_D^{20}$  1.4306 (compare Blanc, A., 1907, i, 710).

1 : 1 : 3 : 3-Tetramethylcyclopentan-2-one, b. p. 155—156° (corr.),  $D_4^{20}$  0.8653,  $n_D^{20}$  1.4288.

In this series the boiling point rises steadily with the introduction of each methyl group, whilst the density and refractive index steadily decrease.

The ethylation of cyclopentanone yielded only a small quantity of a mixture of methylethyl- and methyldiethyl-cyclopentanones, together with a large quantity of condensation products, and was not proceeded with.

The allylation of 1-methylcyclopentan-2-one yielded 1-methyldiallylcyclopentan-2-one  $[(C_3H_5)_2 = 1 : 3 \text{ or } 3 : 3]$ , b. p. 130°/16 mm. (corr.),  $D_4^{20}$  0.9251,  $n_D^{20}$  1.4823, in which the distribution of the allyl groups between the positions 1 and 3 has not been determined. On warming this substance with sodamide in xylene it undergoes decomposition, giving a substance distilling at 135—190°/16 mm. and containing nitrogen.

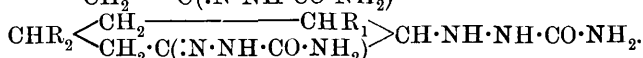
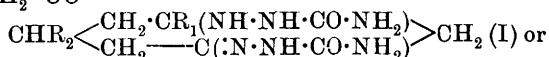
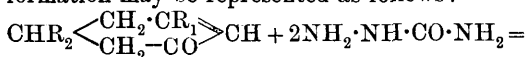
1 : 1 : 3 : 3-Tetramethylcyclopentan-2-one when heated with sodamide in boiling toluene for seven hours is decomposed, giving  $\alpha\alpha\delta$ -trimethylhexamide,  $CH_3 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot CO \cdot NH_2$ , white plates, m. p. 123°, the constitution of which was determined by preparation as follows.

Phenyl isopropyl ketone warmed in benzene solution with sodamide and then with isoamyl iodide yielded dimethylisoamylacetophenone [*phenyl  $\alpha\alpha$ -trimethylamyl ketone*], b. p. 150—151°/16 mm. (corr.),  $D_4^{20}$  0.9361,  $n_D^{20}$  1.5007, giving an oxime, m. p. 131°. This ketone on warming with sodamide in toluene yielded the required amide as above, which on decomposition with sodium nitrite and sulphuric acid gave  $\alpha\alpha\delta$ -trimethylhexoic acid, b. p. 127°/16 mm. (corr.). W. G.

**Preparation of Semicarbazones and Semicarbazidesemicarbazones of cycloHexenones.** IPPOLIT MACUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1925—1936).—With the exception of camphoronesemicarbazidesemicarbazone, no products of reaction of 2 mols. of semicarbazide with unsaturated hydroaromatic ketones have previously been prepared. The author finds, however, that the formation of semicarbazidesemicarbazones takes place with unsaturated  $\Delta^1$ -cyclic ketones in the same way as with unsaturated  $\Delta^\alpha$ -aliphatic ketones. In consequence of the inconstancy of their decomposition temperatures, the semicarbazones are inapplicable to the characterisation of unsaturated  $\Delta^1$ -cyclic ketones. For all the semicarbazones examined, the decomposition temperatures vary within narrow and almost identical limits, and the same is the case with the semicarbazidesemicarbazones, for which the temperatures are somewhat higher. When the cyclic ketone contains an iso-radicle as substituent, the conditions employed for obtaining semicarbazidesemicarbazones yield also a large proportion of the semicarbazone.

Semicarbazidesemicarbazones may be obtained by treating the cyclic ketone (1 mol.) in cold aqueous alcoholic solution with semicarbazide hydrochloride (2 mols.) in presence of sodium acetate. Their formation

occupies about a fortnight, and may be ascertained by boiling a small quantity of the precipitate formed with absolute alcohol, in which they are insoluble; the completion of the reaction occupies a considerable period. Owing to their difficult solubility in all the ordinary solvents, and to their tendency to decompose when boiled for a long time with a solvent, they are best purified by washing on the filter successively with hot water, boiling absolute alcohol, and anhydrous ether. Their formation may be represented as follows:



Or, the second semicarbazide residue may be taken up at the double linking of the first semicarbazide residue, so that four constitutions are possible. The results of Rupe and Kessler (A., 1910, i, 15) and of Harries (A., 1904, i, 427) render formula I. the most probable.

2-Methyl- $\Delta^1$ -cyclohexen-6-one semicarbazone has m. p. about  $174-176^\circ$  (decomp.). Vorländer and Gärtner (A., 1899, i, 259) gave m. p.  $199-201^\circ$ .

2:4-Dimethyl- $\Delta^1$ -cyclohexen-6-one semicarbazone has m. p.  $168-171^\circ$  (decomp.). Knoevenagel (A., 1897, i, 609) gave m. p.  $179-180^\circ$  and  $174-174.5^\circ$ .

2-Methyl-4-ethyl- $\Delta^1$ -cyclohexen-6-one semicarbazone,  $\text{C}_{10}\text{H}_{17}\text{ON}_3$ , forms snow-white, nacreous plates, m. p.  $162-168^\circ$  (decomp.).

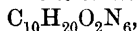
2-Methyl-4-propyl- $\Delta^1$ -cyclohexen-6-one semicarbazone,  $\text{C}_{11}\text{H}_{19}\text{ON}_3$ , forms colourless crystals, m. p. about  $150-153^\circ$  (decomp.).

2-Methyl-4-isopropyl- $\Delta^1$ -cyclohexen-6-one semicarbazone,  $\text{C}_{11}\text{H}_{19}\text{ON}_3$ , decomposes at about  $164-167^\circ$ .

2-Methyl-4-isobutyl- $\Delta^1$ -cyclohexen-6-one semicarbazone,  $\text{C}_{12}\text{H}_{21}\text{ON}_3$ , forms colourless, nacreous scales, m. p. about  $163-167^\circ$  (decomp.).

2-Methyl- $\Delta^1$ -cyclohexen-6-one semicarbazidesemicarbazone,  $\text{C}_9\text{H}_{18}\text{O}_2\text{N}_6$ , forms a pale yellow, microcrystalline powder, decomposing at  $174-179^\circ$ .

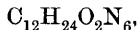
2:4-Dimethyl- $\Delta^1$ -cyclohexen-6-one semicarbazidesemicarbazone,



forms a snow-white, microcrystalline mass, decomposing at  $182-185^\circ$ . Attempts to purify this compound by dissolving it in hydrochloric acid, precipitating it by means of potassium carbonate, and washing with water, alcohol and ether resulted in marked decomposition.

2-Methyl-4-ethyl- $\Delta^1$ -cyclohexen-6-one semicarbazidesemicarbazone,  $\text{C}_{11}\text{H}_{22}\text{O}_2\text{N}_6$ , forms small, snow-white crystals, decomposing at  $183-186^\circ$ .

2-Methyl-4-propyl- $\Delta^1$ -cyclohexen-6-one semicarbazidesemicarbazone,



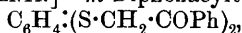
forms snow-white crystals, decomposing at  $183-186^\circ$ .

2-Methyl-4-isopropyl- $\Delta^1$ -cyclohexen-6-one semicarbazidesemicarbazone,  $\text{C}_{12}\text{H}_{24}\text{O}_2\text{N}_6$ , forms snow-white crystals, decomposing at  $186.5-190^\circ$ .

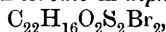
2-Methyl-4-isobutyl- $\Delta^1$ -cyclohexen-6-one semicarbazidesemicarbazone,  $\text{C}_{13}\text{H}_{26}\text{O}_2\text{N}_6$ , decomposing at  $185-188^\circ$ , was not obtained quite pure

The alcoholic solution yielded snow-white crystals of the composition  $C_{12}H_{21}ON_3$ . T. H. P.

**Action of Phenacyl Bromide on Thioresorcinol.** CESARE FINZI (*Gazzetta*, 1913, 43, ii, 643—654. Compare Posner, A., 1908, i, 21).—[With IDA PARENTI.]—*m*-Diphenacylthiolbenzene,



is obtained in 85% yield by the interaction of thioresorcinol, sodium hydroxide (rather more than 2 mols.), and phenacyl bromide (2 mols.); it forms silky needles, m. p.  $95^\circ$ , and is very stable, being hardly decomposed by boiling alkalis. Its *dioxime*,  $C_{22}H_{20}O_2N_2S_2$ , forms tufts of needles, m. p.  $116^\circ$ . *m*-Diphenacylthiolbenzene yields with phenylhydrazine a yellow, amorphous product, but the *di-p-bromophenylhydrazone*,  $C_{34}H_{28}N_4S_2Br_2$ , crystallises in tufts of needles, m. p.  $167$ — $168^\circ$ . When *m*-diphenacylthiolbenzene is treated with 90% nitric acid at the ordinary temperature, a *mononitro*-derivative,  $C_{22}H_{17}O_2S_2\cdot NO_2$ , is produced; it crystallises in yellow, prismatic tablets, m. p.  $166$ — $167^\circ$ . *Dibromo-m-diphenacylthiolbenzene*,



obtained by the action of bromine in chloroform solution, crystallises in colourless leaflets, m. p.  $132^\circ$ . When diphenacylthiolbenzene is oxidised with hydrogen peroxide in acetic acid, the *sulphoxide*,  $C_{22}H_{18}O_4S_2$ , is obtained; it forms small, colourless prisms, m. p.  $149^\circ$ , and when treated (in chloroform solution) with gaseous hydrogen bromide, an unstable *perbromide* is obtained.

*m*-Diphenacylthiolbenzenesulphone,  $C_{22}H_{18}O_6S_2$ , can be obtained by the oxidation of *m*-diphenacylthiolbenzene either with an excess of hydrogen peroxide or, better, with potassium permanganate; it crystallises in long, colourless, prismatic needles, m. p.  $175^\circ$ . The sulphone can be methylated by boiling with methyl iodide and sodium methoxide in alcoholic solution. It yields a *dioxime*,  $C_{22}H_{20}O_6N_2S_2$ , m. p.  $203^\circ$ . R. V. S.

**Unsaturated  $\beta$ -Diketones.** H. HIEMESCH (*Ber.*, 1914, 47, 115—116. Compare Ryan and Dunlea, A., 1913, i, 1067).—The influence of a second carbonyl group in the  $\beta$ -position on the properties of unsaturated ketones is being studied. Attempts had been made to condense ethyl cinnamate with acetophenone, but without the success which Ryan and Dunlea achieved. Their product,  $\alpha$ -diphenyl- $\Delta$ -pentene- $\gamma$ -dione, was obtained, however, by condensing cinnamoyl chloride with sodiobenzoylacetone and shaking the oil left after extraction with ether, with concentrated hydrochloric acid. With phenylhydrazine, it yielded a *compound*, which crystallised in slender, white needles, m. p.  $139$ — $141^\circ$ . J. C. W.

**Lapachonone.** IV. C. MANUELLI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 686—691. Compare A., 1901, i, 216).—Oxidation of lapachonone by means of boiling dilute nitric acid yields phthalic acid, but 50% nitric acid in the hot, although it gives principally phthalic and oxalic acids, yields also: (1) a *nitrodihydroxyquinone* derived from an oxidation product of lapachonone,  $C_{15}H_{13}O_4\cdot NO_2$ , which forms

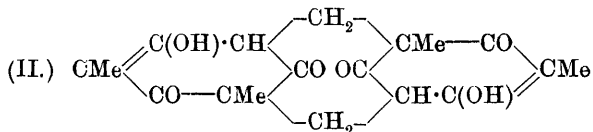
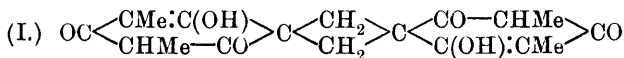
vermillion crystals, m. p.  $206^{\circ}$ , forms a *semicarbazone*,  $C_{16}H_{16}O_6N_4$ , m. p.  $260^{\circ}$  (decomp.), and a dehydrated *acetyl* derivative,  $C_{17}H_{18}O_6N$ , m. p.  $116-117^{\circ}$ , and corresponds with the bromodihydroxyquinone,  $C_{15}H_{15}O_4Br$ , obtained by brominating lapachonone suspended in water; (2) a small proportion of a white *compound*, m. p.  $217^{\circ}$ .

Oxidation of lapachonone with sodium dichromate gives in the hot, phthalic acid, and in the cold, (1) a yellow substance, apparently a mixture, and (2) the *compound*,  $(C_{13}H_{13}O_2)_2$ , which forms shining white prisms, m. p.  $258^{\circ}$ , yields a *diacetyl* derivative,  $(C_{15}H_{15}O_3)_2$ , m. p.  $225-226^{\circ}$ , and forms phthalic acid on oxidation with dilute nitric acid.

T. H. P.

**Cedron.** J. HERZIG and F. WENZEL (*Monatsh.*, 1914, 35, 63—76).—The product of the action of ferric chloride on trimethylphloroglucinol described by Weidel and Wenzel (*A.*, 1898, i, 580) has been further examined by Čečelsky (*A.*, 1900, i, 225). The work of the latter has been repeated, and the conclusions differ in many respects from those previously recorded.

Cedron,  $C_{18}H_{20}O_6$  (instead of  $C_{16}H_{18}O_6$ ), is formed from 2 molecules of trimethylphloroglucinol by the loss of four atoms of hydrogen, and is readily reduced to the original substance. It yields two isomeric dimethyl ethers, which are not interconvertible, and in which the methoxy-groups are evenly distributed between the two nuclei. It also gives two isomeric diacetyl derivatives, whilst the presence of two hydroxyl groups is also shown by Zerewitinov's method. Up to the present, tautomeric reactions of the other four oxygen atoms have not been observed. Two possible formulæ are proposed for cedron (I and II), to the second of which slight preference is accorded as



explaining better the absence of tautomeric reactions.

[With A. GYRI.]—Cedron, the preparation of which from mesitylene is described in detail, has m. p.  $280-282^{\circ}$ , which, when the substance is preserved, sinks to  $260-270^{\circ}$ . A reason cannot be assigned for the change, but the product has the same qualitative reactions as cedron, m. p.  $280-282^{\circ}$ , and yields the corresponding derivatives in the same yield. Čečelsky records  $305^{\circ}$  (decomp.) as m. p. of cedron; this value has not been attained by the present authors, and search for a second compound in cedron has been unsuccessful.

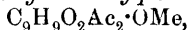
With cold potassium hydroxide, cedron yields the salt,  $C_{18}H_{18}O_6K_2$ , from which cedron is regenerated by acid. Čečelsky describes a tri-potassium salt. It does not react with methyl iodide or methyl sulphate. Diazomethane converts cedron into a mixture of two dimethoxy-compounds, which can be separated by crystallisation from



ethyl acetate into two forms, m. p. 253—256° and 211—214° respectively; the mixed m. p. is 215—232°, and remains unchanged after the substances have been intimately mixed during several weeks. The methyl ethers are stable towards acetylating agents.

When cedron is treated for a few seconds with boiling acetic anhydride and sodium acetate, two *acetyl* derivatives, m. p. 268—270° and 195—197° respectively, are obtained. Protracted action leads to the formation of substances of high melting or decomposition point.

When either of the above dimethoxy-compounds is intimately mixed with zinc dust and anhydrous sodium acetate and boiled with acetic anhydride, *monomethoxydiacetyltrimethylphloroglucinol*,

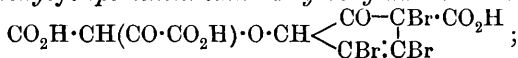


m. p. 66—68°, is obtained in almost quantitative yield. In a similar manner, cedron, when subjected to reducing acetylation, gives *triacetyltrimethylphloroglucinol*, m. p. 165—167°. H. W.

**Action of Sodium Hydroxide on Tetrabromo-*o*-benzoquinone.** C. LORING JACKSON and A. H. FISKE (*Amer. Chem. J.*, 1913, 50, 341—380).—In an earlier paper (A., 1909, i, 657), the authors have shown that when tetrabromo-*o*-benzoquinone is treated with sodium hydroxide, tetrabromocatechol is produced together with one or more acids, according to the strength of the sodium hydroxide used. A further study of these reactions has now been made.

As stated by Zincke (A., 1887, 808), the first effect of a solution of alkali hydroxide on tetrabromo-*o*-benzoquinone is the formation of an unstable, green solid. By the further action of sodium hydroxide of *N*-concentration, an acid, m. p. 217° (decomp.), is produced; with a solution containing 60 grams per litre, two acids are obtained, m. p. 207° (decomp.) and 121°; whilst with a solution containing 200 grams per litre, an acid, m. p. 174° (decomp.), is formed.

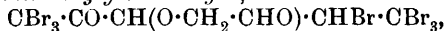
The only one of these acids which has been thoroughly investigated is that of m. p. 207° (decomp.), which has been found to be the *tribromocarboxycyclopentenone ether of hydroxyoxalacetic acid*,



it crystallises in pale yellow needles, and yields a *pyridine* salt, m. p. 122—123°. When a strong aqueous solution of this acid is treated with bromine, carbon dioxide and a little oxalic acid are produced, together with *heptabromomethyldiacetyl* [*tribromomethyl αβββ-tetrabromoethyl diketone*],  $\text{CBr}_3\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CO}\cdot\text{CBr}_3$ , m. p. 97—98°, which crystallises in bright yellow plates, and is gradually decomposed by sodium carbonate solution with formation of bromoform (2 mols.), sodium oxalate (1 mol.), and sodium bromide (1 mol.). If heptabromomethyldiacetyl is heated with water in a sealed tube at 100°, a *compound*, m. p. 71—72°, is obtained, which forms long, slender, pale yellow needles. By the action of methyl alcohol on heptabromodiacetyl, its *methyl hemiacetal*,  $\text{CBr}_3\cdot\text{C}(\text{OH})(\text{OMe})\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CBr}_3$ , m. p. 100—101°, is produced, which crystallises in colourless prisms. The corresponding *ethyl hemiacetal* has m. p. 93—94°.

If a dilute solution of the tribromocarboxycyclopentenone ether of

hydroxyoxalacetic acid is treated with bromine, the *heptabromo-keto-sec.-amyl ether of glycollaldehyde*,



m. p. 96—97°, is formed, which crystallises in short, stout, white prisms, and is converted by sodium carbonate solution into the *hexabromohydroxyketo-sec.-amyl ether of glycollaldehyde*, m. p. 71—72°, which forms white crystals.

The *acid*, m. p. 121°, crystallises in white, rhombic prisms, and probably has the composition  $\text{C}_{10}\text{H}_8\text{O}_7\text{Br}_5$ .

The *acid*, m. p. 174° (decomp.), seems to be the *dibromohydroxy-carboxycyclopentene orthodiether of dihydroxyisocrotonolactonecarboxylic acid*,  $\text{CBr} \begin{array}{c} \diagup \text{C}(\text{OH})(\text{CO}_2\text{H}) \cdot \text{CH} \cdot \text{O} \cdot \text{C} : \text{C}(\text{CO}_2\text{H}) \\ \diagdown \text{CBr} \end{array} \begin{array}{c} \text{CH} \cdot \text{O} \cdot \text{CH} \\ \text{CO} \end{array} \text{O}$ ; it forms pale yellow granules, and when treated with bromine and water yields hepta-bromomethyldiacetyl.

The *acid*, m. p. 217° (decomp.), probably has the composition  $\text{C}_{10}\text{H}_8\text{O}_9\text{Br}_4$ ; it crystallises in yellowish-white prisms, and when treated with bromine and water furnishes a *compound*, m. p. 156°.

E. G.

**Octaiodo-*p*-quinhydrone.** C. LORING JACKSON and E. K. BOLTON (*J. Amer. Chem. Soc.*, 1914, **36**, 301—308).—Although the crystals of octaiodoquinhydrone obtained by the action of sulphurous acid on a benzene solution of iodoanil (compare Jackson and Bolton, A., 1912, i, 476; Torrey and Hunter, *ibid.*, 475) are in appearance very similar to those of iodoanil itself, their behaviour towards organic solvents and sodium hydroxide demonstrates that they are readily resolved into iodoanil and tetraiodoquinol.

The apparent greater stability of octaiodoquinhydrone relative to the unknown corresponding octachloro- and octabromo-compounds is considered to harmonise with Richter's method of formulation of such substances (A., 1911, i, 136), the substance at present under discussion being represented as  $\text{O} : \text{C}_6\text{I}_4 : \text{OH} \cdot \text{O} \cdot \text{C}_6\text{I}_4$ .

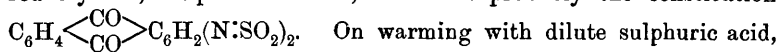
D. F. T.

**Preparation of Nitrogenous Condensation Products of the Anthraquinone Series.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 268454).—When 1:8-diaminonaphthalene is heated with 1-chloroanthraquinone in amyl-alcoholic solution in the presence of copper salts and an acid-fixing agent (such as sodium acetate), 8-amino-1-anthraquinonylamino-naphthalene (m. p. 215°) is produced. If, however, the condensation is effected in a solvent of high boiling point (such as nitrobenzene), or if the above substances are heated alone or in a solvent of high boiling point, new compounds are obtained which give vats and form the starting points for the preparation of colouring matters. The condensation product obtained from the above materials has m. p. 330—340°; that ultimately obtained from 4-chloro-1-methylantraquinone and 1:8-diamino-naphthalene melts at about 280°, and that from 4-chloro-1-amino-anthraquinone has m. p. above 290°.

J. C. C.

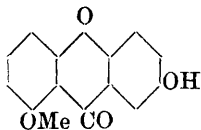
**Preparation of Sulphuric Acid Compounds of 1:4-Diaminoanthraquinone and its Nuclear Substitution Products.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 268592).—

When 1:4-diaminoanthraquinone (5 parts) is warmed with fuming sulphuric acid (45%  $\text{SO}_3$ :100 parts) at 50—60° until a sample is soluble in ammonia and the mixture then diluted with water until the sulphuric acid is about 80% strength, a compound separates in red crystals, m. p. above 300°, which has probably the constitution



On warming with dilute sulphuric acid, hydrolysis takes place; on treatment with nitric acid and subsequent hydrolysis, 5-nitro-1:4-diaminoanthraquinone is obtained, and on warming with aqueous sodium hydroxide, 4-amino-1:2-dihydroxyanthraquinone ( $\alpha$ -aminoalizarin) is produced. Similar compounds are obtained from 2-bromo-1:4-diaminoanthraquinone and 2:3-dichloro-1:4-diaminoanthraquinone. J. C. C.

**Euxanthic Acid.** J. HERZIG and R. STANGER (*Monatsh.*, 1914, 35, 47—61).—The observations of Herzig and Schönbach on the methylation of quercitrin (A., 1912, i, 707) have led the authors to investigate the action of diazomethane on euxanthic acid in the hope



of obtaining a convenient method for the preparation of 1-methyleuxanthone (annexed formula). The action appears to fulfil the desired conditions, but the further hope of finding decisive evidence for the formula,  $\text{C}_{19}\text{H}_{18}\text{O}_{11}$ , for euxanthic acid has not been realised.

When euxanthic acid is dissolved in methyl alcohol and treated with an ethereal solution of diazomethane, white needles or leaflets, m. p. 134—137° (decomp.), are obtained, which have the composition  $\text{C}_{19}\text{H}_{15}\text{O}_8(\text{OMe})_3$ . To a certain extent, an amorphous substance is formed as by-product, and this can be made the chief product of the reaction if methyl alcohol is omitted. It appears to be a tetramethoxy-derivative of the anhydro-compound,  $\text{C}_{19}\text{H}_{12}\text{O}_6(\text{OMe})_4$  (compare Spiegel, A., 1883, 219; Graebe, Aders, and Heyer, A., 1902, i, 39), and is fairly stable towards boiling water.

The crystalline trimethoxy-compound is readily soluble in water, and the solutions, after evaporation, yield an amorphous substance,  $\text{C}_{19}\text{H}_{14}\text{O}_8(\text{OMe})_2$ . When covered with methyl alcohol, it regenerates the crystalline compound,  $\text{C}_{19}\text{H}_{15}\text{O}_8(\text{OMe})_3$ ; the same behaviour is shown by the amorphous product obtained when the crystalline trimethoxy-compound is melted. The amorphous product combines more slowly with ethyl alcohol to yield a substance, m. p. 124—127° (decomp.) which can also be obtained by repeated crystallisation of the trimethoxy-compound from ethyl alcohol. Analyses agree with a formula,  $2\text{C}_{19}\text{H}_{14}\text{O}_8(\text{OMe})_2 \cdot \text{H}_2\text{O} \cdot \text{EtOH}$ . When crystallised from methyl alcohol, or melted and dissolved in the same solvent, it regenerates the trimethoxy-compound.

Methyl euxanthate, m. p. 214—216° (Graebe, Aders, and Heyer, *loc. cit.*, give 218°), is also converted by diazomethane into the

crystalline and amorphous products which are obtained from euxanthic acid.

The potassium salt,  $C_{19}H_{17}O_{11}K$  (compare Graebe, Aders and Heyer, *loc. cit.*), is unaffected by a methyl-alcoholic solution of methyl iodide at  $100^{\circ}$ ; at  $140$ — $150^{\circ}$ , euxanthone, m. p.  $236$ — $237^{\circ}$ , is formed, whilst at  $110$ — $120^{\circ}$ , the main product is methyl euxanthate.

1-Methyleuxanthone, m. p.  $236$ — $239^{\circ}$ , is obtained by the action of warm 10% sulphuric acid on the amorphous substance,  $C_{19}H_{12}O_6(OMe)_4$ , or, more conveniently, by dissolving the latter in concentrated sulphuric acid and pouring the solution on to ice. It can also be prepared from the crystalline methoxy-compound.

In continuation of the work on the methylation of glucosides (A., 1912, i, 707), the authors have studied the action of diazomethane on sucrose, but with negative results. With glycurone, however, a syrupy mass is obtained which appears to contain, as a maximum, two methoxy-groups for each glycurone molecule.

H. W.

**Preparation of Purpurogallin.** C. GRAEBE (*Ber.*, 1914, **47**, 337—338. Compare Nierenstein and Spiers, A., 1913, i, 1367; Herzig, this vol., i, 60).—Purpurogallin has been most conveniently prepared by the oxidation of pyrogallol with sodium nitrite and acetic acid (Perkin and Steven, T., 1903, **83**, 197). The author finds that the yields are considerably improved if formic acid is substituted for acetic acid. In a series of comparative experiments, the maximal yield of purpurogallin was 20% in presence of the latter, 30—31% in presence of the former. The order of addition of the reagents is without influence on the result. Replacement of organic acids by hydrochloric or sulphuric acid leads to much smaller yields.

A further improvement consists in carrying out the reaction with complete exclusion of air. Under these conditions, purpurogallin is immediately obtained in the pure state, m. p.  $274^{\circ}$ , and this result is obtained with acetic as well as with formic acid.

H. W.

**Purpurogallin.** J. HERZIG (*Ber.*, 1914, **47**, 38—39).—The author has been unable to repeat the preparation of a phenylhydrazone of tetra-acetylurpurogallin as described by Nierenstein and Spiers (A., 1913, i, 1367), his only product being purpurogallin itself. The failure is attributed either to insufficient detail in the description of the procedure, or to a lack of identity between specimens of purpurogallin of different origin.

D. F. T.

**Oxonium Salts. Additive Compounds of Cineole.** I. I. BELLUCCI and L. GRASSI (*Gazzetta*, 1913, **43**, ii, 712—735).—This paper records the results of the thermal analysis of the binary systems formed of cineol and a number of aromatic substances containing one or more phenolic hydroxyl groups.

Cineole and phenol form a *compound* in equimolecular proportions, m. p.  $8^{\circ}$ .

Cineole and  $\alpha$ -naphthol form a *compound* also in equimolecular proportions, m. p.  $75^{\circ}$ . The eutectic temperatures lie at  $60^{\circ}$  and  $6^{\circ}$ .

Cineole and  $\beta$ -naphthol form a *compound* in equimolecular proportions, m. p. 48°. The eutectics lie at 43.5° and 3.5°.

Cineole and *o*-cresol form a *compound* in equimolecular proportions, m. p. 50°. Cineole and *m*-cresol form a *compound* in equimolecular proportions, m. p. -5°. Cineole and *p*-cresol form a *compound* in equimolecular proportions, m. p. 1.5°.

Cineole and *o*-nitrophenol do not form any compound; the eutectic lies at 6°. Cineole and *m*-nitrophenol do not form any compound; eutectic temperature, 15°. Cineole and *p*-nitrophenol do not combine; there is an eutectic at 16°.

Cineole and *o*-aminophenol do not combine; the eutectic lies at 0°. Cineole and *m*-aminophenol do not combine; the eutectic lies at 3°.

Cineole and catechol form a *compound* in equimolecular proportions, m. p. 39°. There are eutectics at 31° and 2°. Cineole and resorcinol form a *compound* in equimolecular proportions, m. p. 89°. The eutectics lie at 73° (40% cineol) and 2°. Cineole and quinol form a *compound* in the proportion of 2 mols. cineole to 1 mol. quinol, m. p. 106.5°. The eutectic temperatures are 103° and 2°.

Cineole and guaiacol form a *compound* in equimolecular proportions, m. p. 5°.

Cineole and salicylic acid do not combine. The eutectic temperature is 11°. Cineole and *m*-hydroxybenzoic acid do not combine. The eutectic temperature is 13°. Cineole and *p*-hydroxybenzoic acid form a *compound* which decomposes before melting, but this system could not be investigated beyond 60% of *p*-hydroxybenzoic acid, as the temperatures then reached are above the b. p. of cineol.

Cineole and methyl salicylate form a *compound* in equimolecular proportions, m. p. -15°. Cineole and phenyl salicylate do not combine. The eutectic temperature is 13°. Cineole and naphthyl salicylate do not combine. There is an eutectic at -5°.

Cineole and thymol form a *compound* in equimolecular proportions, m. p. 4.5°.

R. V. S.

**Esters of Chromic Acid.** HEINRICH WIENHAUS (*Ber.*, 1914, 47, 322—331).—With the possible exception of the compound obtained by Gomberg (*A.*, 1902, i, 600) by the action of silver chromate on triphenylmethyl chloride, esters of chromic acid do not appear to have been described. The author finds that they can be readily prepared by shaking a tertiary alcohol, dissolved in light petroleum or carbon tetrachloride, with an aqueous solution of chromic acid or, preferably, with an excess of solid chromium trioxide. The ester remains dissolved or suspended in the organic solvent, from which it can be readily obtained by evaporation. According to analyses and molecular weight determinations, the esters are normal compounds of chromic acid,  $H_2CrO_4$ . They are saponified with difficulty by aqueous alkalis, readily by alcoholic solutions of the latter. With hydrogen peroxide and ether, they do not yield the characteristic test for chromic acid, whilst, also, esters of perchromic acid have not been obtained as yet.

The formation of these substances may also be used to investigate the tertiary alcoholic nature of a given compound. For this purpose the compound under investigation is dissolved in light petroleum or

carbon tetrachloride and shaken with chromium trioxide; if a pure red coloration is developed which persists after some time, the presence of a tertiary alcohol may be regarded as established; on the other hand, should the solution rapidly become discoloured, the absence of a tertiary alcohol cannot be regarded as proved, since many of the latter substances are somewhat readily oxidised.

In general, tertiary alcohols do not readily form crystalline derivatives, so that the formation of a solid chromic ester may frequently be utilised for their isolation in the pure state.

The best results have been obtained in the terpene and sesquiterpene series.

$\alpha$ - and  $\beta$ -Terpineol, *p*-menthan-8-ol, and *p*-menthan-1-ol (Wallach, A., 1911, i, 470) give liquid *chromates* of small stability, the initially yellow, then red solutions becoming rapidly brown. By rapid evaporation of its solution, *p*-menthan-1-ol *chromate*,  $(C_{10}H_{19})_2CrO_4$ , can be obtained as a dark brownish-red oil.

*Methylfenchyl chromate*,  $(C_{11}H_{19})_2CrO_4$ , is readily obtained in wine-red needles or prisms, which can apparently be preserved indefinitely in the dark. It has m. p.  $130^\circ$  (decomp.),  $[\alpha]_D - 30.0^\circ$  in carbon tetrachloride solution (the rotations recorded are all for the Li red line). Determinations of molecular weight are rendered difficult by the gradual decomposition of the dissolved ester, but yield results approximate to those required by a normal ester of chromic acid. An ethereal solution of methylfenchyl chromate is unchanged by agitation with a 30% aqueous solution of hydrogen peroxide. A solution of methylfenchol in light petroleum is not coloured when shaken with an aqueous solution of chromic acid and hydrogen peroxide, unless very concentrated; in that case, it acquires a deep blue colour. Similar results are obtained with solutions of perchromic acid obtained from the salt  $K_2CrO_8$  and dilute sulphuric acid.

In the preparation of methylfenchol by the action of magnesium methyl iodide on fenchone, considerable difficulty is experienced in isolating the tertiary alcohol, owing to the ketone being regenerated on decomposition of the product with water (Wallach and Wienhaus, A., 1907, i, 541). The separation is, however, readily accomplished by converting the alcohol into the above chromate, from which it can be regenerated by saponification or by fission with zinc dust and acetic acid, or with finely-divided palladium and hydrogen.

Ethylfenchol is obtained by the action of an ethereal solution of magnesium ethyl iodide on fenchone, together with fenchyl alcohol, ethane and ethylene, whilst considerable quantities of fenchone are regenerated (compare Konovalov, A., 1907, i, 171). When dissolved in light petroleum and shaken with a solution of chromium trioxide in dilute sulphuric acid, it yields *ethylfenchyl chromate*, cinnabar-red powder or needles, which blackens, without melting, at  $140^\circ$  and at a higher temperature becomes lighter and finally greyish-green. When dissolved in carbon tetrachloride, it has  $[\alpha] + 22.5^\circ$ .

*Methylbornyl chromate*, pale orange needles, is prepared in the same manner as the methylfenchyl compound. It becomes discoloured at  $105^\circ$ , and is laevorotatory in carbon tetrachloride solution.

*Cedrol chromate*,  $(C_{15}H_{25})_2CrO_4$ , yellowish-red prisms, has m. p.  $115^\circ$

after darkening at 100°. In carbon tetrachloride solution, it has  $[\alpha] + 79.4^\circ$ .

Ledol, needles, m. p. 105°, behaves similarly to cedrol, yielding a *chromate*,  $(C_{15}H_{25})_2CrO_4$ , wine-red, apparently monoclinic, prisms, m. p. 92°,  $[\alpha] + 30.0^\circ$  when dissolved in carbon tetrachloride.

Patschali-camphor yields a stable red *chromate*, thus establishing its tertiary alcoholic character, whereas guaiacol (compare Gandurin, A., 1909, i, 98) is fairly readily oxidised, which points to the possibility that it contains the secondary alcoholic group.

Attempts to esterify the tertiary alcoholic groups of more highly oxygenated compounds, such as pinacone, terpin, fenchone-pinacone,  $\alpha$ -hydroxyisobutyric acid, and benzoic acid, with chromic acid have not been completely successful.

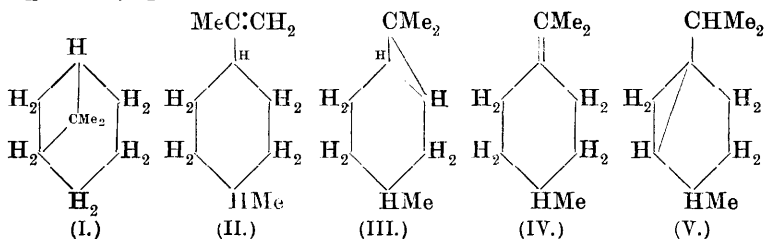
Certain hydroaromatic secondary alcohols (*cyclohexanol*, menthol, fenchyl alcohol, borneol, and *isoborneol*) when dissolved in carbon tetrachloride gave yellow to deep red solutions when shaken with chromium trioxide; after a few seconds, however, brownish-red particles separated in quantity, owing to complete decomposition.

A solution of thymol was coloured blue; eugenol solution reduced chromium trioxide without becoming coloured.

H. W.

**The Constituents of Essential Oils.** *Nopinane*,  $\beta$ -Dihydrolimonene, and *Carane*. F. W. SEMMLER and J. FELDSTEIN (*Ber.*, 1914, 47, 384—389).—In order to obtain a complete knowledge of the physical data of the basal hydrocarbons of the terpene series, some members in which the ring is fully saturated have been prepared. Wolff's method (A., 1912, i, 988) was employed, namely, the conversion of the corresponding ketone into the hydrazone by heating with hydrazine hydrate in a sealed tube, followed by the action of sodium ethoxide under pressure.

*Nopinonehydrazone*,  $C_9H_{16}N_2$ , has m. p. 42—43°, and *nopinane* (I) has b. p. 149°/747 mm.,  $D_{22}^{22}$  0.8611,  $n_D$  1.46141,  $\alpha_D \pm 0^\circ$ .  $\beta$ -Dihydrolimonene (II), from dihydrocarvone, has b. p. 168—169°/750 mm.,  $D_{16}^{21}$  0.8217,  $n_D$  1.45673,  $\alpha_D \pm 0^\circ$ . *Carane* (III) has b. p. 49—50°/9 mm., 165—166°/750 mm. with slight rearrangement,  $D_{20}^{20}$  0.8381,  $n_D$  1.45823,  $\alpha_D - 34^\circ$ . An account of the application of this method to pulegone and tanacetone will appear in another place. *Pulegonehydrazone* has b. p. 129—131°/20 mm.,  $D_{21}^{22}$  0.9563,  $n_D$  1.49261, and *dihydroterpinolene* (IV) has b. p. 169—170°/748 mm.,  $D_{21}^{21}$  0.8189,  $n_D$  1.45823. *Tanacetonehydrazone* has b. p. 128—129°/18 mm.,  $D_{21}^{20}$  0.9502,  $n_D$  1.4965, and *tanacetane* (V) has b. p. 156—157°/747 mm.,  $D_{21}^{22}$  0.8158,  $n_D$  1.44121.



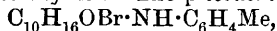
A table of rotations and dispersions is given. The increment in molecular dispersion,  $M_\beta - M_\alpha$ , varies from 1% in the case of  $\beta$ -dihydrolimonene to 9% in tanacetane, in which a three-membered ring is attached to a five-ring, and 10% in carane, in which a three-membered ring is joined to a six-ring. The increment exhibited by compounds containing a *cyclopropane* ring is, therefore, due to that ring alone, and not to any neighbouring ketone or other group (compare Östling, T., 1912, 101, 457). J. C. W.

**System, Sulphur Dioxide-Camphor.** I. BELLUCCI and L. GRASSI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 676—680).—Thermal study of this system revealed no appreciable superfusion and indicated the formation of the two compounds:  $2\text{SO}_2 \cdot \text{C}_{10}\text{H}_{16}\text{O}$ , m. p.  $-45^\circ$  and  $\text{SO}_2 \cdot \text{C}_{10}\text{H}_{16}\text{O}$ , m. p.  $-24^\circ$ . The acceleration produced in the formation of sulphuryl chloride from sulphur dioxide and chlorine by the addition of camphor must therefore be attributed to the interaction of the camphor and sulphur dioxide.

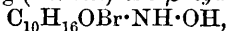
The purified sulphur dioxide employed solidified completely at  $-76^\circ$  (compare Polak-van der Goot, A., 1913, ii, 946). T. H. P.

**Structure of Dibromomenthone and a New Synthesis of Buchu-camphor.** GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 569—575).—The dibromomenthone of Beckmann and Eickelberg (A., 1896, i, 313) can be prepared from 4-bromomenthone by treating its chloroform solution with bromine. When this dibromomenthone is dissolved in 2.5% potassium hydroxide and the solution saturated with carbon dioxide, buchu-camphor (Semmler and McKenzie, A., 1906, i, 373) is precipitated. In addition a *compound*, crystallising in large prisms, m. p. about  $85^\circ$ , and a *carboxylic acid* are obtained. A *monobromo*-buchu-camphor can be obtained by acting on a chloroform solution of the substance with the calculated amount of bromine dissolved in chloroform; it forms rhombic or hexagonal tablets, m. p.  $85^\circ$ . This monobromo-compound yields hydroxythymoquinone when it is dissolved in 2% potassium hydroxide and the solution subsequently acidified and distilled with steam. When heated with acetic anhydride and sodium acetate, the dibromo-derivative is not only acetylated, but also loses HBr, yielding a *substance*,  $\text{C}_{12}\text{H}_{16}\text{O}_3$ , which forms colourless or slightly yellow prisms, m. p.  $106-107^\circ$ .

One of the bromine atoms of the dibromomenthone mentioned above can be substituted by the radicles of amino-bases. The *anilide*,  $\text{C}_{10}\text{H}_{16}\text{OBr} \cdot \text{NHPh}$ , prepared by heating dibromomenthone (1 mol.) with aniline (2 mols.) for half an hour at  $100^\circ$ , forms lemon-yellow prisms, which soften at  $190^\circ$ , melt at  $195^\circ$ , and at a higher temperature the liquid deposits thymol. The *p-toluidide*,



forms pale yellow needles. The *piperidide*,  $\text{C}_{10}\text{H}_{16}\text{OBr} \cdot \text{C}_5\text{NH}_{10}$ , crystallises in colourless prisms, m. p.  $127-129^\circ$ . Hydroxylamine and dibromomenthone yield in addition to the product obtained by Beckmann and Eickelberg (*loc. cit.*) the  $\beta$ -hydroxylamine,



which forms colourless crystals, m. p.  $158-160^\circ$ , and has the reactions



of a  $\beta$ -hydroxylamine. A *substance*, m. p.  $65^\circ$ , crystallising in white needles, is also produced. From the  $\beta$ -hydroxylamine, the *isonitroamine*,  $C_{10}H_{16}BrO \cdot N_2O_2H$ , can be obtained; it is an unstable substance crystallising in long, colourless needles, and yields buchu-camphor when warmed with potassium hydroxide. In the preparation of the *isonitroamine*, a colourless, crystalline *substance*, m. p.  $95^\circ$ , containing bromine and nitrogen, is produced.

In view of the reactions recorded in this paper, the author considers that the dibromomenthone has the constitution of 2:4-dibromo-3-menthanone.

R. V. S.

**Action of Aluminium Chloride on Turpentine.** WILHELM STEINKOPF and MICHAEL FREUND (*Ber.*, 1914, 47, 411—420. Compare Aschan, A., 1902, i, 749; Engler and Routala, A., 1910, i, 2, 160).—French turpentine,  $D_4^{20}$  0.8680,  $\alpha_D - 29.45^\circ$  in 1-dm. tube, 95% of which has b. p.  $152$ — $167^\circ$ , is slowly treated with aluminium chloride at  $0^\circ$ , and the mixture is kept for twelve hours at the ordinary temperature (the longer the mixture is kept the more extensive is the polymerisation and the less is the quantity of residual liquid). The liquid portion, after being decanted and purified, yields by distillation, in addition to unchanged turpentine, a fraction, b. p.  $62$ — $140^\circ/14$  mm.,  $D$  0.9129, a fraction, b. p.  $140$ — $203^\circ$ , 14 mm.,  $D$  0.9487, and a residue of yellow colophony,  $(C_{10}H_{16})_x$ , m. p.  $77$ — $78^\circ$ . The viscous portion yields after purification a fraction, b. p.  $62$ — $140^\circ/14$  mm.,  $D$  0.9119, a fraction, b. p.  $140$ — $203^\circ/14$  mm.,  $D$  0.9503, and a yellow residue, m. p.  $77$ — $78^\circ$ . Similar results are obtained when pure *l*-pinene is treated with aluminium chloride. In some experiments, in order to obtain as much as possible of the more volatile depolymerisation products (b. p. up to  $250^\circ$ ), the turpentine and aluminium chloride, after the initial vigorous reaction, are boiled so long as gas is evolved, the liquid portion is then poured off, and the viscous residue again heated, and so on. The gaseous products thus obtained do not contain acetylene or hydrogen and consist mainly of saturated paraffin and cyclic hydrocarbons. The liquid product has  $D_4^{20}$  0.8821, begins to boil at  $20^\circ$ , has an odour of petroleum, and contains benzene and about 25% of unsaturated constituents. After the removal of these, the residual liquid, consisting of saturated hydrocarbons, is separated into 31 fractions boiling between  $30^\circ$  and  $249^\circ$ . The b. p., density, refractive index, and percentage of carbon and hydrogen of each fraction are tabulated and compared with the corresponding constants of paraffin and naphthene hydrocarbons. The results indicate that the most volatile portions (fractions 1 and 2) of the depolymerised liquid consist of almost pure pentane and isopentane; then naphthenes begin to appear, and become the main constituent in fraction 5. Fraction 13, b. p.  $115$ — $120^\circ$ , is almost pure octanaphthene. The nitration of fraction 22, b. p.  $165$ — $172^\circ$ , yields a tertiary *nitro*-compound,  $C_{10}H_{19}O_2N$ , b. p.  $118$ — $120^\circ/12$  mm.,  $D^{20}$  1.0299,  $n_D^{20}$  1.46572, which is apparently nitrodecanaphthene (Engler and Halmai, A., 1910, i, 160).

The liquid, b. p. above  $250^\circ$ ,  $D_4^{17}$  0.9609, is dark brown and viscous. After further treatment with aluminium chloride and removal of the

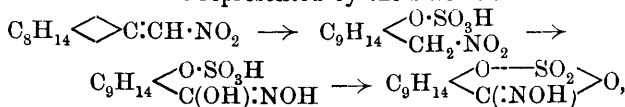
portion boiling below  $250^{\circ}$ , a yellow liquid is obtained, which has  $D_4^{15}$  0.9535,  $n_D^{20}$  1.51048, and is quite analogous to the various artificial and natural lubricating oils.

The experiments show that unsaturated cyclic hydrocarbons like the terpenes yield by treatment with aluminium chloride the same or similar mixtures of hydrocarbons as do olefines, such as pentene or hexene. C. S.

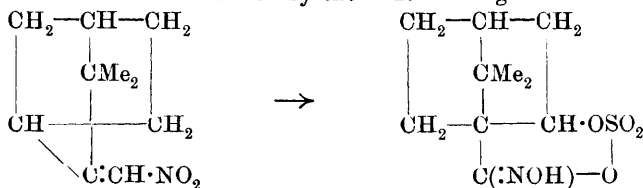
**Nitrocamphene. II. New Connexions between the Camphene and the Camphane Series.** P. LIPP (*Annalen*, 1914, 402, 343—364. Compare A., 1913, i, 1077).—The course of the conversion of nitrocamphene (Jagelki's camphenile nitrite) into tricyclenic acid by means of sulphuric acid (Bredt and May, A., 1910, i, 32) has been examined, and a previous statement of the author (*loc. cit.*) corrected. The nitrogen is eliminated in the form of hydroxylamine, which suggests the intermediate formation of a hydroxamic acid. The first product of the reaction which can be isolated is, however, the neutral sulphuric ester,  $C_{10}H_{15}O_5NS$ , m. p.  $127^{\circ}$  (decomp.). The ester is readily hydrolysed by warm water, yielding a hydroxy-hydroxamic acid,  $C_{10}H_{17}O_3N$ , m. p.  $163$ — $164^{\circ}$  (decomp., corr.), which is not camphenylhydroxamic acid as stated previously (*loc. cit.*), but *hydroxyapocamphanehydroxamic acid*,

$OH \cdot N : C(OH) \cdot C \begin{array}{c} \swarrow CH(OH) \cdot CH_2 \\ \text{---} CMe_2 \text{---} \\ \searrow CH_2 \text{---} CH_2 \end{array} CH$ , since it is converted into keto-

pinic acid, and Bredt and May's hydroxyapocamphanecarboxylic acid, m. p.  $240$ — $242^{\circ}$  (corr.) (*loc. cit.*), by cold 25% hydrochloric acid and sodium nitrite. The latter acid is undoubtedly a camphane derivative, and since it is highly improbable that the change from the camphene to the camphane nucleus is effected by the nitrous acid in the preceding reaction, the only alternative explanation is that the nuclear transformation is accomplished during the addition of the sulphuric acid to nitrocamphene in the formation of the neutral sulphuric ester. The formation of this ester is represented by the scheme :



and the nuclear transformation by the annexed diagram :



Hydroxyapocamphanehydroxamic acid condenses with acetone to form a substance,  $C_{13}H_{21}O_3N$ , m. p.  $209$ — $210^{\circ}$  (corr.), and yields hydroxylamine and tricyclenic acid by boiling with dilute sulphuric acid.

A similar example of the transformation of the camphene into the

camphane nucleus is to be found in the action of fuming hydrobromic acid on nitrocamphene. The transformation is effected during the addition of hydrogen bromide to the nitrocamphene, then follows the change  $\cdot\text{CH}_2\cdot\text{NO}_2 \rightarrow \text{OH}\cdot\dot{\text{C}}\cdot\text{NOH}$ , and the hydroxyl group is replaced by bromine, the product being *bromoapocamphanehydroxamyl*

*bromide*,  $\text{OH}\cdot\text{N}\cdot\text{CBr}\cdot\text{C} \begin{array}{c} \text{CHBr}\cdot\text{CH}_2 \\ \text{CMe}_2 \\ \text{CH}_2-\text{CH}_2 \end{array} \text{CH}$ , m. p. 132—133° (corr.). The

proofs of this formula are the following: By heating at 100° under pressure with fuming hydrochloric acid, the bromide yields hydroxylamine and mainly an unexamined neutral substance, m. p. 150—152°. The two bromine atoms function differently. Only one is displaced by the action of ethereal aniline or ammonia, *bromoapocamphaneanilinoxime*,  $\text{C}_{16}\text{H}_{21}\text{ON}_2\text{Br}$ , m. p. 153·5—154·5° (decomp.), and *bromoapocamphaneamidoxime*,  $\text{C}_{10}\text{H}_{17}\text{ON}_2\text{Br}$ , decomp. 156°, being formed; the latter is converted into *hydroxyapocamphaneamidoxime*,  $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$ , m. p. 180—181° (decomp., corr.), by boiling water. Both halogen atoms are displaced when *bromoapocamphanehydroxamyl bromide* is treated with cold methyl-alcoholic potassium hydroxide, whereby *methyl methoxyapocamphanehydroxamate*,  $\text{C}_{12}\text{H}_{21}\text{O}_3\text{N}$ , m. p. 102·5—104° (corr.), is produced; by brief boiling with 50% sulphuric acid, the methyl ester yields tricyclic acid and hydroxylamine. The final proof of the constitution of *bromoapocamphanehydroxamyl bromide* is furnished by reduction with zinc dust and glacial acetic acid, whereby the *nitrile*, m. p. 171—172° (corr.), of *apocamphanecarboxylic acid* and a little  $\omega$ -aminocamphane are produced.

Aqueous *hydroxyapocamphaneamidoxime hydrochloride* and a slight excess of sodium nitrite yield nitrous oxide and *hydroxycamphenilanonitrile*, m. p. about 145° (decomp.) (annexed formula), which is very stable towards oxidising agents or phosphorus pentachloride, can be converted into an *isomeride*, m. p. 165—170°, and yields camphenilone and hydrogen cyanide by fusion.

Like other nitromethylene derivatives, nitrocamphene reacts additively with potassium cyanide in boiling alcohol, the product after treatment with carbon dioxide yielding a compound,  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2$ , m. p. 165—166°. C. S.

**Additive Reactions of Caoutchouc.** Elucidation of its Constitution and a Theory of Vulcanisation. F. KIRCHHOFF (*Kolloid. Zeitsch.*, 1914, 14, 35—43).—The increase in weight of thin films of caoutchouc on exposure to oxygen and to bromine and sulphur chloride vapour has been determined in a series of experiments in which the caoutchouc was weighed at the end of measured time intervals.

The weight-time curves obtained in this way indicate an absorption of sulphur chloride, which lies between the values required by the formulæ  $\text{C}_{10}\text{H}_{16}\text{S}_2\text{Cl}_2$  and  $(\text{C}_{10}\text{H}_{16})_2\text{S}_2\text{Cl}_2$ . Since hydrogen chloride is evolved during the absorption process, it is probable that the formula  $\text{C}_{10}\text{H}_{16}\text{S}_2\text{Cl}_2$  represents the composition of the compound

which is formed. This conclusion is confirmed by the results obtained in the estimation of the combined sulphur.

The curves representing the data obtained with bromine vapour at 18° point to the formation of the dibromide,  $C_{10}H_{16}Br_2$ , but the corresponding data obtained in experiments at 80° show that the final increase in weight is less than that required by the formula for the monobromide,  $C_{10}H_{15}Br$ . If the additive product obtained at 18° is heated on the water-bath, hydrogen bromide is evolved and the monobromide is formed.

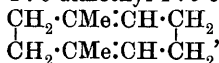
Experiments with oxygen at 75—80° have given indefinite results, and it was found that different samples of caoutchouc behave very differently in regard to their rates of oxidation.

Other observations relate to the changes which occur in the viscosity of solutions of caoutchouc during the addition of sulphur chloride. The initial slight fall in the viscosity is succeeded by a rapid rise, which continues until, ultimately, the solution gelatinises. Gelatinisation occurs much more quickly in light petroleum as compared with benzene solutions.

The later part of the paper is speculative in character and deals with the constitution of caoutchouc and the changes which occur during the additive reactions on the basis of the above observations.

H. M. D.

**Synthetic Caoutchouc from Isoprene.** G. STEIMMIG (*Ber.*, 1914, 47, 350—354).—From experiments on the diozonides (analyses, molecular weight, velocity of decomposition by boiling water, nature of decomposition products) of Para caoutchouc and of the caoutchoucs prepared by autopolymerisation of isoprene and from isoprene by the acetic acid process, Harries (*A.*, 1912, i, 706; 1913, i, 284) has been led to assume the identity of the three products. The author has applied the same method of investigation to the caoutchoucs obtained (1) by heating isoprene in the presence of ozonides or peroxides, and (2) by the action of sodium in the presence of carbon dioxide on isoprene. The ozonides are found to yield succinic acid and acetylacetone in addition to lævulinaldehyde and lævulic acid. Hence, the caoutchoucs must contain 1 : 6-dimethyl-1 : 5-cyclooctadiene,



in addition to 1 : 5-dimethyl-1 : 5-cyclooctadiene, the amount of the former being estimated at about 20%. The two substances may be regarded as formed by the unsymmetrical and symmetrical condensation respectively of two molecules of isoprene. Subsequently, caoutchouc obtained by the autopolymerisation of isoprene has been re-investigated with the result that approximately the same quantities of succinic acid and acetylacetone have been found among the products of decomposition of the ozonide as are yielded by other artificial caoutchoucs. Natural caoutchouc, on the other hand, does not yield a derivative of 1 : 6-dimethyl-1 : 5-cyclooctadiene, and the incomplete identity of the artificial caoutchoucs with the natural product receives an explanation.

The artificial caoutchoucs are purified by repeated treatment with a mixture of benzene and acetone, ozonised in chloroform solution, and

the purified ozonide is decomposed with boiling water. The resulting solution is concentrated in a vacuum until the lævulic acid commences to volatilise and then cooled, when succinic acid separates. The aqueous distillate is treated with an excess of phenylhydrazine acetate, which causes a separation of the oily diphenylhydrazones of lævulin-aldehyde and acetylacetone. The two products can be identified by addition of dilute sulphuric acid and distillation with steam. Lævulin-aldehyde is thereby recognised by the formation of the non-volatile phenylmethyldihydropyridazine, m. p.  $197^{\circ}$  (compare Harries, A., 1898, i, 233), whilst the presence of acetylacetone follows from the formation of the volatile 1-phenylamino-2:5-dimethylpyrrole, m. p.  $90-92^{\circ}$  (Knorr, A., 1885, 995). H. W.

**Synthetic Resins. Condensation Products of Phenolic Substances by Aid of Hexamethylenetetramine.** L. V. REDMAN, A. J. WIETH, and F. P. BROCK (*J. Ind. Eng. Chem.*, 1914, 6, 3-16).—The authors give a synopsis of previous work on the condensation of salicylates, hydroxybenzyl alcohols, aromatic hydrocarbons, etc., with formaldehyde, and record the results of their study on the reaction and the products which are formed when dry hexamethylenetetramine is made to react with anhydrous phenol. The resins formed by this reaction possess higher dielectric properties and are of more uniform character than the resins formed in the wet way, and are more suitable for use in the electrical, varnish, glue, moulding, and other industries. W. P. S.

**Sphingosine. II. The Oxidation of Sphingosine and Dihydrosphingosine.** P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1914, 16, 549-553. Compare A., 1912, i, 284, 575).—On oxidation of sphingosine and dihydrosphingosine in the form of their sulphates by chromic acid in acetic acid solution, the authors have obtained from the first a tridecoic acid, m. p.  $47-47.5^{\circ}$ , and from the latter a pentadecoic acid, m. p.  $60-61^{\circ}$ . Their results are not in entire agreement with those of Lapworth (compare T., 1913, 103, 1029). On the basis of their results, the authors suggest for sphingosine the formula  $C_{12}H_{25}\cdot CH:CH\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot NH_2$ , the exact arrangement of the two hydroxyl and the amino-group not being, however, definitely fixed. W. G.

**Digitoxin and Gitalin.** H. KILIANI (*Arch. Pharm.*, 1913, 251, 562-587).—Attempts to convert gitalin into anhydrogitalin by treatment with absolute alcohol or glacial acetic acid have been unsuccessful (compare Kraft, A., 1912, i, 374). The addition of ether to a solution of gitalin in six parts of methyl alcohol and chloroform (equal vol.) causes the precipitation of about 25% of anhydrogitalin; under similar conditions, Merck's digitoxin yields about 90% of digitoxin but no anhydrogitalin.

The hydrolysis of digitoxin is best effected by boiling for fifteen minutes with ten parts of 50% alcohol containing 1 c.c. of hydrochloric acid (D 1.19), and then adding water, whereby about 41% of digitoxingenin is precipitated and digitoxose remains in the filtrate.

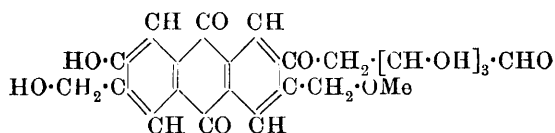
Digitoxose is decomposed extremely easily by hot acids even when very dilute. Although it is a tetrose, it behaves like *L*-arabinose in Bial's reaction. It does not yield furan by Günther, Chalmont, and Tollens' method, and can also be distinguished from arabinose by the phloroglucinol test.

The following salts are suitable for the identification of digitoxonic acid (A., 1909, i, 552): *copper* salt, a green, very hygroscopic syrup obtained by heating the syrupy lactone (*loc. cit.*) with freshly precipitated copper hydroxide (not the carbonate); *quinine* salt, m. p. 164°, long, stout needles or thin prisms, prepared by warming an aqueous solution of the lactone with an alcoholic solution of quinine; *brucine* salt,  $C_6H_{12}O_5 \cdot C_{23}H_{26}O_4N_2 \cdot 3H_2O$ , m. p. 124°, stout prisms, prepared from the lactone and brucine in water, the salt being precipitated from the solution, after concentration, by alcohol and ether.

The author and also other investigators have shown that digitoxin (one sample extracted from the leaves by water or dilute alcohol, other samples purchased from Merck in 1894–5) is obtained in a hydrated form by crystallisation from 85% alcohol. Now it is found that digitoxin (from Merck, 1911–12), after being purified by the methyl alcohol-chloroform method mentioned above, crystallises practically anhydrous from 85% alcohol, a result confirming Kraft's observation (*loc. cit.*). The author is of opinion, therefore, that there must be two kinds of digitoxin, only one of which can be hydrated.

C. S.

**The Constitution of Homonataloin and Nataloin.** E. LÉGER (*Compt. rend.*, 1914, 158, 185–188. Compare A., 1912, i, 708).—By the action of acetic anhydride and sodium acetate on homonataloin the author has obtained three acetyl derivatives, two crystalline and one amorphous, each containing five acetyl groups (compare Tschirch and Klaveness, A., 1901, i, 399), and these he considers to be derived from isomeric homonataloins, the isomerisation taking place during the acetylation. He supports Robinson and Simonsen's formula for



the methyl ether of the aloemodin of nataloin (compare T., 1905, 95, 1085), having obtained a crystalline penta-bromo-derivative

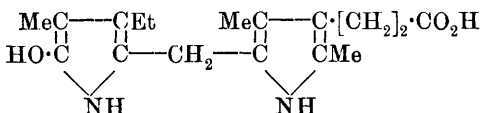
from it. As a result of this work he now assigns the annexed constitution to homonataloin, nataloin being its homologue, in which the group  $\cdot\text{CH}_2\text{OH}$  is replaced by  $\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ .

W. G.

**Bile Pigments. V. Constitution of Bilirubic Acid and Bilirubin.** HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1914, 89, 255–271. Compare A., 1913, i, 71).—When trimethylpyrrolepropionic acid is treated with a concentrated solution of sodium nitrite, the oxime of phonopyrrolecarboxylic acid is produced. This renders probable a formula for bilirubic acid which the authors had regarded as unlikely because bilirubic acid was

found not to be acted on by sodium methoxide. They now find, however, that potassium methoxide effects the expected decomposition, trimethylpyrrolepropionic acid and tetramethylpyrrole (identified as picrate) being formed.

Ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate (compare Benary and Silbermann, A., 1913, i, 651) is destroyed by sodium methoxide, and on reduction with acetic acid and hydriodic acid does not yield 2-methylpyrrole.



$\text{C} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$   
 $\parallel$   
 $\text{CMe}$

In consequence of these results, the constitution

of bilirubic acid is expressed by the annexed formula.

When bilirubin is reduced with hydriodic acid and acetic acid, cryptopyrrole (identified as picrate) and isophenopyrrolecarboxylic acid (identified as picrate) are produced.

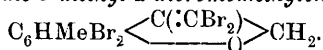
Bilirubic acid behaves similarly.

When bilirubin is treated with sodium methoxide, trimethylpyrrolepropionic acid is formed. When potassium methoxide is used, however, in addition to trimethylpyrrolepropionic acid, phyllopyrrole is obtained.

The significance of these results in regard to the constitution of hemibilirubin and of bilirubin is discussed, and probable formulæ are given for these compounds.

R. V. S.

*o*- $\psi$ -Bromides of Thymol and of *o*-isoPropylphenol and their Conversion into Coumaran Derivatives. II. K. FRIES, W. GROSS-SELBECK, and O. WICKE (*Annalen*, 1914, 402, 261—331. Compare Fries, A., 1910, i, 333).—The substance previously called 1:4:6-tribromo-5-methyl-2-bromomethylcoumarone (*loc. cit.*) exhibits behaviour inharmonious with this formula. Thus it is readily autoxidised in boiling benzene in a current of dry air, yielding the bromide,  $\text{C}_{10}\text{H}_5\text{O}_2\text{Br}_3$ , m. p. 137°, colourless needles, of 4:6-dibromo-5-methylcoumarone-2-carboxylic acid,  $\text{C}_6\text{HMeBr}_2 \langle \text{C}(\text{CO}_2\text{H}) \rangle \text{CH}$ , m. p. 272° (methyl ester, m. p. 154°; ethyl ester, m. p. 123°; anilide, m. p. 210°). Since it is known that keten-haloids frequently autoxidise in the sense,  $\text{CH}_2:\text{CBr}_2 \rightarrow \text{CH}_2\text{Br}\cdot\text{COBr}$ , the substance previously called 1:4:6-tribromo-5-methyl-2-bromomethylcoumarone is now regarded as 4:6 dibromo-5-methyl-2-dibromomethylenecoumaran,



This formula is supported by other evidence. For example, it can be shown that the particularly reactive bromine atom in  $\beta:\beta:3:5$ -tetrabromo-2-hydroxy-4-methyl- $\alpha$ -bromomethylstyrene (from which the tetrabromocoumaran is prepared; *loc. cit.*) is the one in the bromomethyl group, because when this bromine atom is replaced by a hydroxyl group a stable alcohol is produced (see below), from which a coumaran derivative cannot be prepared.

The conversion of 4:6-dibromo-5-methyl-2-dibromomethylenecoumaran into 1:1:4:6-tetrabromo-5-methyl-2-methylenecoumaran, m. p.

140°, can be effected, not only by hydrogen bromide (*loc. cit.*), but also by merely keeping the substance at its m. p., 179°. This intramolecular change is peculiar, but the constitution of the transformed product is established, not only by the evidence already recorded (*loc. cit.*), but also by the fact that 1:4:6-tribromo-1-acetoxy-5-methyl-2-methylenecoumaran, obtained from it by means of silver acetate, yields 4:6-dibromo-5-methyl-2-methylenecoumaran-1-one by hydrolysis and simultaneous loss of hydrogen bromide.

The transformed product might possibly be 1:4:6-tribromo-5-methyl-2-bromomethylcoumarone (the formation of the dibromomethyl-methylenecoumaranone from this is readily explicable in the light of Straus's researches on the behaviour of the keto-haloids of unsaturated ketones [A., 1912, i, 989]), but if such were the case, certainly the alcohol,  $C_6HMeBr_2 \left\langle \underset{\text{O}}{\text{C}(\text{CH}_2 \cdot \text{OH})} \right\rangle CBr$ , should be capable of existence, whereas actually only the coumaranone can be obtained by means of silver acetate and subsequent hydrolysis. Moreover, such a constitution of the tetrabromocoumaran leads to untenable conclusions in connexion with 4:6-dibromo-5-methyl-2-bromomethylcoumaran (see below).

By heating with alcohol at 100°, 1:1:4:6-tetrabromo-5-methyl-2-methylenecoumaran is converted into 1:4:6-tribromo-1-ethoxy-5-methyl-2-methylenecoumaran,  $C_6HMeBr_2 \left\langle \underset{\text{O}}{\text{C}(\text{CH}_2)} \right\rangle CBr \cdot OEt$ , m. p. 115°, from which 4:6-dibromo-5-methyl-2-methylenecoumaran-1-one is obtained by treatment with cold concentrated sulphuric acid. The lactone reacts with boiling methyl or ethyl alcohol in the presence of a little dilute hydrochloric acid to form 4:6-dibromo-1:1-dimethoxy-5-methyl-2-methylenecoumaran,  $C_{12}H_{12}O_3Br_2$ , m. p. 97°, colourless needles, or the corresponding diethoxy-compound, m. p. 66—68°.

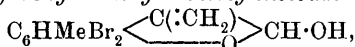
$\beta : \beta : 3 : 5$ -Tetrabromo-2-hydroxy-4-methyl- $\alpha$ -bromomethylstyrene, which contains its reactive halogen atom in the bromomethyl group, reacts with methyl alcohol at 100° to form  $\beta : \beta : 3 : 5$ -tetrabromo-2-hydroxy-4-methyl- $\alpha$ -ethoxymethylstyrene, m. p. 97° (acetate, m. p. 60°), and with silver acetate in hot glacial acetic acid to form  $\beta : \beta : 3 : 5$ -tetrabromo-2-hydroxy-4-methyl- $\alpha$ -acetoxymethylstyrene, m. p. 142°, the hydrolysis of which by boiling aqueous alcoholic potassium hydroxide yields  $\beta : \beta : 3 : 5$ -tetrabromo-2-hydroxy-4-methyl- $\alpha$ -hydroxymethylstyrene, m. p. 85—88° (diacetate, m. p. 85°).

$\beta : \beta : 3 : 5$ -Tetrabromo-2-hydroxy-4-methyl- $\alpha$ -bromomethylstyrene reacts with bromine, not at the ordinary temperature, but at 100° to form an unstable  $\psi$ -bromide from which, by loss of hydrogen bromide, is obtained  $\beta : \beta : 3 : 5$ -tribromo-2-hydroxy-4-methyl- $\alpha$ -tribromomethylstyrene,  $OH \cdot C_6HMeBr_2 \cdot C(CBr_3) \cdot CHBr$ , m. p. 126—127°, stout prisms. The latter forms an acetate, m. p. 150°, and in alcoholic solution is converted by concentrated aqueous potassium hydroxide into a by-product, m. p. 159°, and a main product, m. p. 184°, which is 1:1:4:6-tetrabromo-5-methyl-2-bromomethylenecoumaran,  $C_6HMeBr_2 \left\langle \underset{\text{O}}{\text{C}(\text{CHBr})} \right\rangle CBr_2$ , and is also obtained by the bromination of 1:1:4:6-tetrabromo-5-methyl-2-methylenecoumaran or of 4:6-dibromo-5-methyl-2-bromomethylene-



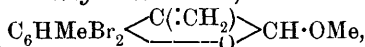
coumaran (see below). 1:1:4:6-*Tetrabromo-5-methyl-2-dibromomethylenecoumaran*,  $C_{10}H_4OBr_6$ , m. p.  $198^\circ$ , is obtained by the bromination of 1:1:4:6-tetrabromo-5-methyl-2-methylenecoumaran or the corresponding 2-bromomethylene derivative at  $50-60^\circ$ .

By heating with copper powder,  $\alpha:\beta:\beta:2:6$ -pentabromo-3-hydroxy-1-methyl- $\alpha$ -bromomethyl-4-ethylbenzene loses two atoms of bromine and yields a substance which is regarded as  $\beta:3:5$ -tribromo-2-hydroxy-4-methyl- $\alpha$ -bromomethylstyrene,  $OH \cdot C_6HMeBr_2 \cdot C(CH_2Br):CHBr$ , m. p.  $107^\circ$ , since it still contains a reactive bromine atom. The substance forms an *acetyl* derivative, m. p.  $105^\circ$ , and in consequence of the presence of the reactive bromine yields  $\beta:3:5$ -tribromo-2-hydroxy-4-methyl- $\alpha$ -methoxymethylstyrene,  $C_{11}H_{11}O_2Br_3$ , m. p.  $104^\circ$ , the corresponding *ethoxy*-derivative, m. p.  $71^\circ$ , and *anilino*-derivative, m. p.  $96^\circ$  (*diacetyl* derivative, m. p.  $167^\circ$ ), by heating with methyl alcohol, ethyl alcohol, and aniline respectively. By treatment with silver acetate and boiling glacial acetic acid,  $\beta:3:5$ -tribromo-2-hydroxy-4-methyl- $\alpha$ -bromomethylstyrene yields  $\beta:3:5$ -tribromo-2-hydroxy-4-methyl- $\alpha$ -acetoxymethylstyrene,  $OH \cdot C_6HMeBr_2 \cdot C(CH_2Br) \cdot CH_2 \cdot OAc$ , (m. p.  $129^\circ$ , stout prisms, from which the *alcohol*,  $C_{10}H_9O_2Br_2$ , m. p.  $128^\circ$  (*diacetate*, m. p.  $63^\circ$ ), is obtained by boiling aqueous alcoholic potassium hydroxide. By treatment with aqueous potassium hydroxide, the alcohol is changed to 4:6-dibromo-1-hydroxy-5-methyl-2-methylenecoumaran,



m. p.  $151^\circ$ , and  $\beta:3:5$ -tribromo-2-hydroxy-4-methyl- $\alpha$ -bromomethylstyrene to 4:6-dibromo-5-methyl-2-bromomethylenecoumaran, m. p. about  $140^\circ$ . The last substance does not contain bromine reactive to silver acetate, and is identical with that obtained by the reduction of 4:6-dibromo-5-methyl-2-dibromomethylenecoumaran; like this compound, it is changed by fusion to the isomeric 1:4:6-tribromo-5-methyl-2-methylenecoumaran,  $C_6HMeBr_2 \left\langle \underset{O}{\underset{|}{C:(CH_2)}} \right\rangle CHBr$ , m. p.

$157^\circ$ , which contains reactive bromine. This bromine is displaced by heating with alcohols, aniline, and silver acetate, 4:6-dibromo-1-methoxy-5-methyl-2-methylenecoumaran,



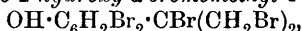
m. p.  $101^\circ$ , and the corresponding *ethoxy*-derivative, m. p.  $65-66^\circ$ , *anilino*-derivative, m. p.  $143^\circ$ , and *acetoxo*-derivative, m. p.  $131-132^\circ$ , being produced. By hydrolysis, the last substance yields 4:6-dibromo-1-hydroxy-5-methyl-2-methylenecoumaran, m. p.  $151^\circ$ , which is identical with the compound mentioned above, and is oxidised to 4:6-dibromo-5-methyl-2-methylenecoumaran-1-one by chromic and acetic acids.

By reduction with zinc dust and alcoholic hydrogen chloride, 1:4:6-tribromo-5-methyl-2-methylenecoumaran is converted into 4:6-dibromo-5-methyl-2-methylenecoumaran, m. p.  $74^\circ$ , colourless needles, and by bromination in chloroform at  $100^\circ$  into 1:4:6-tribromo-5-methyl-2-dibromomethylenecoumaran, m. p.  $177^\circ$ , which contains a reactive bromine atom in position 1, and, therefore, yields a corresponding *methoxy*-derivative,  $C_{11}H_8O_2Br_4$ , m. p.  $184^\circ$ , *ethoxy*-derivative, m. p.  $132^\circ$ , *anilino*-derivative, m. p.  $160^\circ$ , and *acetoxo*-derivative, m. p.  $161^\circ$ ;

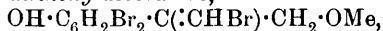
by hydrolysis, the last is converted into 4:6-dibromo-1-hydroxy-5-methyl-2-dibromomethylenecoumaran, m. p. 185°.

2-Hydroxy- $\alpha$ -methylstyrene (Béhal and Tiffeneau, A., 1908, i, 261) rapidly polymerises by treatment with ethereal hydrogen chloride, and yields a bimolecular form,  $C_{18}H_{20}O_2$ , m. p. 97°, small plates, which is depolymerised by heating, forms an *acetyl* derivative,  $C_{20}H_{22}O_3$ , m. p. 96—97°, and *methyl ether*,  $C_{19}H_{22}O_2$ , m. p. 115—117°, prisms, and is converted by bromination in chloroform at about 50° into a *tetrabromo*-derivative,  $C_{18}H_{16}O_2Br_4$ , m. p. 149°, stout prisms (*acetyl* derivative,  $C_{20}H_{18}O_3Br_4$ , m. p. 159—160°).

By bromination in chloroform in a freezing mixture and finally at the ordinary temperature, 2-hydroxy- $\alpha$ -methylstyrene yields a penta-bromo- $\psi$ -bromide, which behaves in general like the hexabromo- $\psi$ -bromide obtained from 2-hydroxy- $\alpha$ :4-dimethylstyrene (*loc. cit.*).  $\alpha$ : $\beta$ :3:5-Tetrabromo-2-hydroxy- $\alpha$ -bromomethyl-1-ethylbenzene,

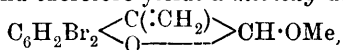


m. p. 126°, prismatic crystals, forms an *acetyl* derivative, m. p. 127°, and is converted by aqueous acetone into a red, very unstable methyl-enequinone, which almost immediately changes to  $\beta$ :3:5-tribromo-2-hydroxy- $\alpha$ -bromomethylstyrene,  $OH \cdot C_6H_2Br_2 \cdot C(CH_2Br) \cdot CHBr$ , m. p. 111°, colourless crystals (*acetyl* derivative, m. p. 102°). By the substitution of the reactive halogen in the bromomethyl group, the last substance yields a *methoxy*-derivative,



m. p. 81° (*acetyl* derivative, m. p. 95—96°), *anilino*-derivative, m. p. 131° (*diacetyl* derivative, m. p. 154°), and *acetoxy*-derivative; by the hydrolysis of the last substance is obtained  $\beta$ :3:5-tribromo-2-hydroxy- $\alpha$ -hydroxymethylstyrene,  $OH \cdot C_6H_2Br_2 \cdot C(CHBr) \cdot CH_2 \cdot OH$ , m. p. 130°, which is converted into 4:6-dibromo-1-hydroxy-2-methylenecoumaran, m. p. 130—132° (see below), by prolonged boiling with dilute sodium hydroxide.

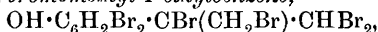
Alcoholic  $\beta$ :3:5-tribromo-2-hydroxy- $\alpha$ -bromomethylstyrene is converted by concentrated aqueous potassium hydroxide into 4:6-dibromo-2-bromomethylenecoumaran,  $C_6H_2Br_2 \left\langle \underset{O}{\text{C}(\cdot CHBr)} \right\rangle CH_2$ , m. p. 140°, which does not contain reactive bromine, but is changed by fusion or by hydrogen bromide in hot, glacial acetic acid into the isomeride, 1:4:6-tribromo-2-methylenecoumaran, m. p. 124°; this contains reactive bromine, and therefore yields a *methoxy*-derivative,



m. p. 72°, *anilino*-derivative, m. p. 140—141°, and *acetoxy*-derivative, m. p. 95°. By hydrolysis, the last substance yields 4:6-dibromo-1-hydroxy-2-methylenecoumaran. The reduction of ethereal 1:4:6-tribromo-2-methylenecoumaran by zinc dust and alcoholic hydrogen chloride yields 4:6-dibromo-2-methylenecoumaran,  $C_9H_6OBr_2$ , m. p. 72° whilst the bromination of the tribromomethylenecoumaran yields 1:4:6-tribromo-2-dibromomethylenecoumaran, m. p. 128°, which reacts instantly with silver acetate.

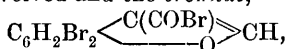
By bromination in chloroform at 100°,  $\alpha$ : $\beta$ :3:5-tetrabromo-2-hydroxy- $\alpha$ -bromomethyl-1-ethylbenzene yields  $\alpha$ : $\beta$ : $\beta$ :3:5-penta-

*bromo-2-hydroxy- $\alpha$ -bromomethyl-1-ethylbenzene*,



m. p. 113—114°, colourless plates (*acetyl* derivative, m. p. 138). This hexabromo- $\psi$ -bromide is changed: (1) by copper powder, in the ethereal solution, to  $\beta:3:5$ -tribromo-2-hydroxy- $\alpha$ -bromomethylstyrene, m. p. 111°; (2) by aqueous acetone to  $\beta:\beta:3:5$ -tetrabromo-2-hydroxy- $\alpha$ -bromomethylstyrene, m. p. 124°, (*acetyl* derivative, m. p. 104°), and (3) by dilute aqueous alkalis to 4:6-dibromo-2-dibromomethylenecoumaran, m. p. 170°.  $\beta:\beta:3:5$ -Tetrabromo-2-hydroxy- $\alpha$ -bromomethylstyrene, which contains a reactive halogen in the bromomethyl group, yields a *methoxy*-derivative,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{C}(\text{CBr}_2) \cdot \text{CH}_2 \cdot \text{OMe}$ , m. p. 145°, and *acetoxy*-derivative, m. p. 94°, the latter forming by hydrolysis the corresponding *alcohol*,  $\text{C}_9\text{H}_6\text{O}_2\text{Br}_4$ , m. p. 154° (*diacetate*, m. p. 103°).

4:6-Dibromo-2-dibromomethylenecoumaran, which is also obtained by the action of aqueous alcoholic alkalis on the preceding tetrabromohydroxybromomethylstyrene, does not contain reactive bromine, but is changed by fusion into the isomeride, 1:1:4:6-tetrabromo-2-methylenecoumaran, m. p. 130—131°, which is reactive and is more conveniently obtained by the bromination of 4:6-dibromo-2-bromomethylenecoumaran in boiling chloroform. 4:6-Dibromo-2-dibromomethylenecoumaran is reduced to 4:6-dibromo-2-bromomethylenecoumaran by zinc dust and hydrogen chloride in alcoholic-ethereal solution, and is readily autoxidised in boiling benzene whereby hydrogen bromide is evolved and the *bromide*,



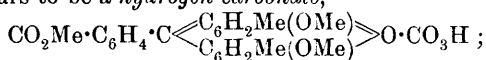
m. p. 144°, of 4:6-dibromocoumarone-2-carboxylic acid, m. p. 277°, is obtained. The acid forms a *methyl* ester, m. p. 155°, and *ethyl* ester, m. p. 106°.

1:1:4:6-Tetrabromo-2-methylenecoumaran forms 1:4:6-tribromo-1-methoxy-2-methylenecoumaran, m. p. 115°, and the *ethoxy*-derivative, m. p. 140°, by treatment with methyl and ethyl alcohol respectively at 100°, and is converted into 4:6-dibromo-2-methylenecoumaran-1-one, m. p. 146°, faintly yellow crystals, by treatment with silver acetate and boiling glacial acetic acid and subsequent hydrolysis of the product. The lactone dissolves rapidly in warm dilute sodium hydroxide and is recovered by acidification; unlike 4:6-dibromo-5-methyl-2-methylenecoumaran-1-one, it does not form ortho-esters with alcohols.

It is noteworthy that all the preceding derivatives of styrene and coumaran which contain reactive bromine do not develop a coloration with concentrated sulphuric acid, whilst the oxygenated derivatives, obtained therefrom by replacing the reactive bromine by the methoxy-, ethoxy-, or acetoxy-group, produce deep blue or bluish-violet colorations with this reagent. C. S.

**Crystalline Oxonium Carbonates.** (Preliminary Communication.) F. KEHRMANN and ADOLF BOHN (*Ber.*, 1914, 47, 82—84).—If at the ordinary temperature a saturated aqueous solution is prepared of the chloride of the trimethyl ether ester of the fluorescein compound obtainable from cresorcinol and phthalic anhydride, namely,

$\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_2\text{Me}(\text{OMe}) \\ \text{C}_6\text{H}_2\text{Me}(\text{OMe}) \end{smallmatrix} \text{OCl}$ , then treatment at  $0^\circ$  with carbon dioxide for ten minutes, followed by the addition of an equal bulk of saturated potassium hydrogen carbonate solution, causes the separation of golden-yellow crystals. The new substance gives a yellow aqueous solution with a bitter taste, similar to that of the chloride; the solution is alkaline to litmus, and, although fairly stable at  $0^\circ$ , decomposes rapidly on warming. Even in the dry condition the substance undergoes decomposition in the course of twenty-four hours, water of crystallisation which is probably present producing apparently a similar hydrolysis to that which occurs in solution. From its analysis the salt appears to be a *hydrogen carbonate*,



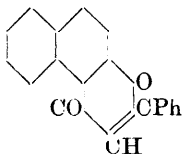
the existence of the corresponding normal carbonate is possible, for on boiling the solution a portion of the carbon dioxide is retained more tenaciously than the rest, and the solution becomes more strongly alkaline.

In an analogous manner, but by salting out with solid potassium hydrogen carbonate, yellow leaflets of a *carbonate* can be obtained from the chloride of the methyl ester of fluorescein dimethyl ether,  $\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OMe}) \\ \text{C}_6\text{H}_3(\text{OMe}) \end{smallmatrix} \text{OCl}$ . This carbonate which dissolves in mineral acids with effervescence is less stable than the preceding one.

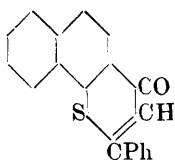
D. F. T.

**Naphthaflavones and Naphthathioflavones.** SIEGFRIED RUHEMANN (*Ber.*, 1914, **47**, 119—125).—The preparation of  $\beta$ -substituted cinnamic esters by the condensation of the naphthols or naphthyl mercaptans with ethyl phenylpropionate is not so simple as in the case of phenol and phenylmercaptan (*A.*, 1913, i, 891, 1374), partly owing to the difficulty of preparing the pure sodium compounds and partly owing to the poor yields. The condensation to flavones is easily effected.

$\beta$ - $\alpha$ -Naphthoxycinnamic acid (*T.*, 1900, **77**, 989) was treated in benzene with phosphorus pentachloride followed by aluminium chloride, and converted into  $\alpha$ -naphthaflavone (Kostanecki, *A.*, 1898, i, 373). In the same way (*loc. cit.*),  $\beta$ -naphthol was transformed into *ethyl  $\beta\beta$ -naphthoxycinnamate*,  $\text{C}_{10}\text{H}_7 \cdot \text{O} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ , which forms colourless, shining leaflets, m. p.  $161$ — $162^\circ$ , b. p.  $285$ — $290^\circ/23$  mm.  *$\beta\beta$ -Naphthoxycinnamic acid* forms colourless needles, decomp.  $164^\circ$ , and furnishes an almost quantitative yield of  $\beta$ -naphthaflavone (annexed formula), which crystallises in colourless needles, m. p.  $164$ — $165^\circ$ , and gives a colourless solution with intense blue fluorescence in concentrated sulphuric acid.



Similarly, *ethyl  $\beta$ - $\alpha$ -naphthylthiolcinnamate*, b. p.  $278$ — $280^\circ/12$  mm, was hydrolysed to  *$\beta$ - $\alpha$ -naphthylthiolcinnamic acid*, which was obtained in colourless needles, m. p.



183—184°, and condensed to  $\alpha$ -naphthathioflavone (annexed formula). The latter forms almost colourless leaflets, m. p. 182°, and in contrast to the benzothioflavones, it exhibits a faint green fluorescence in sulphuric acid. Ethyl  $\beta$ -naphthylthiolcinnamate was also obtained in colourless needles, m. p. 102—103°.  $\beta$ -Naphthylthiolcinnamic acid forms yellow prisms, m. p. 165—166°, and is converted into  $\beta$ -naphthylthiolstyrene,  $C_{10}H_7 \cdot S \cdot CPh : CH_2$ , yellow needles, m. p. 84—85°, b. p. 238—239°/12 mm., on distillation in vacuum, and into  $\beta$ -naphthathioflavone, colourless needles, m. p. 155°, by the above method.

J. C. W.

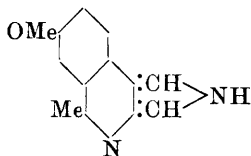
**3-Aceto-2:5-thioxen** [**3-Acetyl-2:5-dimethylthiophen**]. (Mlle.) F. ZILBERFARB (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1936—1940).—Two acetylthioxens are already known: that obtained from coal-tar thioxen, b. p. 223—224°,  $D_4^{17}$  1.091, giving an oxime, m. p. 65°, and 2-acetyl-3:5-dimethylthiophen, b. p. 226—228°, the oxime of which has m. p. 70°.

**3-Acetyl-2:5-dimethylthiophen**,  $S \begin{smallmatrix} \swarrow CMe : CAc \\ \searrow CMe : CH \end{smallmatrix}$ , obtained by acetylating the 2:5-dimethylthiophen prepared by the action of phosphorus trisulphide on acetonylacetone, is a colourless liquid, b. p. 223—224.5°,  $D_4^{13.5}$  1.0979,  $D_4^{17}$  1.0973,  $n_D^{13.5}$  1.5441. Its semicarbazone,  $C_9H_{11}ON_3S$ , m. p. 197°, and its oxime,  $C_8H_{11}ONS$ , m. p. 83°, were prepared.

Hence the thioxen from coal-tar cannot be either 2:5- or 3:5-dimethylthiophen.

T. H. P.

**Harmine and Harmaline.** O. FISCHER [with (Frl.) L. ANGERMANN and E. DIEPOLDER] (*Ber.*, 1914, 47, 99—107).—Hitherto, no direct evidence of the existence of a pyridine and a pyrrole nucleus in the molecule of harmine has been obtained, although the various formulæ advanced by O. Fischer, and by Perkin and Robinson (*T.*, 1912, 101, 1775) and Hasenfratz (*A.*, 1912, i, 383, 797) incorporate those systems. By heating harmine acid, or what amounts to the same, apoharminecarboxylic acid, with dilute nitric acid in a sealed tube at 180—200°, oxidation to isonicotinic acid (4-pyridinecarboxylic acid) has been effected. The product was isolated by decomposition of the copper salt, and completely identified with material prepared by Weidel's method (m. p., platinum- and auri-chlorides). The nitrogen of the pyrrole nucleus cannot therefore be ortho to the pyridine ring, as a nitropyridinecarboxylic acid might have been expected in that case. Attempts have also been made to prove the presence of the pyrrole nucleus by conversion into a dioxime according to Ciamician and Zanetti, but without success. Harmine does not react with hydroxylamine, and harmaline only forms an additive compound. Furthermore, the formation of a bisazo-derivative of harmaline (*A.*, 1912, i, 645) would suggest that the methyl group is attached to the pyridine rather than to the pyrrole nucleus. The formula for harmine which agrees most nearly with the accumulated



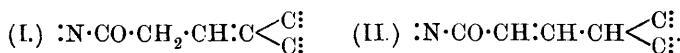
evidence, including the fact that it gives the quinophthalone reaction is the one annexed.

When harmaline is heated with methyl iodide and methyl alcohol, methylharmaline hydroiodide separates, but the highly concentrated mother liquor deposits *dimethylharmaline iodide*,  $C_{15}H_{19}ON_2I \cdot \frac{1}{2}H_2O$ , in stout, yellow crystals, m. p. about  $220^\circ$ . The primary iodide was converted into *methylharmaline hydrochloride*,  $C_{14}H_{17}ON_2Cl \cdot 4H_2O$ , which formed twinned crystals with pearly lustre, decomp.  $265^\circ$ . From this, the *picrate*, slender, yellow needles, m. p.  $216^\circ$ , the *nitrate*, stout, yellow, shimmering prisms or tablets, decomp. over  $230^\circ$ , the *aurichloride*, reddish-violet needles, decomp.  $153^\circ$ , and the *platinichloride*, orange leaflets, decomp.  $220^\circ$ , were prepared. The hydrochloride was also reduced by means of sodium in amyl alcohol to *methyldihydroharmaline*,  $C_{14}H_{18}ON_2$ , which was obtained in almost colourless leaflets, m. p.  $173-174^\circ$ . The *hydrochloride* forms slender, white scales, decomp.  $142-146^\circ$ . With methyl iodide, it yields *dimethyldihydroharmaline iodide*,  $C_{15}H_{21}ON_2I$ , in colourless crystals, m. p.  $203^\circ$ . Unlike the above dimethylharmaline iodide, it does not produce trimethylamine when heated with sodium hydroxide, but yields a substance of the composition of *dimethylharmaline ammonium hydroxide*,  $C_{15}H_{22}O_2N_2$ , which forms colourless needles, m. p.  $129^\circ$ , from light petroleum.

When treated with hydroxylamine, harmaline yields a compound,  $C_{13}H_{17}O_2N_3$ , which is insoluble in alkalis, but soluble in mineral acids, and forms colourless needles, m. p.  $180^\circ$ . Benzylideneharmine and benzylidenediharmaline (Perkin and Robinson) were also prepared. Dihydroharmaline also condenses with benzaldehyde, giving *benzylidenebisdihydroharmaline*,  $C_{38}H_{26}O_2N_4$ , in colourless flakes, the *hydrochloride* forming very slender needles.

J. C. W.

**Strychnos Alkaloids. XX. Oxidation of Acetylbrucinolone.** HERMANN LEUCHS and HUBERT RAUCH (*Ber.*, 1914, 47, 370—380).—Two acids, acetylbrucinolic acid and a dibasic acid,  $C_{23}H_{24}O_{10}N_2$ , were obtained by the oxidation of acetylbrucinolone (A., 1912, i, 210, 898). The latter has now been hydrolysed and, besides acetic acid, oxalic acid and an amino-acid,  $C_{19}H_{22}O_6N_2$ , have been isolated from the products. This similar behaviour of the two acids points to the conclusion that the addition of oxygen to acetylbrucinolone has taken place at the same part of the molecule. The formation of two acids presupposes that the ethylene linking which is attacked must be in two different positions. Thus, the grouping (I) leads to acetylbrucinolic acid and (II.) to the dibasic acid.



This difference is not due to displacement of the ethylenic linking during oxidation, but to the presence of an isomeride, for pure acetylbrucinolone, prepared from brucinoline hydrate I., only yields acetylbrucinolic acid. Attempts were therefore made to purify acetylbrucinolone, either by destroying one isomeride or by causing a

displacement of the double linking into a common position. Success was attained by heating the crude product with alcoholic ammonia. Pure brucinolone was thus obtained, and the results indicated that in all probability the process was mainly that of the displacement of the bond in the isomeride.

The barium salt of the acid,  $C_{23}H_{24}O_{10}N_2$  (*loc. cit.*), was heated with hydrochloric acid, when the barium chloride which crystallised was converted into the sulphate and filtered. The filtrate deposited the *hydrochloride* of an *amino-acid*,  $C_{19}H_{22}O_6N_2 \cdot 2HCl$ , on freezing, and also contained oxalic, but no malonic acid. A by-product was also obtained from the last mother liquors in shining, broad needles, decomp. about  $272^\circ$ , when the whole filtrate was evaporated and the oxalic acid extracted with ether. The above hydrochloride forms hexagonal prisms, m. p.  $235-236^\circ$  with gas evolution, and does not give the brucine reaction or precipitates with ferric, mercuric or platinic chlorides. The free base could not be isolated, but a *compound*,  $C_{26}H_{27}O_7N_3$ , with phenylcarbimide was obtained, in small, colourless prisms, decomp. towards  $210^\circ$ , which give the brucine reaction and dissolve in alkalis.

Crude brucinolone is yellow, but the pure substance, prepared by adding the requisite amount of sodium hydroxide to brucinoline hydrate I. and dehydrating the amino-acid so obtained at  $135^\circ$  in vacuum over phosphoric oxide, is colourless and has  $[\alpha]_D^{20} - 37^\circ$ . Pure brucinolone was acetylated and then oxidised by permanganate in acetone as in A., 1912, i, 211. The extraction of the products was carried out in a modified way when a small amount of a neutral oxidation product II.,  $C_{23}H_{24}O_8N_2 \cdot 4H_2O$ , of acetylbrucinolone was isolated. It lost  $4H_2O$  at  $100^\circ$  in vacuum over sulphuric acid and then had m. p.  $175-180^\circ$ , but reabsorbed  $1H_2O$  in the air. It gives the brucine reaction.

Crude acetylbrucinolone was heated with methyl-alcoholic ammonia at  $95^\circ$  when the tube soon became full of colourless crystals of pure brucinolone. The mother liquor contained a base which was isolated as the *hydrochloride*,  $C_{21}H_{25}O_5N_3 \cdot HCl$ , in the form of rectangular prisms, m. p.  $320^\circ$  (decomp.). The free *base* crystallises in four-sided tablets from ethyl acetate, m. p.  $220^\circ$  (decomp.), and is alkaline to litmus and turmeric.

J. C. W.

**Pyrrole.** HANS FISCHER and W. ZIMMERMANN (*Zeitsch. physiol. Chem.*, 1914, 89, 163—169).—Tetramethylpyrrole reacts with hydroxylamine according to the equation

$$\begin{array}{c} \text{CMe}:\text{CMe} \\ | \quad | \\ \text{CMe}:\text{CMe} \end{array} > \text{NH} + 2\text{NH}_2\cdot\text{OH} =$$

$$\begin{array}{c} \text{CHMe}\cdot\text{CMe}:\text{NOH} \\ | \\ \text{CHMe}\cdot\text{CMe}:\text{NOH} \end{array} + \text{NH}_3 \text{ (compare Ciamician and Zanetti, A., 1890, 264, 1155; 1891, 1502), the dioxime obtained being identical with that of Ciamician and Silber (A., 1912, i, 174, 538).}$$

Hydroxylamine acts on porphyrinogen as an oxidising agent, mesoporphyrin and ammonia being formed.

When ethyl 2-methylpyrrole-3-carboxylate and acetone are heated



together in presence of a little hydrochloric acid, a condensation product of the annexed formula is formed. The substance has the composition and molecular weight required by this

formula, and gives the Ehrlich aldehyde reaction in the warm (but not in the cold).

When 5-acetyl-2:4-dimethylpyrrole and formaldehyde are heated at  $130^\circ$  for five hours, a substance,  $\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$ , is obtained; it crystallises in compact prisms, m. p.  $136-138^\circ$ . On heating with sulphuric acid and water on the water-bath for two hours, it yields 2:4-dimethylpyrrole.

Acetaldehyde reacts in the same circumstances as formaldehyde, yielding a substance,  $\text{C}_8\text{H}_{11}\text{ON}, 2\text{MeCHO}$ , m. p.  $142^\circ$ .

When 3-acetyl-2:4-dimethylpyrrole is treated with pyridine and cyanogen bromide, two substances are formed, of which the chief product has the formula  $\text{C}_{14}\text{H}_{15}\text{ON}_3$ . It crystallises in compact prisms, m. p.  $208^\circ$ , and is probably a cyanamide derivative. R. V. S.

**Bases Formed by the Alkylation of Pyrroles.** I. G. PLANCHER and C. RAVENNA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 703—707).—It has been shown by Plancher and his pupils (1897—1908) that the action of methyl iodide on sodium pyrrolocarboxylate yields a pentamethylpyrrolidine, and from this or from 1-methylpyrrole, by methylation, pentamethylmethylenepyrroline is obtained. Further methylation then gives pentamethylisopropylidenepyrroline, and if, as has been supposed, the constitution of this compound is represented by the formula  $\text{NMe} \begin{array}{c} \text{C}(\text{CMe}_2) \cdot \text{CMe}_2 \\ | \\ \text{CMe} = \text{CMe} \end{array}$  or  $\text{NMe} \begin{array}{c} \text{CMe}_2 - \text{CMe} \\ | \\ \text{C}(\text{CMe}_2) \cdot \text{CMe} \end{array}$ , it should be obtainable from either 2:5-dimethylpyrrole, or 2:4:5-trimethylpyrrole, or 2-methyl-5-isopropylpyrrole.

In the present paper the action of methyl iodide on 2-methyl-5-isopropylpyrrole is considered. With excess of methyl iodide, a base,  $\text{C}_{12}\text{H}_{21}\text{N}$ , is formed, giving an aurichloride,  $\text{C}_{12}\text{H}_{21}\text{N}, \text{HAuCl}_4$ , m. p.  $86-87^\circ$ , which is not identical with the aurichloride, m. p.  $99.5-100.5^\circ$ , prepared by Anderlini (A., 1890, 1431), whose results were confirmed by the authors. With deficit of methyl iodide, a mixture is obtained giving, on purification, a base,  $\text{C}_{12}\text{H}_{21}\text{N}$ , the aurichloride of which has m. p.  $95^\circ$ .

It seems probable that Anderlini's product is not quite pure, and that the purest product is that obtained from 2-methyl-5-isopropylpyrrole. Preparation of pentamethylisopropylidenepyrroline in some other way is hence desirable.

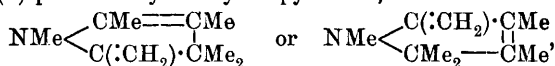
If the bases obtained by the above two methods prove to be identical, the constitution would be demonstrated, since the preparation from 2-methyl-5-isopropylpyrrole would fix the positions of one methyl and of the isopropyl group. In order to determine the positions of the other methyls, attempts have been made to prepare more highly methylated bases from Korschun's 2:3:5-trimethylpyrrole (A., 1905,



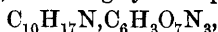
i, 373) and from 2:5-dimethylpyrrole. The first of these, when heated with methyl iodide, methyl alcohol and potassium carbonate in a sealed tube for ten hours at  $140^{\circ}$  gives a base,  $C_{10}H_{17}N$ , corresponding in composition with Ciamician and Anderlini's 1-methyltetramethylenepyrroline (A., 1889, 58), and forming an aurichloride, m. p.  $100^{\circ}$ . Similar treatment of 2:5-dimethylpyrrole yields a semi-solid hydrochloride, which gives indications of the presence of a base,  $C_9H_{15}N$ , a small proportion of a picrate, m. p.  $168^{\circ}$ , being obtained. This experiment is being repeated.

T. H. P.

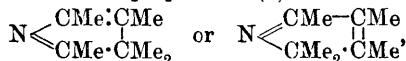
**Bases Formed by the Alkylation of Pyrroles. II.** G. PLANCHER and T. ZAMBONINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 708—712. Compare preceding abstract).—The interaction of 2:3:4:5-tetramethylpyrrole and methyl iodide in presence of potassium carbonate and methyl alcohol in a sealed tube at  $110^{\circ}$  yields: (1) pentamethylmethylenepyrroline,



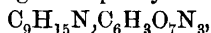
which has a sweetish, faintly geranic odour recalling that of the analogous indole derivative obtained by Fischer; its deliquescent hydrochloride, m. p.  $125^{\circ}$ , its orange-yellow picrate,



m. p.  $148^{\circ}$ , and its aurichloride,  $C_{10}H_{17}N, HAuCl_4$ , m. p.  $101-102^{\circ}$ , decomposing at  $220^{\circ}$ , were prepared. (2) Pentamethylpyrrolenine,



b. p.  $70-90^{\circ}/26$  mm., which has an odour intermediate to those of camphor and menthol and gives a pale yellow picrate,



m. p.  $168-169^{\circ}$ . The colours of these two picrates are precisely similar to those of the corresponding indole derivatives, trimethylindolenine and trimethylmethylenindoline.

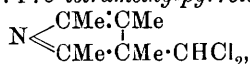
The action of magnesium methyl iodide on 2:3:4:5-tetramethylpyrrole yields only pentamethylpyrrolenine, which is the first of these bases to be obtained pure.

The esters of pyrrolocarboxylic acids with a methyl group in the 1-position do not undergo complete methylation even under prolonged treatment with methyl iodide at a high temperature. Thus, ethyl 2:5-dimethyl-1-ethylpyrrole-3:4-dicarboxylate and ethyl 1:2:5-trimethyl-3:4-dicarboxylate do not lose their carbethoxyl groups, but are simply hydrolysed, whereas Korschun's ethyl 2:3:5-trimethylpyrrole-4-carboxylate (A., 1905, i, 373) and esters of other secondary pyrrole derivatives yield secondary tetramethylpyrrole. Further, 1:2:5-trimethylpyrrole remains unaltered even when heated for fifteen hours at  $260^{\circ}$  with sodium methoxide. It seems certain, then, that pyrrole derivatives are acted on by sodium ethoxide only when the iminic hydrogen is not substituted. Again, organo-magnesium compounds are without action on 3:5-dimethyl-1-ethylpyrrole.

T. H. P.

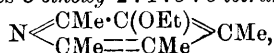
**Action of Chloroform on Tetramethylpyrrole.** III. G. PLANCHER and T. ZAMBONINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 712—716. Compare preceding abstracts).—The results obtained by Plancher and Ponti in their study of the action of chloroform on 2:5-dimethylpyrrole (A., 1910, i, 132) indicate that with the pyrroles, just as with the indoles, the initial action of chloroform is perfectly analogous to that of the alkyl iodides, a dichloromethylpyrrolenine being formed; this compound subsequently loses a molecule of water, yielding a chloropyridine derivative. It is now found that a similar reaction occurs with 2:3:4:5-tetrachloropyrrole and chloroform.

3-Dichloromethyl-2:3:4:5-tetramethylpyrrolenine,



obtained by the action of chloroform on 2:3:4:5-tetrachloropyrrole in presence of alcohol and aqueous alcoholic potassium hydroxide, forms hard, colourless crystals, m. p. 86—87°, which tend to turn red and lose hydrogen chloride in the air; it forms an orange-red *picrate*, m. p. about 189°, and with nitrous acid gives pale yellow scales, m. p. 155°. The mother liquors contain other bases to be examined later.

When treated with sodium ethoxide, 3-dichloromethyl-2:3:4:5-tetramethylpyrrolenine gives 3-ethoxy-2:4:5:6-tetramethylpyridine,



as an oily liquid, forming a *picrate*, m. p. 124°.

3-Chloro-2:4:5:6-tetramethylpyridine,  $\text{N} \begin{array}{c} \diagup \text{CMe}:\text{CMe} \\ \diagdown \text{CMe} - \text{CCl} \end{array} \text{CMe},$

obtained by the action of aqueous alcohol on the dichloromethyltetramethylpyrrolenine, has an odour resembling that of quinoline and gives a *picrate*,  $\text{C}_9\text{H}_{12}\text{NCl} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , in dark yellow scales, m. p. 152°.

T. H. P.

**Complex Compounds of Organic Salts with Some Organic Bases.** G. ROSSI (*Gazzetta*, 1913, 43, ii, 654—665).—This paper describes the results of measurements of the electrical conductivity of solutions containing water, pyridine, and the following salts (taken one at a time): nickelous nitrate, cobaltous nitrate, sodium bromide, copper acetate, and also of solutions containing water, hexamethylenetetramine, and each of the following salts: cobaltous nitrate, nickelous nitrate, copper acetate. From the experiments it appears that pyridine can unite with certain cations giving complex cations which are stable below 40°. With water, these complex cations behave like simple cations, giving unstable hydrates of the type  $n\text{Py} \cdot \text{R} \cdot n'\text{H}_2\text{O}$ , which are resolved into water and complex cations  $n\text{Py} \cdot \text{R}$  at a temperature below 40°. Hexamethylenetetramine does not form complex ions, but when it combines with salts it behaves like water of crystallisation.

R. V. S.

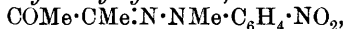
**Two Compounds of Zirconium Chloride with Pyridine.** ED. CHAUVENET (*Compt. rend.*, 1914, 158, 128—130).—In addition to the compound  $\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ , prepared by Matthews (compare A., 1899, ii, 295), the author has obtained a compound,  $\text{ZrCl}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$ , by

saturating pyridine with zirconium chloride, and allowing the solution to evaporate in a dry atmosphere. The crystals are freed from excess of pyridine by washing with light petroleum, which, however, tends to remove small quantities of the combined pyridine. The crystals are prismatic, and act energetically on polarised light. They possess a high dissociation pressure at the ordinary temperature. From a study of the heat of fixation of the pyridine molecules, the author shows that a third compound cannot exist between the two described. The compound  $\text{ZrCl}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$  decomposes slowly at the ordinary temperature, and rapidly at  $50^\circ$  to give  $\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ . The heats of fixation of the two and four molecules of pyridine are respectively 54 Cal. and 70 Cal., or for one molecule 27 Cal. in the one case, and 17.5 Cal. in the other.

W. G.

**2-Acetyl-1-methylindole.** OTTO DIELS and WALTHER DÜRST (*Ber.*, 1914, **47**, 284—290).—2-Acetyl-1-methylindole has a physiological effect resembling that of morphine, but is only sparingly soluble, so that the authors have now introduced an amino group into the molecule with the object of obtaining a compound giving more soluble salts. The new compound has, however, no physiological action.

*Diacetyl-p-nitrophenylmethylhydrazone*,



obtained by nitrating diacetylphenylmethylhydrazone (see Diels and Köllisch, A., 1911, i, 230), forms brownish-yellow needles, exhibiting orange-blue dichroism, m. p.  $157-158^\circ$ . On reduction it undergoes decomposition, yielding *p*-phenylenemethyldiamine.

**5-Nitro-2-acetyl-1-methylindole**,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CH} \\ \text{NMe} \end{smallmatrix} \text{CAc}$ , obtained by nitrating 2-acetyl-1-methylindole or, better, by the indole-transformation of diacetyl-*p*-nitrophenylmethylhydrazone, forms dark brown needles, m. p.  $199^\circ$ .

Reduction of this nitro-derivative by means of stannous chloride and hydrochloric acid yields the *chloroindoline* base,



in the form of olive-brown needles with a marked bluish reflection.

**5-Amino-2-acetyl-1-methylindole**,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CH} \\ \text{NMe} \end{smallmatrix} \text{CAc}$ , prepared by reducing the corresponding nitro-compound in moist ethereal solution by means of zinc dust, forms olive-green leaflets, m. p.  $173^\circ$ . The *hydrochloride* gives an intense blue coloration with ferric chloride in aqueous solution, and with nitrous acid forms a diazonium salt, which with R-salt yields a fine red azo-colouring matter. T. H. P.

**Isatin and Allied Compounds. I.** W. BORSCHKE and W. JACOBS (*Ber.*, 1914, **47**, 354—363).—The properties assigned by Gysae to "isaphenic acid," the condensation product of isatin and phenylacetic acid, are not in agreement with the proposed constitution (A., 1894, i, 29). The substance is now identified with 2-hydroxy-3-phenylquinoline-4-carboxylic acid (Hübner, A., 1908, i, 288). This reaction of isatin has been extended to other acids with an active

methylene group, particularly malonic acid. A similar condensation takes place, but the carboxyl group which should be in position 3 is at the same time destroyed. Thus, isatin and malonic acid yielded 2-hydroxyquinoline-4-carboxylic acid. This was identified with the product obtained by Camps' method (A, 1900, i, 310) from *N*-acetyl-isatin. The attachment of malonic acid to isatin does not take place at the nitrogen atom, since *N*-methylisatin also reacts.

The ease with which the pyrrole ring passes into another cyclic system led the authors to attempt the rearrangement of isatoxime. Neither by means of dilute mineral acids, alkalis, nor by acetic anhydride could any change be effected, and the expectation that a quinoxaline or quinazoline would result by the Beckmann transformation was also unfulfilled, the product being *o*-cyanophenylcarbimide, or *o*:*o*'-dicyanocarbanilide.

The identity of "isaphenic acid" was established by converting the substance into 2-chloro-3-phenylquinoline-4-carboxylic acid, and the 2-hydroxyquinoline-4-carboxylic acid obtained by heating isatin with malonic acid and glacial acetic acid, first at 100°, then at 120°, was identified by conversion into the chloro-acid and the esters, the latter by direct means, using sulphuric acid. 5-Bromoisatin, prepared by adding bromine in glacial acetic acid to a boiling solution of isatin in the same solvent, yielded with malonic acid grey, insoluble, high melting 6-bromo-2-hydroxyquinoline-4-carboxylic acid, which was analysed as the *ethyl* ester,  $C_{12}H_{10}O_3NBr$ , colourless needles, decomp. about 220°. Similarly, 5:7-dibromoisatin formed 6:8-dibromo-2-hydroxyquinoline-4-carboxylic acid as a yellowish-white powder which did not melt.

*N*-Methylisatin was also condensed with malonic acid in glacial acetic acid, and the solution obtained was diluted and allowed to evaporate. The product, which was probably *o*-methylaminophenyl-fumaric acid,  $C_{11}H_{11}O_4N$ , formed colourless crystals, m. p. 163–164°, and the *monomethyl* ester crystallised from ether in colourless prisms, m. p. 131–132°.

Experiments have already been commenced with the aim of condensing *N*-methylisatins with acetophenone to 2-phenylcinchonic acid alkyl haloids, but the only products which have been isolated as yet are apparently compounds with two molecules of the ketone through the loss of two molecules of water. Thus *N*-methylisatin was dissolved in 33% potassium hydroxide and heated with alcoholic acetophenone for two days, when the solution was diluted and the concentrated filtrate from neutral substances was acidified. A small amount of an acid,  $C_{25}H_{21}O_3N$ , was obtained as a blood-red, crystalline powder, m. p. 240–242° (decomp.). Similarly, 5-bromo-*N*-methylisatin,  $C_9H_6O_2NBr$ , slender, red needles, m. p. 172–173°, obtained by direct bromination or methylation with methyl sulphate, formed a red acid,  $C_{25}H_{30}O_3NBr$ , m. p. 253–254°. J. C. W.

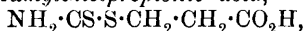
**Preparation by Catalysis of Decahydroquinoline and 2-Methyldecahydroquinoline.** PAUL SABATIER and M. MURAT (*Compt. rend.*, 1914, 158, 309–311. Compare Ipatiev, A., 1908, i, 332).—By bubbling hydrogen through quinoline at 100° and passing

the issuing gas on to very active nickel at 130—140° a good yield of decahydroquinoline, b. p. 204—207°, is obtained. 2-Methylquinoline can be similarly hydrogenated using active nickel at 180°, and gives 2-methyldecahydroquinoline,  $C_{10}H_{19}N$ , a colourless liquid, b. p. 216°/752 mm.,  $D_4^{20}$  0.9489,  $D_4^{20}$  0.9308,  $n_D^{20}$  1.497. It is soluble in water, alcohol and ether, and like decahydroquinoline it turns litmus blue, fumes in air, and fixes carbon dioxide, giving a solid carbonate. The following derivatives have been prepared: *hydrochloride*, a very deliquescent, crystalline powder, m. p. 284°; *platinichloride*, deliquescent, brown crystals; *acid oxalate*, colourless, deliquescent needles; *dichromate*, greenish-yellow; *picrate*, yellow plates, m. p. 134°; *methiodide*, m. p. 230°; *phenylurethane*, a white, crystalline powder, m. p. 148°. W. G.

**Preparation of Hydroxyanthrapyridones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 268793).—Chloroanthrapyridones, in which the chlorine is contained in the pyridone ring, when treated with alkali hydroxides yield hydroxyanthrapyridones. *Hydroxy N-methylantrapyridone*, yellow needles, m. p. 280°, is obtained by boiling an alcoholic solution of chloro-*N*-methylantrapyridone with alcoholic potassium hydroxide or by heating the chloro-derivative with aqueous potassium hydroxide in an autoclave. Similarly, 4-bromohydroxy-1-*N*-methylantrapyridone, *hydroxy-1-N-p-tolylantrapyridone*, and *hydroxyanthrapyridone* are obtained from the corresponding chloro-derivatives. Dichlorodi-*N*-methylantradiipyridone also yields the corresponding hydroxypyridone derivative. J. C. C.

**Propiorhodanines.** BROR HOLMBERG (*Ber.*, 1914, 47, 159—165).—Some condensations of  $\beta$ -iodopropionic acid with dithiocarbamates, ammonium thiocarbamate, and potassium trithiocarbonate are described.

A solution of sodium  $\beta$ -iodopropionate was left with ammonium dithiocarbamate for twelve hours, then acidified with hydrochloric acid, when  $\beta$ -thiocarbamylthiolpropionic acid,

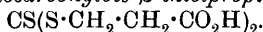


was precipitated. It crystallised in very pale yellow tablets, m. p. about 125°, but was not purified. A different product was obtained by leaving the mixture for two days, namely, thiocarbonylbis- $\beta$ -thiolpropionic acid (see below). Unlike thiocarbamylthiolacetic acid (*A.*, 1909, i, 286), the above lactic acid was not dehydrated by boiling in aqueous solution, but required acetic anhydride. The

product, *propiorhodanine*,  $S < \begin{array}{c} CS \\ \text{CH}_2 \cdot CH_2 \cdot \text{CO} \end{array} \text{NH}$ , crystallised in long, yellow prisms, m. p. 120—121°. Aniline, carbon disulphide, and aqueous potassium hydroxide were stirred together, and the filtrate from diphenylthiocarbamide was left with sodium  $\beta$ -iodopropionate for two days. Acetic acid precipitated  $\beta$ -thiocarbonylbispropionic acid,  $C_{10}H_{11}O_2NS_2$ , which crystallised from alcohol in small, colourless prisms, m. p. 153—154°. Acetic anhydride dehydrated it to *N-phenylpropiorhodanine*,  $C_{10}H_9ONS_2$ , which formed yellow, prismatic

needles, m. p. 173—173.5°. It did not react with benzaldehyde, but it combined with alcohol, forming 2-thiol-2-ethoxy-5-phenylpenthiarolid-4-one,  $\text{CO} \begin{array}{c} \text{NPh} \text{---} \text{C}(\text{SH}) \cdot \text{OEt} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{S} \end{array}$ , in shining, colourless, short prisms, m. p. 85—85.5°.

Ammonium thiocarbamate and sodium  $\beta$ -iodopropionate were left for a day and then acidified, when Langlet's carbamyl- $\beta$ -thiolpropionic acid (A., 1892, i, 440) was gradually deposited. A solution of potassium trithiocarbonate, obtained by shaking potassium sulphide with carbon disulphide, was also left with sodium  $\beta$ -iodopropionate and converted into thiocarbonylbis- $\beta$ -thiolpropionic acid,



This forms thin, golden-yellow leaflets, m. p. 109.5—110°, and behaves like the corresponding trithiocarbodiglycollic acid (A., 1905, i, 323) on heating in neutral, alkaline or ammoniacal solution, but it is decomposed by aniline into  $\beta$ -thiolpropionic acid and diphenylthiocarbamide and not into phenylpropiorhodanine. The barium salt forms yellow, prismatic needles, with 4H<sub>2</sub>O. J. C. W.,

[Preparation of Derivatives of *p*-Phenylenediaminesulphonic Acid.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 268794. Compare this vol., i, 88).—Instead of condensing *p*-aminodiphenylaminesulphonic acids with 4-chloro-1:3-dinitrobenzene, aminophenylnaphthylaminesulphonic acids or their derivatives may be condensed to give similar products. 5-*op*-Dinitroamolino-2- $\beta$ -naphthylaminobenzenesulphonic acid,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , is prepared in this way from sodium *p*-aminophenylnaphthylamine *o*-sulphonate. J. C. C.

Action of Sodium Peroxide on Benzidine in the Presence of Ethyl Alcohol. G. ROSSI (*Gazzetta*, 1913, 43, ii, 671—673).—When a boiling alcoholic solution of benzidine is cautiously treated (explosions may occur) with sodium peroxide, glyoxime *N*-phenyl ether,  $\text{NPh} \begin{array}{c} \text{O} \text{---} \text{CH} \cdot \text{CH} \text{---} \text{O} \\ \text{NPh} \end{array}$ , is produced; the substance has already been obtained in various other ways. R. V. S.

Phototropy of Hydrazones. F. BOVINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 460—465).—In this paper a number of hydrazones derived from acetophenone and benzophenone are described. Some of them are already known; none is phototropic.

Acetophenone-*p*-tolylhydrazone,  $\text{CMePh} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms colourless needles, m. p. 122°.

Benzophenone-*p*-tolylhydrazone,  $\text{CPh}_2 \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , crystallises in pale yellow prisms, m. p. 90°.

Benzophenone- $\beta$ -naphthylhydrazone,  $\text{CPh}_2 \cdot \text{N} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , forms colourless crystals, m. p. 159.5—160.5°.

Benzophenonephenylmethyllhydrazone,  $\text{CPh}_2 \cdot \text{N} \cdot \text{NMePh}$ , forms yellow crystals, m. p. 81—82°.

Benzophenonephenylbenzylhydrazone,  $\text{CPh}_2 \cdot \text{N} \cdot \text{NPh} \cdot \text{CH}_2\text{Ph}$ , crystallises in pale yellow scales, m. p. 105—106°.

R. V. S.

**Phototropy.** F. BOVINI and F. GRAZIANI (*Gazzetta*, 1913, **43**, ii, 674—692).—In this paper are described a large number of hydrazones derived from diphenyl-, ditolyl-, phenylmethyl-, phenylbenzyl-, and phenyl- $\beta$ -naphthyl-hydrazines; none of them is phototropic. Of them, the following have not been prepared previously.

*Anisaldehydediphenylhydrazone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}_2$ , has m. p.  $76^\circ$ .

*Benzaldehyde-p-ditolylhydrazone*,  $\text{CHPh}\cdot\text{N}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})_2$ , forms small, yellow prisms, m. p.  $99^\circ$ .

*Anisaldehyde-p-ditolylhydrazone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})_2$ , forms slightly yellow, flattened needles, m. p.  $128^\circ$ .

*Cuminaldehyde-p-ditolylhydrazone*,  $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}\cdot\text{N}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})_2$ , crystallises in long, silky needles, m. p.  $104^\circ$ .

*Cinnamaldehyde-p-ditolylhydrazone*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})_2$ , forms deep yellow, flattened needles, m. p.  $143^\circ$ .

*Salicylaldehyde-p-ditolylhydrazone*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})_2$ , is a greenish-yellow, crystalline powder, m. p.  $126^\circ$ .

*Piperonaldehyde-p-ditolylhydrazone*,  
 $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{N}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})_2$ ,  
 crystallises in colourless leaflets, m. p.  $134^\circ$ .

*Cuminaldehydophenylmethylhydrazone*,  $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}\cdot\text{N}\cdot\text{NMePh}$ , forms slightly yellow needles, m. p.  $54^\circ$ .

*Cinnamaldehydophenylmethylhydrazone*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{NMePh}$ , crystallises in minute, deep yellow needles, m. p.  $114^\circ$ .

*p-Tolualdehydophenylmethylhydrazone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{N}\cdot\text{NMePh}$ , forms greenish-yellow leaflets, m. p.  $122^\circ$ .

*Vanillinphenylmethylhydrazone*,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}\cdot\text{N}\cdot\text{NMePh}$ , forms colourless needles, m. p.  $122^\circ$ .

*Cinnamaldehydophenylbenzylhydrazone*,  
 $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}\cdot\text{CH}_2\text{Ph}$ ,  
 is a lemon-yellow, crystalline powder, m. p.  $167$ — $168^\circ$ .

*Piperonaldehydophenylbenzylhydrazone*,  
 $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}\cdot\text{CH}_2\text{Ph}$ ,  
 forms slightly yellow needles, m. p.  $124^\circ$ .

*p-Tolualdehydophenylbenzylhydrazone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}\cdot\text{CH}_2\text{Ph}$ , crystallises in silky needles, m. p.  $123$ — $124^\circ$ .

*Phenyl- $\beta$ -naphthylhydrazine* can be prepared by reducing with zinc and acetic acid the corresponding nitrosoamine described by Streiff (A., 1881, 176).

*Benzaldehydophenyl- $\beta$ -naphthylhydrazone*,  $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{C}_{10}\text{H}_7$ , forms yellow needles, m. p.  $92$ — $93^\circ$ .

*Anisaldehydophenyl- $\beta$ -naphthylhydrazone*,  
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}\cdot\text{C}_{10}\text{H}_7$ ,  
 forms large, prismatic needles, m. p.  $116$ — $117^\circ$ .

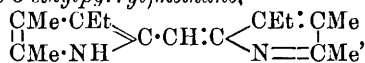
*Cuminaldehydophenyl- $\beta$ -naphthylhydrazone*,  
 $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}\cdot\text{C}_{10}\text{H}_7$ ,  
 forms small needles, m. p.  $118^\circ$ .

*Cinnamaldehydophenyl- $\beta$ -naphthylhydrazone*,  
 $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}\cdot\text{C}_{10}\text{H}_7$ ,  
 forms minute, pale yellow, acicular crystals, m. p.  $156^\circ$ .

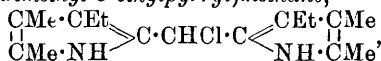
*p*-Tolualdehydphenyl- $\beta$ -naphthylhydrazone forms yellow, acicular crystals, m. p.  $154^{\circ}$ . R. V. S.

**Constitution of the Colouring Matter of Blood. Coloured Dipyrromethane Derivatives.** O. PILOTY, J. STOCK, and E. DORMANN (*Ber.*, 1914, 47, 400—406).—The colour of the following substances, like that of dehydrobilic acid (Piloty and Thannhauser, A., 1912, i, 925), is due possibly to the presence of a system of conjugated double linkings.

*Di*(4 : 5-dimethyl-3-ethylpyrrolyl)methane,

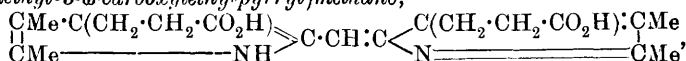


m. p.  $99.5$ — $100^{\circ}$ , brown, rhombic leaflets with a bronze lustre (*hydrochloride*,  $\text{C}_{17}\text{H}_{25}\text{N}_2\text{Cl}$ , m. p. about  $206^{\circ}$ , long, green, prismatic leaflets), and *chlorodi*(4 : 5-dimethyl-3-ethylpyrrolyl)methane,



yellow, felted needles subliming almost without decomposition, are produced by gently warming hæmopyrrole-*b*, chloroform, alcohol, and aqueous potassium hydroxide (1 : 1), and are separated by means of the insolubility of the hydrochloride of the former in cold dilute hydrochloric acid.

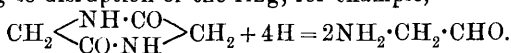
By a similar reaction, phonopyrrolecarboxylic acid-*a* yields *di*(4 : 5-dimethyl-3- $\omega$ -carboxylethylpyrrolyl)methane,



m. p.  $240^{\circ}$ , red prisms with a faintly green lustre, which forms a *hydrochloride*,  $\text{C}_{19}\text{H}_{25}\text{O}_4\text{N}_2\text{Cl}$ , decomp. about  $215^{\circ}$ , brick-red, prismatic needles with a green lustre.

The absorption spectra of the preceding coloured substances present some similarity to that of bilirubin, but none to that of the colouring matter of blood. C. S.

**Fission of the Diketopiperazine Ring by Electrolytic Reduction.** GEO. W. HEIMROD (*Ber.*, 1914, 47, 338—350).—The author has studied the electrolytic reduction of glycine anhydride and similar substances, and finds that amino-aldehydes are thereby produced owing to disruption of the ring, for example,



Since, in general, the  $-\text{CO} \cdot \text{NH}-$  group is electrolytically reduced to the group  $-\text{CH}_2 \cdot \text{NH}_2$ , he is led to discuss the possibility that the constitution of diketopiperazine may be more correctly represented by the formula  $\text{CH}_2 \begin{array}{c} \diagup \text{NH} \\ \diagdown \text{CO} \end{array} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{NH} \end{array} \text{CH}_2$ , or that in solution an equilibrium may exist between this form and that usually assumed.

A solution of glycine anhydride in hydrochloric or sulphuric acid is scarcely reduced by sodium amalgam. Aluminium amalgam is also without effect.

Electrolytic reduction is effected in a divided cell, the anode



(platinum, lead or Acheson graphite) being immersed in a porous pot. Cathodes of platinum, platinised platinum, copper, silver, gold, lead, cadmium, palladium, and mercury have been tried, but, of these, only the last mentioned gave useful results. Considerable irregularities have been encountered which can only be avoided by a most careful purification of the metal from grease. The cathode solution consists partly of a suspension, partly of a solution of the anhydride in sulphuric or hydrochloric acid, and, as a result of a large number of experiments, 2*N*-hydrochloric acid is found to yield the most satisfactory results. Even in this case, the current yields are very poor and the excess voltage required is high. The temperature is maintained at  $-5^{\circ}$  to  $0^{\circ}$ .

The solution obtained by the reduction of glycine anhydride, after concentration and treatment with phenylhydrazine and acetic acid, yields the osazone of  $\alpha$ -aminoacetaldehyde, m. p.  $175.5^{\circ}$ ; Neuberg (A., 1908, i, 323) gives  $176^{\circ}$ .

Glycine alanine anhydride,  $\text{CHMe} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CH}_2$ , gives a solution which readily reduces ammoniacal silver oxide and Fehling's solution and yields an osazone. An attempt to purify the latter was not made, since it probably consists of a mixture of the osazones of aminoacetaldehyde and  $\alpha$ -aminopropaldehyde.

Alanine anhydride (compare Fischer, A., 1906, i, 145) is prepared by the condensation of  $\alpha$ -bromopropionyl bromide with alanine and esterification of the product with alcohol and hydrogen chloride. *Ethyl bromopropionylaminopropionate* so obtained crystallises in long needles, m. p.  $139^{\circ}$ , and is converted by alcoholic ammonia at  $100^{\circ}$  into alanine anhydride. On reduction and treatment with phenylhydrazine it yields the osazone of methylglyoxal, m. p.  $154.8^{\circ}$ , for which Nef (A., 1905, i, 2) gives m. p.  $149-154^{\circ}$ .

C-Phenylglycine anhydride is ill-adapted for electrolytic reduction on account of its practical insolubility in water and dilute acids. An attempt to isolate the osazone was not made, but the solution was found to reduce ammoniacal silver oxide and Fehling's solution.

Sarcosine anhydride,  $\text{CH}_2 \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix} \text{CH}_2$ , is prepared in the following manner: A 40% solution of formaldehyde (1.5 mols.) is allowed to react with molecular quantities of potassium cyanide and methylamine hydrochloride. The nitrile formed is extracted with ether and hydrolysed with concentrated hydrochloric acid. The solution is evaporated in a vacuum, treated with barium hydroxide, and excess of the latter removed by carbon dioxide. The filtered solution is evaporated to dryness and the sarcosine extracted with absolute alcohol and converted into the anhydride by heating at  $215-220^{\circ}$ . On reduction and subsequent treatment in the usual manner, an osazone, m. p.  $168-175^{\circ}$ , is obtained, which is apparently identical with that obtained from glycine anhydride. H. W.

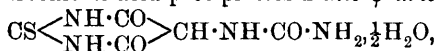
**Pyrimidines. LXVI. The Formation of Pyrimidines from Ethyl Aminomalonate and Aminomalononitrile.** TREAT B. JOHNSON and BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1914, 36, 345-355. Compare Johnson, this vol., i, 366).—As

an outcome of the recent paper in which it was suggested (*loc. cit.*) that the purines in plants may be formed from pyrimidines of the barbituric acid series, such as dialuric acid and uramil, the authors consider the possibility that hydrogen cyanide may be the parent substance from which these are derived. It is already known that hydrogen cyanide can polymerise to aminomalononitrile (compare Bamberger and Rudolf, A., 1902, i, 364), and the results now published show that it is possible to convert this into pyrimidine substances.

Ethyl aminomalonate was prepared by reducing ethyl nitrosomalonate with hydrogen sulphide in the presence of an equimolecular amount of potassium hydroxide, the process being less troublesome than reduction with aluminium amalgam (compare Piloty and Neresheimer, A., 1906, i, 146); ethyl nitromalonate resisted reduction in this manner. When ethyl aminomalonate, which is isolated as the hydrochloride, is shaken with an aqueous solution of sodium hydrogen carbonate and a benzene solution of ethyl chloroformate, *ethyl carbethoxyaminomalonate*,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , is obtained in colourless needles, m. p.  $63^\circ$ .

The ester condenses also with ethyl benzoyldithiocarbamate in alcoholic solution, giving *ethyl benzoylthiocarbamidomalonate*,  $\text{NHBz}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , rectangular plates, m. p.  $123^\circ$ .

With thiocarbamide in alcoholic solution containing sodium ethoxide, ethyl aminomalonate reacts in the usual manner of malonic esters, condensing to *2-thiouramil*,  $\text{CS}\langle\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\rangle\text{CH}\cdot\text{NH}_2$ , a yellow powder which is unaltered at  $300^\circ$ . When warmed in aqueous solution with potassium cyanate, this thiouramil undergoes condensation, and the addition of hydrochloric acid precipitates *2-thio- $\psi$ -uric acid*,

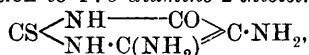


a practically colourless, crystalline powder which on loss of its water of crystallisation becomes deep purple; it decomposes above  $300^\circ$ . The anhydrous substance gives a deep green solution in alkali, the colour being changed to red by acetic acid and destroyed by hydrochloric acid which precipitates the substance. It was not found possible to cause this substance to pass into thiouric acid.

Ethyl nitrosomalonate condenses with thiocarbamide in alcoholic solution containing sodium ethoxide, with formation of *2-thiovioluric acid*,  $\text{CS}\langle\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\rangle\text{C}\cdot\text{NOH}$ , a yellow powder which does not melt below  $300^\circ$ .

Potassium cyanate in concentrated aqueous solution immediately condenses with the hydrochloride of ethyl aminomalonate, giving *ethyl carbamidomalonate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , octahedral crystals, m. p.  $173^\circ$ , which did not condense further with carbamide to give  $\psi$ -uric acid.

A mixture of aminomalononitrile and thiocarbamide in alcoholic solution containing sodium ethoxide, when heated for several hours undergoes condensation to 4 : 5-diamino-2-thiotetrahydro-6-pyrimidone,

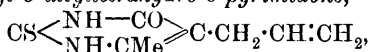


a colourless substance which decomposed when heated.

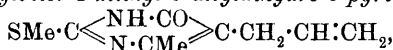
D. F. T.

**Researches on Pyrimidines. LXVII. The Condensation of Thiocarbamide with Ethyl Allylacetoacetate.** TREAT B. JOHNSON and ARTHUR J. HILL (*J. Amer. Chem. Soc.*, 1914, **36**, 364—372).—On account of the abnormal behaviour of ethyl allylmalonate, ethyl diallylmalonate, and ethyl benzylallylmalonate towards thiocarbamide (Johnson and Hill, A., 1911, i, 502) as compared with carbamide, the authors have chosen ethyl allylacetoacetate as a  $\beta$ -ketonic ester for an investigation of the behaviour towards thiocarbamide.

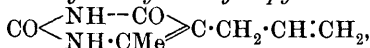
When heated with thiocarbamide in alcoholic solution containing sodium ethoxide for ten hours, ethyl allylacetoacetate is converted into 2-thio-4-methyl-5-allyltetrahydro-6-pyrimidone,



flat prisms, m. p. 187°; this substance reacts, in an alcoholic solution containing a molecular proportion of sodium ethoxide, with methyl iodide, producing 2-methylthiol-4-methyl-5-allyldihydro-6-pyrimidone,

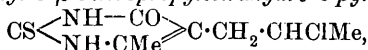


colourless, flat prisms, m. p. 189—191°. Both this methyl derivative and the parent thio-compound are hydrolysed by aqueous chloroacetic acid, giving 2:6-diketo-4-methyl-5-allyltetrahydropyrimidine,



barrel-shaped prisms, m. p. 218°. Heating with hydrochloric acid converts both the last-named substance and also 2-methylthiol-4-methyl-5-allyldihydro-6-pyrimidone into 2:6-diketo-4-methyl-5- $\beta$ -chloropropyltetrahydropyrimidine,

$\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CMe} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{CHClMe}$ , rosettes of minute prisms, m. p. 233° (decomp.), whilst 2-thio-4-methyl-5-allyldihydro-6-pyrimidone under similar but more prolonged treatment yields 2-thio-4-methyl-5- $\beta$ -chloropropyltetrahydro-6-pyrimidone,



ovate prisms, m. p. 218—220° (decomp.), without loss of sulphur.

The last product exhibits interesting behaviour when heated with an alcoholic solution of an equimolecular quantity of sodium ethoxide, forming a bridge between the 2 and 5 positions, the resulting substance,

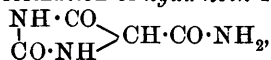
$\text{C} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \cdot \text{CHMe} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} \text{---} \text{CMe} \end{array} \text{C}$ , needles, m. p. 225—227°, being the first member

of a new class of pyrimidines, and the name 2:5-cyclopropylthiol-4-methyldihydro-6-pyrimidone is given. When heated with hydrochloric acid the bridge undergoes fission at the C-S bond with formation of the 2-thio-4-methyl-5- $\beta$ -chloropropyltetrahydro-6-pyrimidone described above.

By heating an aqueous solution of 2-ethylthioldihydro-6-pyrimidone and chloroacetic acid for an hour, uracil can be obtained. D. F. T.

**Researches on Hydantoins. XXVII. Synthesis of Hydantoin-4-carboxylamide.** TREAT B. JOHNSON and BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1914, **36**, 355—364).—Nitromalonamide (Ruhemann and Orton, T., 1895, 67, 1002), of which the

m. p. is said to vary between  $168^{\circ}$  and  $182^{\circ}$  with the rate of heating, was obtained by the gradual addition of finely divided malonamide to seven times its weight of fuming nitric acid (D 1.5—1.55) cooled in a freezing mixture. It was reduced by aluminium amalgam in ammoniacal aqueous solution, giving aminomalonalamide  $\text{NH}_2\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)_2$ , which when warmed with barium hydroxide solution is converted into barium aminomalonate, colourless prisms. By heating at  $100^{\circ}$  with 85% formic acid, aminomalonalamide gives the formyl derivative (compare Conrad and Schulze, A., 1909, i, 213), whilst treatment with ethyl chloroformate and alkali produces *carbethoxyaminomalonalamide*,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)_2$ , rosettes of colourless leaflets, m. p.  $178^{\circ}$ , which readily undergoes internal condensation in warm alkaline alcoholic solution with formation of *hydantoin-4-carboxylamide*



hexagonal prisms or thin plates, m. p.  $249^{\circ}$  (decomp.); this did not give rise to uric acid when heated with carbamide.

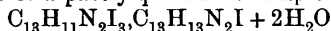
Aminomalonalamide reacts smoothly with cyanic acid in cold aqueous solution, giving *carbamidomalonalamide*  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)_2$ , prismatic needles, decomp. at  $200$ — $225^{\circ}$ , which when warmed at  $100^{\circ}$  with barium hydroxide solution is converted into the barium salt (with  $2\text{H}_2\text{O}$ ) of carbamidomalonic acid. When treated with ethyl acetyl-dithiocarbamate,  $\text{COMe}\cdot\text{NH}\cdot\text{CS}_2\text{Et}$ , aminomalonalamide yields *acetylthiocarbamidomalonalamide*,  $\text{NHAc}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)_2$ , fine needles, m. p.  $254^{\circ}$  (decomp.), which on hydrolysis with hydrochloric acid produces 2-thiohydantoin. Ethyl benzoylthioncarbamate,  $\text{NHBz}\cdot\text{CS}\cdot\text{OEt}$ , in a similar manner converts aminomalonalamide into *benzoyl-ethyl-ψ-carbamidomalonalamide*  $\text{NHBz}\cdot\text{C}(\text{OEt})\cdot\text{N}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)_2$ , colourless, hair-like needles, m. p.  $230$ — $240^{\circ}$  (decomp.). D. F. T.

**Chromoisomerism of Onium Compounds. Methylphenazonium Iodides.** I. F. KEHRMANN and A. DANECKI (*Ber.*, 1914, 47, 279—284).—This paper constitutes an initial reply to Hantzsch's criticisms (A., 1913, i, 393, 903; this vol., i, 91) on the authors' previous results (A., 1913, i, 298, 522, 1241).

The following methylphenazonium iodides have been prepared:

(I) The normal iodide,  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{I}$ , in dark brownish-red, flat needles or leaves showing steel-blue reflection.

(II) The periodide of a partly-quinonoid complex,



(or +  $\text{EtOH}$ ), which forms large, blackish-green needles with a bluish reflection, and is obtained only in presence of excess of hydrogen iodide from the holoquinonoid salt; one-half of the latter is reduced to the leuco-compound with liberation of 2 atoms of iodine, which combine with the non-reduced half to form the tri-iodide. These two iodides, (I) and (II), have been repeatedly prepared and analysed, and there is no doubt that they are neither chromo-isomeric nor even isomeric.

(III) The meriquinonoid iodide,  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{I}, \text{C}_{13}\text{H}_{13}\text{N}_2\text{I} + \text{H}_2\text{O}$ , which forms greyish-green crystals.

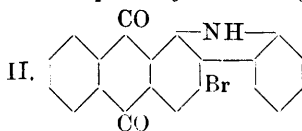
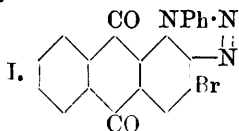
(IV) Various periodides, obtained by the action of iodine-potassium iodide solution on the normal iodide (I). T. H. P.

[Constitution of Benzoylhydrazicarbonyl.] R. STOLLÉ (*Ber.*, 1914, 47, 427).—Freund and Kuh proposed the dihydro-oxadiazole formula of benzoylhydrazicarbonyl in 1890, not Rupe and Gebhardt in 1899 as stated previously by the author (*A.*, 1913, i, 898).

C. S.

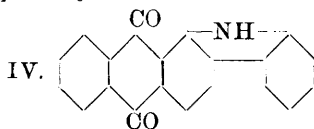
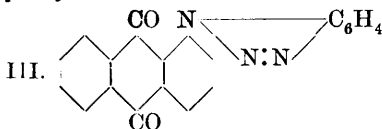
**Carbazoles of the Anthraquinone Series.** FRITZ ULLMANN and ERICH ILLGEN (*Ber.*, 1914, 47, 380—383).—Since the acridone derived from 1-aminoanthraquinone (*A.*, 1911, i, 489) is not sensitive towards alkalis as is the isomeride from 2-aminoanthraquinone (*A.*, 1911, i, 468), the authors have attempted the synthesis of carbazoles derived from the former base.

1:3-Dibromo-2-aminoanthraquinone was boiled with potassium acetate and aniline when a 97% yield of 3-bromo-2-amino-1-anilinoanthraquinone was obtained in long, dark red needles, m. p. 208° (corr.). It was treated with isoamyl nitrite in glacial acetic acid when the red solution became pale and, on cooling, deposited 3-bromo-N-phenyl-2:1-aziminoanthraquinone (I.) in yellow needles, m. p. 315—316° (corr.). This was gradually added to gently boiling diphenylamine and condensed to 4-bromo-1:2-phthaloylcarbazole (II.).



The latter forms brick-red, shining leaflets, m. p. 304° (corr.), gives a cornflower-blue solution in cold sulphuric acid which becomes violet on warming, and dyes cotton pale brown in the red, alkaline hyposulphite vat.

A new method for the preparation of azimines was investigated in the case of 1-chloroanthraquinone. This substance was boiled with aziminobenzene, potassium acetate and a little copper acetate in nitrobenzene, when 1-anthraquinonylbenzotriazole, III, was obtained in pale yellow leaflets, m. p. 269° (corr.), which were added to boiling diphenylamine and converted into 1:2-phthaloylcarbazole, IV.



This compound forms brick-red needles, m. p. 255° (corr.), dyes cotton pale orange and colours sulphuric acid blue. J. C. W.

**Anomalous Solubility of Uric Acid (Colloidal Uric Acid).** F. GUDZENT (*Zeitsch. physiol. Chem.*, 1914, 89, 253—254).—An additional argument against the existence of a colloidal form of uric acid (compare Schade and Boden, *A.*, 1913, i, 404) is to be found in the fact that if solutions prepared according to the directions of these authors are subjected to ultrafiltration, no change can be detected in the amount of total nitrogen in them. R. V. S.

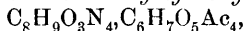
**Quadriurates.** W. E. RINGER (*Zeitsch. physiol. Chem.*, 1914, 89, 321—324).—Polemical. The author is in agreement with Kohler (this vol., i, 94) that chemical compounds having the composition of quadriurates do not exist, but points out that his view was, and is, that such quadriurates exist as solid solutions. R. V. S.

**Synthetic Glucosides of the Purines.** EMIL FISCHER and BURCKHARDT HELFERICH (*Ber.*, 1914, 47, 210—235).—Several glucosides of the purines have been synthesised by the interaction of acetobromoglucose or allied compounds with the salts of the purines with the heavy metals, especially silver. The possibility of the formation of isomerides renders the purification of the tetra-acetylglucosides rather difficult and hydrolysis to the free glucosides without further decomposition into the purine and sugar also requires special precautions in many cases. Besides the difficulty of obtaining a suitable salt of uric acid, the isolation of a glucoside would be especially opposed by the above obstacles. The glucosides of hypoxanthine, xanthine, guanine, and adenine were prepared by indirect methods, from trichloropurine or dichloroadenine. It is expected that the combination of the purine-glucosides with phosphoric acid, and therefore the synthesis of nucleotides will soon be accomplished.

The silver salt of theophylline was boiled with acetobromoglucose in dry xylene for one minute, when *tetra-acetyltheophylline-d-glucoside*,  $C_7H_7O_2N_4 \cdot C_6H_7O_5Ac_4$ , was obtained in long, flat prisms by the addition of light petroleum to the filtrate. The compound seems to exhibit dimorphism, for it has m. p. 147—149° (corr.) when crystallised from alcohol and m. p. 168—170° (corr.) from water, although the two specimens have  $[\alpha]_D^{20} - 12.21^\circ$  and  $-12.36^\circ$  in acetylene tetrachloride respectively, and both yield the same theophylline-*d*-glucoside. The latter was prepared by saturating a methyl-alcoholic solution of the acetyl derivative with ammonia at 0°, when an ammonia compound of the glucoside crystallised, which was filtered and dissolved in methyl alcohol. The solution was evaporated in vacuum, and the *theophylline-d-glucoside* was obtained as a heavy powder consisting of rhombic plates, m. p. 278—280° (corr.). It crystallises with  $2H_2O$  from hot water, has a bitter taste and very powerful diuretic action, and does not reduce Fehling's solution. The dry substance has  $[\alpha]_D^{20} - 2.33^\circ$ ,  $-2.28^\circ$  in water, but  $+1.08^\circ$ ,  $1.09^\circ$  in *N*-hydrochloric acid. Neutralisation of the acid solution reverses the rotation, but the rotation of an alkaline solution gradually falls from  $-3.48^\circ$ , probably owing to disruption of the purine nucleus. The glucoside is readily hydrolysed by hot *N*-hydrochloric acid, but emulsin and yeast are without action. The dextrose residue is probably in position 7. In the same way the *galactoside*,  $[\alpha]_D^{20} + 23.4^\circ$ , and the *rhamnoside*,  $[\alpha]_D^{20} - 76.5^\circ$ , of theophylline have been prepared.

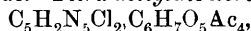
*Tetra-acetyltheobromine-d-glucoside*,  $C_7H_7O_2N_4 \cdot C_6H_7O_5Ac_4$ , forms colourless needles,  $[\alpha]_D^{20} - 18.42^\circ$  in acetylene tetrachloride, but is readily resolved into its components, even in hot water. For the hydrolysis with ammonia, great care was necessary, but *theobromine d-glucoside* was isolated in small, bitter prisms with  $1H_2O$ ,  $[\alpha]_D^{20} - 49.58^\circ$

(ten minutes after solution in water). It is gradually hydrolysed in water and, therefore, reduces Fehling's solution. *Tetra-acetylchlorotheophylline-d-glucoside*,  $C_7H_6O_2N_4Cl.C_6H_7O_5Ac_4$ , forms flat prisms, m. p. 166—167° (corr.),  $[\alpha]_D^{21} - 15.47^\circ$ ,  $- 15.95^\circ$  in toluene, and *chlorotheophylline-d-glucoside* crystallises with 1MeOH or 1H<sub>2</sub>O, in bitter prisms, m. p. 159° (corr.),  $[\alpha]_D^{20} + 18.88^\circ$ ,  $18.35^\circ$  in water, and does not reduce Fehling's solution. *Tetra-acetylhydroxycaffeine-d-glucoside*,



forms very slender needles, m. p. 235°,  $[\alpha]_D^{23} + 1.36^\circ$ ,  $1.81^\circ$  in acetylene tetrachloride, but it could not be hydrolysed without complete resolution into the components.

*Tetra-acetyltrichloropurine-d-glucoside*,  $C_5N_4Cl_3.C_6H_7O_5Ac_4$ , crystallises in long prisms, m. p. 168—169° (corr.),  $[\alpha]_D^{19} - 26.48^\circ$ ,  $[\alpha]_D^{20} - 26.02^\circ$  in acetylene tetrachloride. *Tetra acetyldichloroadenine-d-glucoside*,



forms pale yellow, curved needles, m. p. 213—215° (corr.),  $[\alpha]_D^{17} - 16.41^\circ$ ,  $- 16.52^\circ$  in acetylene tetrachloride, and is hydrolysed by ammonia to *dichloroadenine-d-glucoside*, which crystallises in very sparingly soluble, slender needles, m. p. 250° (corr.),  $[\alpha]_D^{20} + 8.3^\circ$ ,  $9.2^\circ$  in water. The latter was shaken with hydriodic acid and phosphonium iodide at 0°, when it formed a pale yellow solution. This was poured into ice water, treated with lead acetate, filtered, then silver nitrate was added to remove the remaining hydriodic acid, and finally, the solution of the lead salt was decomposed by hydrogen sulphide. The crude glucoside obtained on evaporating the filtrate was converted into the *picrate*, which formed long, yellow tablets, m. p. 250°. *Adenine-d-glucoside* was obtained in long, flat prisms, which melt at 210° with gas evolution, then crystallise, and melt finally at 275° (decomp.);  $[\alpha]_D^{19 \text{ or } 20} - 10.5^\circ$  in water,  $+ 5.67^\circ$  in *N*-hydrochloric acid. It has a slightly bitter taste, forms precipitates with phosphotungstic acid and silver nitrate, and is only slowly hydrolysed. It was treated with an excess of nitrous acid, and *hypoxanthine-d-glucoside* was isolated from the product, through the lead salt, in the form of long needles, m. p. 245°,  $[\alpha]_D^{20} - 34.5^\circ$  in *N*-sodium hydroxide,  $+ 12.92^\circ$  in *N*-hydrochloric acid.

Dichloroadenineglucoside was shaken with zinc dust and water in a sealed tube at 140°, and reduced to *chloroadenine-d-glucoside*,  $C_5H_3N_5Cl.C_6H_{11}O_5$ . The latter forms sparingly soluble sheaves of needles,  $[\alpha]_D^{20} - 7.66^\circ$ ,  $[\alpha]_D^{21} - 7.69^\circ$  in water. It was treated with nitrous acid, and the crude, syrupy chlorohypoxanthineglucoside was heated with alcoholic ammonia at 145—150°, when, by the intervention of the lead salt, a small amount of not quite pure *guanine-d-glucoside*,  $C_5H_4ON_5.C_6H_{11}O_5$ , was obtained in slender, glistening needles, m. p. 298° (corr.).

J. C. W.

**Transformation of Diphenyldibenzylidenehydrotetrazone into Dehydrobenzaldehydephenylhydrazone and into Benzil-osazone.** R. CIUSA and B. TOSCHI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 489—494).—The authors suggest a mechanism for this transformation and suggest that a similar explanation may apply to the reaction

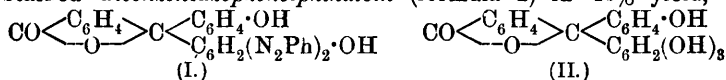
of diphenylamine with oxidising agents in sulphuric acid solution, to the benzidine and semidine transformations, and to others.

When the substance,  $C_{26}H_{20}O_4N_6$  (m. p. 236—238°), obtained from the nitroso-derivative of benzaldehyde-*p*-nitrophenylhydrazone (Bamberger and Pemsel, A., 1903, i, 285), is heated with benzoyl chloride at 130—135°, a substance,  $C_{40}H_{30}O_4N_6$ , m. p. 259°, is obtained; it is not a benzoyl derivative.

R. V. S.

**Constitution of Bisazophthaleins and of the Coloured Salts of Phenolphthalein.** P. SCHESTAKOV and TH. NOCKEN (*Ber.*, 1914, 47, 331—336).—Derivatives of the quinone form of phenolphthalein have not yet been obtained from the coloured solutions of phenolphthalein salts, since the reagents which have been used are those which react with the portions of the molecule which, by their change, determine the structure of the tautomeric form. Such derivatives are only to be expected when reagents are used which cause the substitution of hydrogen atoms in the quinone- or phenol-rings and do not react with the oxygen groups.

The authors have therefore investigated the action of benzenediazonium chloride on an alkaline solution of phenolphthalein, and have obtained *dibenzeneazophenolphthalein* (formula I) in 40% yield, the



constitution of which follows from its reduction to the corresponding diamino-compound and conversion of the latter into *pyrogallol-phenolphthalide* (formula II). It is therefore probable that the derivatives prepared by Oddo (A., 1913, i, 1111) from phenolphthalein and diazotised solutions of *p*-toluidine and *o*-nitroaniline respectively contain the substituents in the same ring, and not, as previously assumed, in different rings.

*Dibenzeneazophenolphthalein*, yellow, crystalline substance, m. p. 189—190°, is prepared by adding a diazotised solution of aniline (2 mols.) to a solution of phenolphthalein (1 mol.) in aqueous sodium hydroxide and subsequent acidification with hydrochloric acid. When reduced with sodium thiosulphate in alkaline solution or, better, with a slight excess of tin and hydrochloric acid, it gives diaminophenolphthalein (compare Gattermann and Bamberg, A., 1899, i, 514; Oddo, *loc. cit.*; Meyer and Hantzsch, A., 1907, i, 932), which, when diazotised and poured into a boiling aqueous solution of copper sulphate, yields pyrogallolphenolphthalide. The latter forms a yellowish-brown, hygroscopic mass, m. p. above 300°, and has not been isolated in the pure condition. Boiling acetic anhydride and sodium acetate convert it into a *tetra-acetyl* derivative, which separates from alcohol as a colourless mass, m. p. 84—86°, from aqueous alcohol in crystals, m. p. 145°.

H. W.

**Changes in the Physical Condition of Colloids. XVII. Optical Rotation of Protein Salts.** WOLFGANG PAULI, MAX SAMEC, and ERWIN STRAUSS (*Biochem. Zeitsch.*, 1914, 59, 470—495).—A salt-free solution of native protein, prepared by prolonged dialysis, undergoes no change of optical rotation on the addition of a neutral salt, or



of an acetate-acetic acid "buffer" mixture up to the isoelectric point. From the last fact it will be noticed that small changes in the condition of ionisation of the proteins have but little effect on the rotation, which is in marked contrast to the effects already observed on viscosity and precipitability by alcohol. On addition of acids, the rotation is increased up to a certain maximal point; addition of more acid (provided that not sufficient to cause proteolysis is added) causes no further change. This point of maximal rotation corresponds with that of maximal viscosity and minimal precipitability, or, as has already been shown, the point of maximal ionisation of the acid protein. The depression of the ionisation by addition of further acid affects the viscosity and precipitability, but not the rotation. This constant depends therefore on the formation of a protein acid salt, and is independent of the ionic dissociation of the latter. The general action of all acids is similar, but the amount of change in rotation produced by each individual acid varies, and depends on the character of the anion, and not on the strength of the acid. The order of action of the acids is hydrochloric > oxalic and monochloroacetic > sulphuric and trichloroacetic acids (the latter two about equal). There is a marked parallelism between the viscosity and rotation effects due to these acids.

Alkalis also cause increased rotation, and again there is a marked parallelism between rotation and viscosity changes produced. In this case, the amount of change produced depends on the strength of the alkali.

Addition of normal salts to acid proteins produces a depression of the rotation, and again there is a marked parallelism between viscosity and rotation changes. The change depends on the anion. In the case of the alkali proteins, no change is produced in the rotation by the salts of alkalis, whereas the salts of alkaline earths diminish the rotation. The anions here have little action. In all these reactions of normal salts there is a parallelism between the optical changes produced and the changes in the coagulation temperatures. These actions are possibly due to the production of salt complexes.

Caffeine and theophylline produce a marked increase in the rotation, just as they do in the viscosity of the proteins. These changes are apparently due to the formation of a complex of the protein with the purine base.

The action of acids on gelatin was also investigated, and it was found that whereas this protein undergoes the most marked changes in hydration (recognised by the water imbibition and viscosity), under influence of acids and alkalis its optical rotation is but little changed. This fact is ascribed to the presence of large quantities of the optically inactive glycine in gelatin. The authors discuss in some detail the causes of the change in rotation on formation of salts from neutral proteins, and call attention to the possible tautomerism in the molecule.

S. B. S.

**Historical Notes on Egg-albumin and Peptone Solutions.**  
L. BERCZELLER (*Kolloid. Zeitsch.*, 1914, 14, 1—2).—A reference to early discussions (1870) on the nature of the peptonisation process.

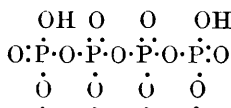
H. M. D.

**The Nucleo-protein (Hammarsten) from the Ox-pancreas.**

I. MARTIN KNOPF (*Zeitsch. physiol. Chem.*, 1914, 89, 170—174) — According to the analyses of other workers, the nucleo-protein separated from the pancreas by Hammarsten's method contains 4·5% of phosphorus. As guanylic acid contains 8·5% of phosphorus, the nucleo-protein in question should contain nearly 50% of guanylic acid, if this latter substance is the only phosphorus-containing component of the nucleo-protein. No observer has obtained more than 12% of guanylic acid from the nucleo-protein, and with the guanine estimations in the present research the figure was smaller; there are no grounds for believing that this is due to loss of material during the manipulations. It cannot therefore be doubted that the nucleo-protein contains other phosphorised constituents, and one was obtained of a very soluble nature in the mother liquor after removal of the potassium guanylate: it has not yet been obtained free from protein, but further work is in progress. W. D. H.

**The Partial Enzymatic Hydrolysis of Yeast Nucleic Acid.**

WALTER JONES and A. E. RICHARDS (*J. Biol. Chem.*, 1914, 17, 71—80) — Thymus-nucleic acid yields on hydrolysis phosphoric acid, guanine, adenine, cytosine, thymine, and a hexose. Yeast-nucleic acid yields the same except that uracil and pentose replace thymine and hexose respectively. The structure at the



base of the complex in both cases appears to be that annexed. Bang's discovery of guanylic acid in animal tissues (yielding phosphoric acid, guanine, and pentose only) was followed by the work of Levene and Jacobs, who showed that by

the loss of phosphoric acid, the crystalline compound guanosine (guanine + pentose) could be obtained. Guanylic acid is thus a mono-nucleotide, whereas the yeast acid is a tetra-nucleotide, the four oxygen atoms placed lowermost in the above formula being united respectively to the four basic groups. If cleavage took place vertically, four mono-nucleotides should be obtained, one of which would be guanylic acid. To obtain this acid from the yeast acid would therefore be a confirmation of Levene and Jacobs' view of its structure. The action of extract of pig's pancreas is variable according to the time it is kept at 40°, so that the enzymes in it are gradually destroyed, but the first action of the fresh extract is to split the yeast acid into two di-nucleotides, one of which contains guanine and cytosine, and the other adenine and uracil. Both of these compounds (each containing one purine and one pyrimidine base) were separated; the enzyme responsible for this cleavage is termed *tetra-nuclease*. Continued action of the extract decomposes the two di-nucleotides into their constituent mono-nucleotides (one of which is guanylic acid), and these in turn are converted into nucleosides (that is, base + pentose), from which the free bases are finally produced. The task set out upon was thus accomplished, but owing to the uncertainty of the condition of the enzymes in the extract, the final outcome is uncertain also, and only occasionally successful. There is, however, another method which has no element of chance in it at all, and that is to allow yeast to act on the

yeast-nucleic acid; guanylic acid is then always obtained as an end product, and it was thoroughly identified with Bang's acid.

W. D. H.

**The Changes in the Physical Condition of Colloids. XVI. Deaminogelatin.** LEOPOLD BLASEL and JOH. MATAJA (*Biochem. Zeitsch.*, 1914, 58, 417—450. Compare Pauli, A., 1913, i, 108).—The substance employed for these investigations was obtained from gelatin by treatment with nitrous acid according to Skraup's method. Its behaviour towards acids and alkalis was compared with that of the proteins, from which it differs chemically in that the terminal amino-groups have been removed. It was treated in solution with hydrochloric acid in varying concentrations, and the hydrogen and chlorine ion concentrations in various dilutions were measured. The results indicate a distinct amount of combination between the protein derivative and the acid, although the amount is less than in the case of the natural proteins. This fact is of interest in view of the absence of amino-groups. There is, however, a marked difference between the combination of deaminogelatin and of natural proteins with acids. In the case of the latter, there is a large increase in the viscosity of the solutions, with addition of small amounts of acids, which increases up to a maximum. Addition of acids beyond this maximum causes a diminution of viscosity. The point of maximum viscosity corresponds with the point of maximum difference between the amounts of combined hydrogen and chlorine ions. This is explained by Pauli by assuming the combination of the hydrochloric acid to form a chloride giving rise to protein and chlorine ions, the former of which give rise to the high viscosity of the solution. Addition of excess of mineral acid depresses the dissociation of the protein salt and diminishes the number of protein ions. A similar phenomenon as regards viscosity was not observed in the case of deaminogelatin. In the case of the latter substance however, the point of maximum difference between the bound hydrogen and chlorine ions corresponds with the point of minimal precipitability by phenol, as in the case with the natural proteins. The precipitability by phenol is increased by the addition of neutral salts, which depress the electrolytic dissociation of the salt.

The behaviour of deaminoglutin towards alkalis is similar in many respects to that of the natural proteins, the viscosity passing through a maximal point with addition of increasing amounts of alkali hydroxide, the maximal point again corresponding with the largest amounts of protein ions in solution. Electrometric measurements indicate a binding of the hydroxyl ions (namely, combination with hydrogen set free from the carboxyl group of the proteins by the alkali). There is in this case no maximal precipitation point for phenol, less and less precipitate being obtained as the amount of alkali is increased. The authors give an account of the precipitability of alkali deaminogelatin by phenol in the presence of salts. Here various minimal points can be observed, but the phenomena appear to be somewhat complex and are not yet explained in a satisfactory manner.

S. B. S.

**Cerebrosides of the Brain.** IV. and V. H. THIERFELDER (*Zeitsch. physiol. Chem.*, 1914, 89, 236—248, 247—250. Compare A., 1913, i, 747).—IV. This paper deals with the more readily soluble portions of the mixture previously mentioned (*loc. cit.*), after the cerebrone and kersin fractions have been removed. By fractionations with various solvents it is possible to isolate from it a substance free from sugar as well as products containing sugar (cerebrosides closely related to cerebrone and kersin). The substance which contains no sugar begins to melt above 80°, and has  $[\alpha]_D^{20} = 3.38^\circ$  (in 8% solution in chloroform and methyl alcohol), and contains about 77% C, 12.5% H, and 2.3% N. Acid hydrolysis yielded sphingosine sulphate, dimethylsphingosine sulphate, sugar derived from admixed cerebroside, and kersinic acid (compare *loc. cit.*). Acetylation yields an *acetyl* derivative, m. p. 104°. The substance is probably a compound of sphingosine with kersinic acid or a mixture of compounds of sphingosine with various fatty acids similar to kersinic acid.

V. A *hexa-acetylcerebrone* can be obtained from crystalline cerebrone with acetic anhydride and sodium acetate. It becomes damp at 31°, and is quite liquid at 40—41°;  $[\alpha]_D^{20} = 3^\circ$  (in 10.1% solution in chloroform and methyl alcohol). A *penta-acetylkersin* can be obtained in the same way. A summary is given of the conclusions which can be drawn as to the constitution of cerebrone and the cerebrosides in view of the results hitherto obtained by the author. R. V. S.

**Nomenclature of Enzymes.** EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1914, 38, 81. Compare A., 1903, i, 304).—The author points out that considerable confusion is caused by the arbitrary system of nomenclature adopted for enzymes, and that a rigid system is impossible so long as the name is derived from one word. He proposes to compound the name from two words, the first of which indicates the substance acted on, the second the sole or most characteristic product formed. Thus, amyloglycase yields glucose from starch, amyломaltase gives maltose from starch, lactoglycase forms glucose (and galactose) from lactose. H. W.

**Chemical Constitution of Invertase.** I. J. M. NELSON and SIDNEY BORN (*J. Amer. Chem. Soc.*, 1914, 36, 393—403).—The results of this investigation generally confirm those of O'Sullivan and Tompson (*T.*, 1890, 57, 834).

The invertase was obtained by the autolysis of 91 kilos of pressed yeast, the 22—27 litres of liquid obtained being treated with alcohol and the precipitate purified by several stages, including re-solution and re-precipitation, and finally ending with dialysis and re-precipitation. The yield of purified invertase amounted to approximately 200 grams. The product was a colourless powder, which gave a slightly opalescent solution in water, and responded to the biuret, Millon, and xanthoproteic tests, although it gave no precipitate with phosphotungstic acid, mercuric acetate, or lead acetate. Its solutions did not coagulate on heating, and could not be salted out by magnesium, ammonium, or zinc sulphates. The average content of nitrogen,

phosphorus, and ash was 1.3, 0.3, and 0.9% respectively. The activity towards sucrose was  $\pm 0^\circ = 37$  mins. at  $37^\circ$  (see O'Sullivan and Tompson, *loc. cit.*)

The polysaccharide of the invertase (yeast gum) was separated from invertase solution by precipitation with Fehling's solution (Salkowski, A., 1900, i, 180); after purification by repeated re-precipitation by alcohol from aqueous solution, it was found to be free from nitrogen and ash, but to contain practically all the phosphorus originally present in the invertase.

The action of acetyl bromide and of acetic anhydride on invertase gave colourless, amorphous products of m. p.  $198^\circ$  (decomp.) and  $184\text{--}198^\circ$  (decomp.) and of acetyl values 44.4% and 42.5% respectively. The latter product, after hydrolysis, yielded a considerable quantity of mannosazone on treatment with phenylhydrazine acetate.

Although a 10% solution of invertase is not affected by the usual protein reagents, after hydrolysis with dilute sulphuric acid at  $100^\circ$  and neutralisation, copious precipitates are formed on addition of phosphotungstic acid, phosphomolybdic acid, or mercuric chloride, whilst the hydrolysed solution also gives a small amount of gelatinous precipitate on treating with a solution of ammonium, magnesium, or zinc sulphate. Evidently, therefore, the properties of the protein are effectually masked in the invertase itself.

The polysaccharide of invertase is unaffected by ptyalin, pancreatic amylase or castor bean lipase. D. F. T.

**Conditions of Action of the Salivary Diastase.** L. MICHAELIS and H. PECHSTEIN (*Biochem. Zeitsch.*, 1914, 59, 77—99).—In complete absence of salts, diastase is inactive. It forms double compounds with a large number of salts, each one of which has its own characteristic properties, which are due almost entirely to the anion. All such complexes possess diastatic properties, but differ from one another (a) in the affinity of the salt to the diastase, which will effect the completeness of the combination, (b) in the magnitude of its action on starch, or, in other words, the affinity of the salt-diastase compound for starch, (c) in the acid dissociation constant, and consequently in the isoelectric point and the  $[H^+]$  concentration of optimal activity. The diastase complexes are active in the form of their anions. As regards the affinity of diastase to salt, the latter can be divided into three classes: (1) nitrates with very great affinity, (2) chlorides and bromides with smaller, but still great, affinity, (3) sulphates, phosphates, and acetates with low affinity. As regards the action of the complexes on starch, they can be arranged in the following order: Chlorides, bromides > iodides, nitrates > sulphates, acetates and phosphates. These results are arrived at by investigating the action of salts separately and combined on the activity of dialysed saliva. The results in mixtures were not necessarily additive, as the addition of a salt of great affinity, yielding a less active diastatic complex, to a more active complex, formed from a salt of smaller affinity, would diminish the activity of the latter. The isoelectric point of all the complexes lies between  $10^{-5}$  and  $10^{-6}$ . It was not possible to determine this point with such accuracy as in the case of other ferments, as it varied

with the different complexes (for phosphate, acetate, sulphate,  $p_H = 6.1-6.2$ ; for chloride and bromide,  $6.7$ ; for nitrate,  $6.9$ ). The more acid, therefore, is the point of optimal action, the less the affinity of the anion for the diastase. S. B. S.

**The Emulsin-like Ferments.** L. ROSENTHALER (*Biochem. Zeitsch.*, 1914, 59, 498).—A reply to a criticism of Bayliss (this vol., i, 919), who ascribes to the author's so-called  $\sigma$ -emulsin the property of synthesising a glucoside. The author has only ascribed to the ferment thus designated the property of causing the formation of the cyanohydrin from benzaldehyde and hydrogen cyanide. S. B. S.

**The Esterase of Blood.** V. P. RONA and Z. BIEN (*Biochem. Zeitsch.*, 1914, 59, 100—112).—The point of optimal activity of the blood esterase of rabbits lies at about  $[H^+] = 10^{-8}$ , the anions of the ferment being the active agents. The acid dissociation constant is about  $10^{-6}$ . The esterase differs, therefore, from the lipase of the stomach and probably also that of the small intestine. The rate of activity on various esters varies, and is probably a function of the chemical constitution of the latter. S. B. S.

**I. Fermentation Equilibria. II. Division and Displacement in an Alcoholic Medium containing Dextrose and Two Glucosidases.** ÉM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1914, 158, 370—373; *J. Pharm. Chim.*, 1914, [vii], 9, 155—158).—In the action of  $\alpha$ -glucosidase on a solution of dextrose in dilute alcohol, the equilibrium is reached when the ratio of combined dextrose to free dextrose is as  $32.6 : 67.4$ . With  $\beta$ -glucosidase the ratio is  $23.39 : 76.61$ . If the two ferments are allowed to act simultaneously on the same solution of dextrose in alcohol, or if the second ferment is introduced after equilibrium has been reached with the first, the final equilibrium is reached when the amount of free dextrose bears respectively the above ratios to the two forms of combined dextrose, each ferment being without action on the glucoside synthesised by the other. W. G.

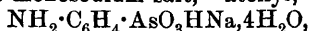
**The Effect of Acids and Alkalis upon the Catalase of Taka-diastase.** RAY E. NEIDIG (*J. Amer. Chem. Soc.*, 1914, 36, 417—429).—Euler (A., 1905, i, 400) has obtained results on the inhibition of various catalases by acids indicating that the catalases of various origin are not identical. The author is extending this examination to the catalase obtainable from lower fungi, and has selected commercial taka-diastase obtained from *Aspergillus oryzae* as especially suitable for this purpose.

The activity of the catalase was measured by the rate of decomposition induced in hydrogen peroxide. The results indicate that the inhibiting effect of acids and alkalis follows the order of their dissociation constants. Neutralisation of the solution after fifteen minutes contact with acid or alkali does not restore the original activity of the enzyme, whilst it is found that although with alkali hydroxides the effect is proportional to the period of contact, the time of contact with sulphuric or hydrochloric acid has little or no influence on the activity of the enzyme. D. F. T.

**"Glyoxalase" a Ferment which Converts Methylglyoxal into Lactic Acid.** H. D. DAKIN and H. W. DUDLEY (*Biochem. Zeitsch.*, 1914, 59, 193—194).—The authors claim priority over Neuberg for the discovery of this enzyme. They also state that the "glyoxalase" is not identical with aldehydemutase, and state reasons for maintaining their nomenclature, assigning the name glyoxalase to ferments which convert glyoxals into hydroxy-acids.

C. NEUBERG replies affirming his former conclusions. S. B. S.

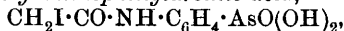
**Experiments on the Adherence of Arsenic Acid to the Aromatic Nucleus.** E. SCHMITZ (*Ber.*, 1914, 47, 363—370).—Although free arsanilic acid or an alkaline solution is stable towards heat, solutions of the monosodium salt, "atoxyl,"



cannot be sterilised without decomposition into arsenic acid. Solutions of arsanilic acid with various proportions of alkali have therefore been heated at 100°, or in an autoclave at 130°, and the amount of free arsenic acid estimated as magnesium pyroarsenate, the unchanged arsenic acid being precipitated by acid in a freezing mixture and the last traces removed as the resorcinol azo-dye. It was found that the replacement of the second hydrogen by an alkali metal, even lithium, gave stable solutions. Carbamide also stabilised the solutions of sodium arsanilate. The maximum instability was found in a solution containing sodium to arsanilic acid in the proportion 8 : 10, whereas complete stability was reached when the proportion was 15 : 10. That the amino-group also plays an active part was shown by the fact that the sodium salts of substituted amino-compounds (acetyl-, chloroacetyl-, benzoyl-derivatives, the carbamide, resorcinol azo-dye, phloroglucin-aldehyde compound and sodium acetanthranilarsinate) all gave stable solutions. The cause of the decomposition must therefore lie with some interaction between the amino-group and the second hydroxyl group of the arsenic acid residue. Perhaps a free hydrogen atom in the para-position is a criterion, for sodium *p*-phenolarsinate is also unstable, whereas the disodium salt, or sodium *p*-methoxyphenylarsinate, is stable. In arsanilic acid itself it may be that the formation of an inner salt neutralises the groups in question, for free *p*-phenolarsinic acid, in which this is impossible, is very unstable in solution.

J. C. W.

**Preparation of Acyl Derivatives of *p*-Aminophenylarsinic Acid.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 268983).—*p*-Iodoacetylaminophenylarsinic acid,



prepared by treating sodium *p*-aminophenylarsinate with iodoacetyl chloride or iodoacetic anhydride, forms white needles, m. p. 196° (decomp.). *p*-Iodopropionylaminophenylarsinic acid, white needles, m. p. 224° (decomp.), is similarly prepared from iodopropionyl chloride.

J. C. C.

**Aromatic Arsenic Compounds. V. *p*-Iodoso- and *p*-Iodoxyphenylarsinic Acid.** P. KARRER (*Ber.*, 1914, 47, 96—98. Compare A., 1913, i, 413; 1912, i, 740, 929).—*p*-Iodoso and *p*-iodoxy-phenyl-

arsinic acids can both be obtained directly or indirectly from *p*-iodophenylarsinic acid (Mameli and Patta, A., 1909, i, 543).

Chlorine is led into a cooled solution of *p*-iodophenylarsinic acid in acetic acid, when *phenylarsinic acid p-iodochloride*,  $\text{ICl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , crystallises. This is a yellow substance always giving an odour of chlorine. When treated cautiously in aqueous suspension with sodium hydroxide solution, it is converted into *p-iodosphenylarsinic acid*,  $\text{IO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ , a colourless, crystalline powder of marked oxidising power, which decomposes explosively when heated.

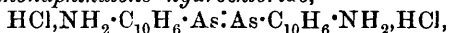
Oxidation of *p*-iodophenylarsinic acid or of *p*-iodosphenylarsinic acid in ice-cold *N*-sodium hydroxide solution by chlorine yields *p-iodoxyphenylarsinic acid*, as a colourless, granular solid. It is a stronger oxidising agent than the *p*-iodoso-compound.

*p*-Iodo-, *p*-iodoso-, and *p*-iodoxy-phenylarsinic acids have almost equal toxic effects on mice, but the two former, unlike the iodoxy-compound, affect mice with jaundice.

D. F. T.

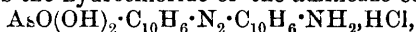
**Derivatives of Naphthylarsinic Acid.** N. ANDREEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1980—1985).—1-Nitronaphthyl-4-arsinic acid,  $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{AsO}(\text{OH})_2$ , obtained by nitrating  $\alpha$ -naphthylarsinic acid, forms pale yellow needles and is converted into  $\alpha$ -nitronaphthalene by heating with concentrated hydrochloric acid at  $120^\circ$ , into  $\alpha$ -naphthol by fusion with potassium hydroxide, and into 1:4-chloro-nitronaphthalene by treatment with phosphorus pentachloride. Just as with *m*-nitrophenylarsinic acid, the arsenic in 1-nitronaphthyl-4-arsinic acid is so stably connected with the naphthalene that it is not replaced by iodine and only slightly by bromine; on the other hand, the arsenic of *p*-nitrophenylarsinic acid is readily replaced by either bromine or iodine. Reduction of the nitronaphthylarsinic acid to the corresponding amino-derivative is rendered difficult by the ease with which the arsenic grouping undergoes reduction.

*Diaminoarsenonaphthalene hydrochloride*,



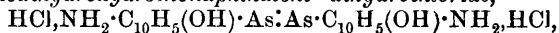
obtained by reducing 1-nitronaphthyl-4-arsinic acid in methyl-alcoholic solution by means of stannous chloride and hydrochloric acid, forms a fine, pale yellow precipitate, and both the hydrochloride and the free base readily oxidise in the air, especially if the latter is moist.

1-Aminonaphthyl-4-arsinic acid,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{AsO}(\text{OH})_2$ , is prepared by fusing  $\alpha$ -naphthylamine arsenate or, better, by heating a mixture of  $\alpha$ -naphthylamine and arsenic acid gradually to  $175^\circ$  (compare Adler and Adler, A., 1908, i, 492), the yield being very greatly diminished if traces of moisture are present. Diazotisation of the amino-acid yields the hydrochloride of the aminoazo-compound,



as a dark raspberry-red precipitate.

*Diaminodihydroxyarsenonaphthalene dihydrochloride*,

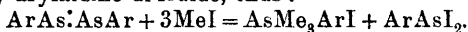


obtained by nitrating Adler and Adler's hydroxynaphthylarsonic acid (*loc. cit.*) and reducing the product by means of stannous chloride and hydrochloric acid, forms a fine, brownish-yellow powder.

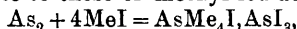
T. H. P.



**Splitting of Arseno-compounds by Methylation.** A. BERTHEIM (*Ber.*, 1914, **47**, 271—277).—The action of methyl iodide on arseno-compounds results in the formation of a quaternary arsonium iodide and a primary arylarsine diiodide, thus :



The tertiary aryltrimethylarsine,  $\text{AsMe}_3\text{Ar}$ , must be assumed to be an intermediate product, and the true addition, which represents a transformation from the primary to the quaternary series, extends only to one half of the molecule, which is resolved at the double linking. The reaction is intermediate to those of methyl iodide on arsenic,



and on the cacodyls,  $\text{AsR}_2 \cdot \text{AsR}_2 + 2\text{MeI} = \text{AsMe}_2\text{R}_2\text{I} + \text{AsR}_2\text{I}$  (compare Cahours, *Annalen*, 1862, **122**, 198, 206).

The yellow oily compounds obtained by Auger (A., 1904, i, 724) by the action of sodium hypophosphite and sulphuric acid on methyl- and ethyl-arsinic acid are similarly decomposed on methylation, and must, therefore, be regarded as arsenomethane, etc.

The actions of ethyl iodide and higher homologues on arseno-compounds are more complicated. When heated in a sealed tube at  $100^\circ$ , arsenobenzene and methyl iodide yield phenyltrimethylarsonium iodide, the corresponding periodide, and phenyldi-iodoarsine,  $\text{AsPhI}_2$ . Arsenobenzene and ethyl iodide give (1) iodoarsenobenzene, (2) a quaternary iodide, probably phenyltriethylarsonium iodide, (3) phenyldi-iodoarsine, and (4) a colourless oil of strong cacodyl-like odour, which is apparently a second or tertiary compound, or a mixture of these.

*p*-Arsenotoluene and methyl iodide yield *p*-tolyltrimethylarsonium iodide, m. p.  $274\text{--}275^\circ$  (frothing) (compare Michaelis, A., 1902, i, 411), and *p*-tolylarsenic oxide,  $\text{C}_7\text{H}_7 \cdot \text{AsO}$ .

*p*:*p'*-Di-iodoarsenobenzene and methyl iodide give (1) *p*-iodophenyltrimethylarsonium iodide,  $\text{C}_6\text{H}_4\text{I} \cdot \text{AsMe}_3\text{I}$ , which contracts considerably above  $285^\circ$ , and melts and boils at  $300^\circ$ , and (2) the corresponding substituted arsenic oxide.

*p*-Anisylarsinic acid, prepared by methylating hydroxyphenylarsinic acid, has m. p.  $179\text{--}180^\circ$ , but softens much below this temperature. Michaelis (A., 1902, i, 411) gave m. p.  $203^\circ$ .

*p*:*p'*-Dimethoxyarsenobenzene and methyl iodide yield (1) *p*-anisyltrimethylarsonium iodide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{AsMe}_3\text{I}$ , m. p.  $213^\circ$ , with previous softening, and (2) *p*-anisyl-di-iodoarsine.

T. H. P.

**Compounds of Chlorine, Bromine, and Iodine with Diaminodihydroxyarsenobenzene and Silver.** J. DANYSZ (*Compt. rend.*, 1914, **158**, 199—201).—The compounds referred to are obtained by adding drop by drop a solution of the silver haloid in aqueous potassium cyanide to a solution of diaminodihydroxyarsenobenzene hydrochloride until a permanent precipitate is just formed. This is just redissolved by addition of hydrochloric acid and the silver halogen compound is precipitated as its sulphate by addition of sulphuric acid. The last traces of potassium cyanide are removed by washing with a solution of potassium chloride. In the formation of these compounds

one molecule of the silver haloid reacts with one molecule of the arsenobenzene. The compounds obtained vary in colour from orange-yellow to deep brown, and the chloro-compound is less active as regards antiseptic and therapeutic properties than the iodo-, and still less so than the bromo-compound. The toxicity of the bromo-compound is almost the same as that of salvarsan itself, whilst its sterilising power *in vitro* and *in vivo* is much greater. W. G.

**Preparation of Arseno-metallic Derivatives Containing Noble Metals.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 268220, 268221).—Aqueous solutions of the salts of 3:3'-diamino-4:4'-dihydroxyarsenobenzene and of gold or the metals of the platinum group are mixed, whereby additive compounds are obtained in which the metal is not precipitated by the ordinary reagents. The compounds are separated by evaporation in a vacuum, or by precipitation with alcohol and ether, or alcohol and acetone.

The second patent describes similar compounds obtained from the sodium formaldehydesulphoxylate compound of 3:3'-diamino-4:4'-dihydroxyarsenobenzene, employing copper, silver, gold and platinum salts. J. C. C.

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## Physiological Chemistry.

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**Influence of Intravenous Infusions of Acids, Alkalis, and Neutral Salt Solutions on the Respiratory Exchanges.** ALFRED LEIMDÖRFER (*Biochem. Zeitsch.*, 1914, **59**, 451—469).—By means of the Zuntz-Geppert apparatus used with tracheotomised rabbits under urethane narcosis, the following results were obtained. Immediately after intravenous infusion of acid solutions, the exchange drops to below its normal value. A diminution also follows the injection of alkalis when their concentration reaches a certain percentage. Administration of a large amount of sodium chloride also causes a diminution of the oxydative processes. All these results appear to depend on some action of salts in the organism.  
S. B. S.

**Variations in the Gaseous Metabolism and Blood-Flow in the Human Lungs Due to the Respiratory Movements.** A. KROGH and J. LINDHARD (*Biochem. Zeitsch.*, 1914, **59** 260—280).—Gaseous metabolism of the lungs is subject to considerable variations. The oxygen intake, which should be nearly proportional to the blood-flow, is increased when breathing is chiefly diaphragmatic (up to 40%) during inspiration, and decreased during expiration. In costal respiration, on the other hand, the oxygen intake is increased during expiration. The controlling factor is here the variations in the abdominal pressure. Carbon dioxide

output increases steadily and strongly during expiration, as a consequence of the increased carbon dioxide tension in the alveolæ. The amount of carbon dioxide excreted increases with increased blood-flow, but only to a small extent (0.4:1). The amount excreted is larger during inspiration than during expiration. This is due to the fact that during expiration, carbon dioxide is stored in the lung tissue in amount corresponding with its increased tension, and is then given up again during inspiration. S. B. S.

**The Laws of Absorption of Carbon Monoxide by the Blood in vivo.** MAURICE NICLOUX (*Compt. rend.*, 1914, 158, 363—365).—The law of mass action applies to the absorption of carbon monoxide from a mixture of that gas and oxygen by blood *in vivo* just as *in vitro* (compare this vol., ii, 111). For a given mixture of carbon monoxide and air, which is not fatal, breathed by an animal, the carbon monoxide is fixed by the blood up to a certain limit, which cannot be passed. Oxygen displaces carbon monoxide from the blood, and thus this gas is the best antidote for carbon monoxide poisoning. W. G.

**The Protein Sugar of Blood Plasma.** HENRI BIERRY and ALBERT RANC (*Compt. rend.*, 1914, 158, 278—280. Compare A., 1913, i, 923; this vol., i, 218).—The "combined" sugar in the blood is found to occur in the protein constituents, being removed by reagents which precipitate protein. The ratio of combined sugar in arterial blood to that in venous blood is of the same order as that of their protein content. Fibrinogen, serum-globulin, and serum-albumin when prepared and purified yielded sugar on hydrolysis. The ratio of protein nitrogen to combined sugar in blood plasma varies with animals of different species, the variation being less important with animals of the same species. W. G.

**Detection of Free Amino-acids in Blood under Normal Conditions.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, 88, 478—483).—After the proteins had been completely removed from 50 litres of blood serum, it was found possible by precipitation with mercuric acetate to isolate a number of amino-acids, including proline, leucine, valine, alanine, glycine, aspartic acid, glutamic acid, arginine, lysine, and histidine. The identification was supported by analyses in many cases. The previous removal of protein (on the completeness of which the significance of the work depends) was effected by coagulation (under particular conditions) and also by dialysis. The experimental data will be published in a later paper. R. V. S.

**The Iron Content of Leucocytes and Lymphocytes.** S. SANEYOSHI (*Biochem. Zeitsch.*, 1914, 59, 339—346).—The iron content was determined in the following: Pus from rabbit (two samples, one fresh and one preserved in alcohol), pus from dog, cells from lymph glands, and thymus cells. In a large number of determinations the iron varied from 0.0943 to 0.1451<sup>o</sup>/<sub>100</sub>. There was no

marked difference found between the iron content of lymphocytes and leucocytes. S. B. S.

**The Physico-chemical Mechanism of Hæmolysis by Specific Hæmolysins.** UPENDRA NATH BRAHMACHARI (*Biochem. J.*, 1913, 7, 562—567).—Corpuscles, after treatment with a serum containing a specific amboceptor, in which the complement has been destroyed, are found to be more resistant to hæmolysis by water than normal corpuscles, or corpuscles which have been treated with a serum which does not contain a specific amboceptor. The explanation suggested is that the amboceptor fills in the pores between the molecules of the outer walls of the erythrocytes. It was found that there was no reduction in the volume of the corpuscles after treatment with amboceptor; the increased resistance is not due, therefore, to a reduction in the volume. S. B. S.

**Lipoproteins. III. The Hæmolytic Action of the Lipoproteins.** GUIDO IZAR and PAOLO FERRO (*Biochem. Zeitsch.*, 1914, 59, 238—243).—The various synthetic lipoproteins exert a hæmolytic action, which is inhibited by serum, cholesterol, lecithin (only slightly), and to a very small extent by calcium chloride. Boric acid, potassium oxalate, and saturated sodium chloride solutions exert no action on the inhibitory property of serum; the cholesterol inhibition is neutralised by boric acid and potassium oxalate, whilst the action of calcium chloride is increased by potassium oxalate and not affected by boric acid or salt solution. S. B. S.

**Lipoproteins. IV. The Behaviour of Blood-serum from Different Species of Animals.** GUIDO IZAR and PAOLO FERRO (*Biochem. Zeitsch.*, 1914, 59, 244—246).—The sera of ox, rabbit, dog or goat, after mixture with emulsions of the myristyl derivatives of peptone, edestin, elastin, histidine, and albumose (which have not been heated), exhibit somewhat larger changes in the stalagmometric measurements than are produced by the addition of the same emulsions to non-tumorous human sera. The changes produced by the sera of pigeons, sparrows, and fowls are still larger; by heating the latter sera with the emulsions for one hour at 50°, very little change in the surface tension is produced, whereas in the former series of sera a diminution in this constant is produced, a change not observed by a similar treatment of the lipoproteins and human non-tumorous sera. S. B. S.

**The Hæmolytic Action of Terpenes.** NOBUKICHI ISHIZAKA (*Arch. expt. Path. Pharm.*, 1914, 75, 194—229).—Comparisons between surface tension, solubility, capillary activity, and chemical constitution were made stalagmometrically for a series of terpene alcohols and ketones. Their degree of hæmolytic action depends on purely physical properties, namely, capillary activity, but also on chemical properties; the degree of saturation has no influence. Within certain limits, a diminished degree of saturation increases the solubility in water, and diminishes capillary and hæmolytic action.

Some of the substances investigated change the blood-pigment into methæmoglobin; this is especially the case for unsaturated compounds.

W. D. H.

**The Metabolism of Infants during Starvation. II.** ARTHUR SCHLOSSMANN and HANS MURSCHEHAUSER (*Biochem. Zeitsch.*, 1914, 58, 483—502. Compare A., 1913, i, 1407).—The authors give details of further metabolism experiments on one of the children used in the previous research during a preliminary period of feeding on a fixed diet (butter-milk, cream, and banana flour), during a succeeding period of starvation lasting for seventy-six hours, and during a final period with the same diet as in the preliminary period. They estimate the nitrogenous metabolism during these periods, the water exchanges, the excretion of acetone substances, and the respiratory exchanges. They thus obtain the data for estimating the basal metabolism during starvation (as the child exhibited few movements during the period in which the respiratory exchanges were measured), and determining the constituents of the body which supported the caloric needs of the organism when food was withheld. They compare their results with those of the former investigation, and confirm the statement there made, that the poorer the diet in proteins in the period before starvation, the less is the amount of body protein destroyed during starvation. A sparing diet before starvation protects the organism, therefore, during starvation.

S. B. S.

**The Value in Metabolism of Protein Cleavage Products Injected Intravenously. I.** C. OEHME (*Zeitsch. physiol. Chem.*, 1914, 89, 312—320).—A preliminary statement of an investigation on dogs in relation to the question of the nutrition value of "erepton," a commercial product containing 75% of formaldehyde-titratable nitrogen. The animals were in a state of inanition, or on a carbohydrate-fat diet. The injections were made slowly to avoid, so far as possible, toxic effects. The result was that the nitrogen of the injected material participates in metabolism, and that nitrogenous equilibrium can be maintained. So far, however, no evidence was obtained that the injected material protected the body-nitrogen from decomposition.

W. D. H.

**The Metabolism of Endogenous and Exogenous Purines in the Monkey.** ANDREW HUNTER and MAURICE H. GIVENS (*J. Biol. Chem.*, 1914, 17, 37—53).—A number of data are given in relation to the fate of certain purine derivatives given to monkeys subcutaneously or by the mouth. Many protocols are given in full, but no general conclusions are stated. The results confirm, and to some extent correct or amplify, conclusions previously published.

W. D. H.

**Comparative Value of Various Sugars in the Feeding of Infants.** CHAS. C. HASKELL (*Lilly Sci. Bull.*, 1914, 1, 136—150).—The results, which are mainly of clinical interest, indicate that the best feeding results were on a diet containing "malt-soup

extract." Next in order was lactose, followed by a mixture of dextrins with maltose. S. B. S.

**Effects of Nutrition with Maize. VI. Nutritive Value of Zein, Gliadin and Ovalbumin.** S. BAGLIONI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 721—728. Compare A, 1913, i, 214).—Nutrition experiments were made with albino rats, which were fed with zein, gliadin, or ovalbumin, the other constituents of the food being the same in the three cases. The balance of nitrogen and the weight and general condition of the animals were studied.

The results show that each of these three proteins is capable, not only of maintaining in equilibrium the balance of nitrogen in either adult or adolescent rats, but of leading to the formation of a reserve of nitrogen in the organism. When, however, ovalbumin is supplied, the animals keep or increase their weight, whilst with gliadin, and more especially with zein, constant diminution in weight occurs.

The conclusion is drawn that, owing to their chemical structures, zein and gliadin cannot completely replace animal proteins in the food of man and animals not adapted to their ingestion. These vegetable proteins seem to produce serious disturbance of the metabolism of the fats and carbohydrates, with the result that the assimilative processes undergo relative retardation. Such deleterious action is due to the lack or presence of certain amino-acid residues in the protein molecule. T. H. P.

**The Sulphur-content of the Cerebral Cortex in Normal and Demented Persons.** S. WOSKRESSENSKI (*Zeitsch. physiol. Chem.*, 1914, 89, 228—231).—In healthy persons, and in those who suffer from various forms of mental disease (seven cases), the mean percentage of sulphur in the cortex of the brain was 0.66. The variations are from 0.64 to 0.69. The increase of neutral sulphur in the urine noted in the urine in cases of psychosis can hardly be related to the sulphur in the brain, neither is there any relation between the latter and mental disease. W. D. H.

**The Effect of Chemical Products of Muscular Activity on the Frequency and Force of the Heart-beat.** M. S. PETERSEN and H. S. GASSER (*Amer. J. Physiol.*, 1914, 33, 301—312).—The effect of extracts of tetanised muscle on the isolated cat's heart is to cause an increase in the size of the heart beat, but not in the rate. W. D. H.

**The Action of Serum on the Perfused Heart of the Rabbit.** A. R. CUSHNY and J. A. GUNN (*J. Pharmacol. Expt. Ther.*, 1913, 5, 1—19).—The addition of serum to Ringer's solution, perfused through an excised rabbit's heart, first stimulates and then depresses the heart, and reduces the coronary flow. The latter is not due to increase of viscosity. Egg-albumin, starch, and even the animal's own serum or plasma have the same effect, which is

attributed, not to any special poison, but to an abnormal state of the heart induced by isolation and perfusion. W. D. H.

**The Sugar Consumption of the Surviving Heart.** P. RONA and G. G. WILENKO (*Biochem. Zeitsch.*, 1914, 59, 173—182).—The rabbit's heart, when perfused with sugar dissolved in Tyrode's solution, consumes more sugar than when perfused with Locke's fluid. The latter differs from the former chiefly in that it contains less sodium hydrogen carbonate. By reducing the concentration of this salt in Locke's solution, results were obtained similar to those got with Tyrode's solution. The authors draw the conclusion that the sugar consumption of the heart is markedly affected by relatively small changes in the hydrogen ion concentration. S. B. S.

**The Glycogen Content of the Liver after Diets of Proteins and their Degradation Products; the Functions of the Liver in the Utilisation of Proteins and Degradation Products.** ALFRED TSCHANEN (*Biochem. Zeitsch.*, 1914, 59, 202—224).—The effect of feeding rats on peptones, with addition only of small amounts of substance to render the diet palatable, is to make the liver free of glycogen. On addition of small amounts of carbohydrates to this diet, the liver stores up only very small amounts of glycogen. The inhibitory action of the peptones on the formation of glycogen can be counteracted only by relatively large amounts of carbohydrates and caseinogen. Peptones exert in the case of rats, as has already been observed in the case of dogs, an irritant action on the liver, causing an excretion of bile in the urine. In contrast to the peptones, meat, freed from carbohydrates, causes a formation of glycogen in the liver, which is, however, small in amount. Caseinogen, on the other hand, is a good glycogen former, although its degradation products exert an inhibitory action, which is not so great as that of peptone. Degradation products can be employed instead of the corresponding proteins in the maintenance of the organism, but these researches indicate that the liver functions in a different manner in the two diets. Alanine favours, whereas glutamic acid inhibits, the formation of glycogen in the liver.

S. B. S.

**Protein Storage in the Liver.** N. TICHMENEV (*Biochem. Zeitsch.*, 1914, 59, 326—332).—Mice were starved, and some were killed without feeding and served as controls, whilst others received a diet of meat for a few days after the period of starvation, and were then killed. The weights of the livers, the amount of nitrogenous matter precipitable by tannic acid, and also the nitrogen-phosphorus ratio in this precipitate in the two series of animals were estimated and compared. It was found that the fed animals showed (as compared with the controls) marked increase in the weights of the livers, in the proteins of these organs, and in the nitrogen-phosphorus ratio. The latter factor indicates, according to the author, an increase in the proteins, as apart from increase of cells, which latter phenomenon should be accompanied by increase of phos-



phorus (nucleoproteins). The conclusion drawn from these experiments is that protein feeding increases the proteins in the liver. The author discusses whether the increased proteins should be regarded as "reserve material" in the sense that glycogen and fats are. S. B. S.

**The Influence of Pregnancy and Castration on the Iodine and Phosphorus Metabolism of the Thyroid Gland.** FREDERIC FENGER (*J. Biol. Chem.*, 1914, 17, 23—28).—The thyroid of female animals shows greater functional activity than in the male, and is heavier in relation to body-weight and contains more iodine. It is not affected by pregnancy, but in males, castration leads to a diminution of thyroid tissue and a drop in iodine content. The phosphorus content is constant throughout. The iodine present occurs in a compound with a garlic-like odour. W. D. H.

**Estimation of Creatinine and Creatine in Muscle.** VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1914, 17, 65—69).—In order to estimate creatine and creatinine separately, it is necessary to remove proteins from the muscle extract. Heat must not be employed, and the removal is best accomplished by colloidal iron or alumina cream. Creatinine exists in small amount in fresh muscle (4 to 8 mg. per 100 grams); on autolysis, it increases uniformly at the expense of the creatine, until equilibrium is reached. Added creatine shares the same fate, but added creatinine inhibits the process, or in sufficient amount, reverses it. W. D. H.

**The Extractives of Muscle. IV.** TEMISTOCLE JONA (*Zeitsch. physiol. Chem.*, 1914, 89, 160—162. Compare A., 1913, i, 422).—From the extract previously described two further substances can be isolated. One of these is a *substance* which reduces ammoniacal silver solution, and has the composition and molecular weight required by the formula  $C_7H_{16}ON_2$ ; m. p.  $261^\circ$  (corr., decomp.),  $[\alpha]_D^{25} - 73.33^\circ$  (in 1.5% solution in 95% alcohol). The other *substance* is of similar appearance; it reduces ammoniacal silver solution, and has the composition and molecular weight required by the formula  $C_6H_{16}O_2N_2$ ; m. p.  $215^\circ$  (corr., decomp.),  $[\alpha]_D^{25} - 30.0^\circ$  (in 1.5% solution in 95% alcohol). R. V. S.

**The Part Played by Lipoids in the Formation of Potential Differences at the Surface of Animal Organs.** JACQUES LOEB and R. BEUTNER (*Biochem. Zeitsch.*, 1914, 59, 195—201).—It is known that when the uninjured end of a frog's muscle is immersed in a potassium salt solution, this end acquires a more negative potential than when immersed in a similar solution of a sodium salt with the same anion. The same phenomena have now been observed when, instead of the uninjured muscle, a guaiacol extract of the same is used, or a solution of lecithin in guaiacol. The influence of the anions on the potential of a muscle immersed in salt solutions has been studied by Höber, who has shown that the tissue

becomes less positive as it is immersed in salts with anions in the following order: CNS, NO<sub>3</sub>, I, Br, Cl, SO<sub>4</sub>. A similar influence of the anions has now been observed at the interface of a salt solution and a guaiacol solution of lecithin. These results are opposed to all theories of the surface potential which assume the latter to be due to injury of the membrane or selective permeability. They may be ascribed to the solubility of small quantities of salts in the lipid; potassium salts are more soluble than sodium salts. From the results, the authors draw the conclusion that a lipid layer or membrane exists in the surface of organs. S. B. S.

**Protozoan Protoplasm as an Indicator of Pathological Changes.** III. In Fatigue. FRANK P. UNDERHILL and LORANDE LOSS WOODRUFF (*J. Biol. Chem.*, 1914, 17, 9—12).—Extracts prepared from fatigued muscles produce no change in the division rate of *Paramoecium* as compared with that obtained with extracts of normal muscles. W. D. H.

**The Fatigue Threshold as Affected by Adrenaline and by Increased Arterial Pressure.** CHARLES M. GRUBER (*Amer. J. Physiol.*, 1914, 33, 335—355).—Adrenaline causes a rapid recovery of the normal irritability of voluntary muscle (cat's tibialis anticus) after fatigue and improves the contractive power. This is not entirely due to circulatory conditions, but is an effect on the muscle itself, and partly on the neuro-muscular function. W. D. H.

**The Osmotic Properties of the Adductor Muscle of the Clam (*Venus mercenaria*).** EDWARD B. MEIGS (*J. Biol. Chem.*, 1914, 17, 81—98).—This muscle contains only 0.3% of chlorine, although the surrounding medium contains 1.6%. The impermeability of the mantle to this element leads to this result; the elements of the muscle itself are not surrounded by semi-permeable membranes, but take up chlorine readily when immersed in seawater. About 38% of the water in muscle is combined with colloids in such a way that it cannot dissolve sugar or salts; the same is true for vertebrate smooth muscle, although the irritability to electric currents is different in the two cases. W. D. H.

**The Rôle and State of the Fluorine in the Animal Economy.** ARMAND GAUTIER (*Compt. rend.*, 1914, 158, 159—166.\* Compare A., 1912, ii, 681, 805, 806; 1913, i, 789, 1017).—A study of the fluorine content of different organs of the body, taken in conjunction with the phosphorus content of these organs, shows that they may be divided into three groups:

(1) The tissues, such as the muscles, glands, nervous tissues, etc., which are most active in life functions, and the different secretions destined to function as nutrients, such as milk, in which the fluorine is bound to the phosphorus in the form of some organic nitrogenous substance, the ratio of fluorine to phosphorus varying from 1:350 to 1:750, and in one case 1:1493.

(2) The tissues, such as the bones, cartilages, tendons, etc., where

\* and *Bull. Soc. chim.*, 1914, [iv], 15, 241—248.

life is less active, in which one part of fluorine is only associated with from 130 to 180 parts of phosphorus, these two elements being apparently partly mineralised.

(3) The organs of simple, mechanical protection or ornamentation, such as the nails, hair, teeth, etc., where the ratio of fluorine to phosphorus is such as is found in fluorophosphatic minerals, and in particular in apatite.

W. G.

**The Hydroxybutyric Acid Content of the Organs of Normal and Diabetic Individuals.** RENPEI SASSA (*Biochem. Zeitsch.*, 1914, 59, 362—377).—Two satisfactory methods for the estimation of hydroxybutyric acid have been found. The one depends on the production of acetone by oxidation with dichromate and sulphuric acid (Schaffer's method), in the course of which acetaldehyde is formed at the same time by the oxidation of the lactic acid. The acetone and aldehyde can be separated by Mond-schein's process, by oxidising the aldehyde by hydrogen peroxide in alkaline solution. The acetone can then be distilled off and titrated by the iodometric method. The second method of estimating hydroxybutyric acid depends on the production of crotonic acid on distillation with sulphuric acid, the amount of the former acid being determined by titration with bromine water. The latter method contains a source of error due to fatty acids, when applied to tissues, but these can be eliminated by a process described by the author, which consists essentially in their separation as insoluble barium salts.

The blood and organs of normal individuals contain a fairly constant quantity of hydroxybutyric acid (0·01—0·02%). The magnitude of the elimination of acetone substances by starving dogs, as a result of phloridzin treatment, depends on various factors, especially the fat content of the organism, and reaches its maximum generally on the second or third day of treatment. If the animal is killed at this point, the organs are found to contain two to three times the normal amount of hydroxybutyric acid. The amount stored is small compared with the amount eliminated in the urine. The amount found in the organs of man, dead after diabetic coma, reaches as much as eight times the normal, the liver containing the largest quantity.

S. B. S.

**Glycine Synthesis in the Organism.** RENPEI SASSA (*Biochem. Zeitsch.*, 1914, 59, 353—361).—The possible origin of glycine from glyoxylic acid is discussed, but no evidence to indicate this method of synthesis in the organism was found. An increased excretion of hippuric was not produced by the simultaneous administration to a rabbit of ammonium or sodium glyoxylate with benzoic acid, nor was any increase in the nitrogen titratable by the formaldehyde method found when the glyoxylate was digested with liver pulp at body temperature.

S. B. S.

**The Source of Creatine in the Animal Organism.** KARL THOMAS (*Zeitsch. physiol. Chem.*, 1913, 88, 465—477).—A considera-

tion of the way in which creatine, a guanidino-compound (thus resembling arginine), originates in the body led to the investigation of how arginase or similar enzymes, or extracts of tissues, act on guanidine compounds.

$\epsilon$ -Guanidinohexoic acid is obtained by the action of cyanamide on  $\epsilon$ -aminohexoic acid as microcrystalline needles; the *hydrochloride*, m. p.  $165^{\circ}$ ; *aurichloride*,  $C_7H_{15}O_2N_3 \cdot HAuCl_4$ , octahedra, m. p.  $166^{\circ}$ ; *nitrate*, stout prisms, m. p.  $154-155^{\circ}$ ; and *acetate* were prepared.

Liver press juice does not cleave this acid, but splits  $\gamma$ -guanidinobutyric acid into urea and  $\gamma$ -aminobutyric acid. Muscle press juice, which probably contains no arginase, does not possess the latter activity.

W. D. H.

**Detection and Estimation of Acetone, Physiological Acetonuria. Influence of Certain Drugs and Hunger.** C. CERVELLO and F. GIRGENTI (*Arch. expt. Path. Pharm.*, 1914, **75**, 153—167).—Lieben's method, applied after distillation, was found to be the best and most delicate method for detecting acetone in urine. Acetone is a normal and constant constituent of the urine of man, dog, and rabbit; its amount is increased by hunger.

W. D. H.

**The Absence of Sugar in the Urine after Pancreatectomy in Pregnant Bitches near Term.** A. J. CARLSON, J. S. ORR, and W. S. JONES (*J. Biol. Chem.*, 1914, **17**, 19—22).—Removal of the pancreas is fatal in such animals, but glycosuria is absent; the foetuses also die. This may be explained on the detoxication theory of pancreas activity, the hypothetical toxins being accumulated in the foetal pancreas, or by the passage of the internal secretion of the foetal pancreas into the maternal blood, or excess of sugar may pass into the foetal blood to be stored and oxidised.

W. D. H.

**The Nitrogen Excretion of the Monkey.** ANDREW HUNTER and MAURICE H. GIVENS (*J. Biol. Chem.*, 1914, **17**, 55—59).—The daily average composition of the urine of one monkey is given.

W. D. H.

**The Occurrence of "Urogon" in Human and Animal's Urine.** ERNST FRICKE (*Pflüger's Archiv*, 1914, **156**, 225—252).—The occurrence of phenol or phenolic derivatives, the precise chemical nature of which is still uncertain, was first noted by Städeler in 1851, and confirmed by numerous later workers, whose writings are quoted. The term urogon is employed for this constituent of the urine. It occurs in the urine of man and domestic animals, is especially abundant in herbivora, and its quantity in human urine is increased by a vegetable diet.

W. D. H.

**The Variations in the Excretion of Endogenous Uric Acid Produced by Changes in Diet.** GEORGE GRAHAM and E. P. POULTON (*Quart. J. Med.*, 1913, **7**, 13—28).—A diet of protein

and fat of insufficient caloric value causes a fall in the output of endogenous uric acid of between 30 and 50%. If most of the fat is replaced by carbohydrate, no such fall occurs. A fall also occurs during the first few days of starvation, and during the consumption of fat and carbohydrate diet. The fall cannot be accounted for by lessening of protein metabolism, or a loss of body protein, nor by acidosis or increased metabolism of fat; the probable explanation is an interaction between protein and carbohydrate metabolism.

W. D. H.

**The Influence of the Rate of Urine Flow on the Secretion of Uric Acid.** J. H. ROBERTSON (*Amer. J. Physiol.*, 1914, 33, 324—334).—The experiments recorded on dogs and hens did not definitely settle whether increased water excretion or the change in the blood flow is responsible for the parallelism between increase in urine flow and uric acid excretion.

W. D. H.

**The Chemistry of the Blood in Conditions of Anæmia.** EMIL MEDAK (*Biochem. Zeitsch.*, 1914, 59, 419—428).—Estimations were made of the cholesterol and cholesteryl ester contents of the blood of patients with various diseases. The iodine numbers of the fats, both before and after separation of the cholesteryl substances, were also determined by the methods described by the author. Although the results give some indication of the momentary condition of the disease, they do not throw any light on the cause of the anæmia or of the hæmolytic processes.

S. B. S.

**The Cholesterol Content of Cancer in Rats.** C. B. BENNETT (*J. Biol. Chem.*, 1914, 17, 13—14).—The injection of cholesterol into rats does not markedly affect the cholesterol content of cancer tissue. In cancer, as in normal tissues, the cholesterol content increases with age. Quickly growing cancer tissue contains less cholesterol than that which grows slowly.

W. D. H.

**Lipoproteins. V. Immunisation Experiments.** GUIDO IZAR and PROSPERO MAMMANA (*Biochem. Zeitsch.*, 1914, 59, 247—248).—Human tumour sera, and sera from sarcomatous rats, cause no specific complement deviation in presence of synthetic antigens for the meiotigmin reaction. Repeated injections of the myristyl derivatives of peptone, elastin, edestin, histidine, or arginine into rabbits produce no specific anti-substances which can be detected by the methods of either complement deviation or the meiotigmin reaction.

S. B. S.

**Synthetic Antigens to the Meiotigmin Reaction for Malignant Tumours. II. Some Compounds of Fatty Acids with Proteins.** GUIDO IZAR and GIUSEPPE DI ZUATTRO (*Biochem. Zeitsch.*, 1914, 59, 226—233).—An account is given of some attempts to replace the pancreas antigen in the above-mentioned meiotigmin reaction. The preparation of myristyl derivatives of Witte's peptone is described, and the precautions necessary for obtaining a

satisfactory preparation are specified in detail. A large number of myristyl derivatives of various proteins and degradation products (peptones, amino-acids, etc.) have been prepared, some of which act as satisfactory antigens, whilst others do not. In addition to those of myristic acid, derivatives from other fatty acids or mixtures of fatty acids have been obtained. None of the pure fatty acids gave with proteins a compound which acted as an antigen. On the other hand, the mixture of fatty acids isolated from cocoa butter, pancreas, and various malignant tumours yielded compounds with proteins, and their degradation products, which were active as antigens, but only, however, with those proteins and derivatives of which myristyl derivatives were active. The activities of the myristyl and these other derivatives were about equal.

S. B. S.

**Synthetic Antigens to the Meistigmin Reaction for Malignant Tumours. III. The Mannitol Esters.** GUIDO IZAR and PAOLO FERRO (*Biochem. Zeitsch.*, 1914, 59, 234—235).—Addition of aqueous suspensions of mannitol esters of various fatty acids to blood-serum causes a diminution of its surface tension. If the serum-emulsion mixture is warmed for one hour at 50°, a marked rise in the surface tension is produced. Sera from both non-tumourous and tumourous individuals (man and rats) behave towards the mannitol esters in the same way.

S. B. S.

**Synthetic Antigens to the Meistigmin Reaction for Malignant Tumours. IV. Cholesteryl Esters.** GUIDO IZAR and PAOLO FERRO (*Biochem. Zeitsch.*, 1914, 59, 236—237).—The emulsions added to blood-sera cause a diminution of the surface tensions; warming the mixture for one hour at 50° causes no appreciable change in these tensions. Tumourous and non-tumourous sera are affected in the same way.

S. B. S.

**The Various Actions of Colloidal Sulphur, with Special Reference to the Mode of Introduction into the Organism.** L. SABBATANI (*Biochem. Zeitsch.*, 1914, 59, 378—407).—The author reviews in detail the literature on the pharmacological action of colloidal sulphur, and draws the conclusion that the varied results obtained by different investigators is due to the differences of the dispersion grade of the preparations used. His own experiments were carried out with a preparation prepared by Raffo's method. This preparation in the presence of salts, etc., passes from the condition of hydrosol into a hydrogel, then into an amorphous, insoluble form, and finally into the crystalline form. These changes in the presence of various tissues have been studied by the author both *in vivo* and *in vitro*. He has also studied the chemical changes of sulphur in the body. When injected subcutaneously, hydrogen sulphide is formed only very slowly. After interperitoneal injection it is formed more rapidly, but yet not sufficiently quickly for it to be detectable in the expired air. When injected intravenously, it is readily formed, and for this reason

the highly colloidal sulphur is very toxic. As the sulphur aggregates get larger, the toxicity diminishes. Numerous experiments on dogs and rabbits with colloidal sulphur were performed. The dog can tolerate relatively large doses when the sulphur is introduced into the stomach. With the larger doses vomiting occurs, and the animal rapidly recovers. The sulphur is more toxic under the same condition in rabbits, as these animals cannot vomit. A little more than 0.1 gram per kilo. of body-weight can produce death. This dose can be well tolerated when introduced intraperitoneally or subcutaneously, although larger doses can act toxically. When given intravenously, doses of 0.0065 to 0.0203 gram are toxic, the toxicity depending on the rate at which the sulphur is introduced. S. B. S.

(Pharmacological) Action of Colloidal Carbon Prepared by a Chemical Method. L. SABBATANI (*Biochem. Zeitsch.*, 1914, 59, 408—417).—Colloidal carbon was prepared by the action of sulphuric acid on sugar. A preparation made in this way is not toxic, whatever its method of administration. It is very slowly absorbed. When introduced intravenously, it only passes very slowly from the circulation into the organs. It is fixed chiefly by the endothelial cells, to the greatest extent by those of the lungs. Even these are not functionally affected. S. B. S.

Gluconeogenesis. VI. The Effects of Acetaldehyde and Propaldehyde on the Formation of Sugar and Acidosis in the Diabetic Organism. A. I. RINGER and E. M. FRANKEL (*J. Biol. Chem.*, 1914, 16, 563—579).—The injection of acetaldehyde or propaldehyde into female dogs, in which glycosuria had been induced by prior injection of phloridzin, results in a marked depression of the nitrogen elimination, which lasts for about twenty-four hours after the aldehyde administration, a rise in the absolute amount of dextrose eliminated during the period of aldehyde administration, in spite of the drop in the nitrogen, accompanied by a very high rise in the ratio dextrose/nitrogen. There is also a very marked depression in the acetone, acetoacetic acid, and  $\beta$ -hydroxybutyric acid eliminations, where acidosis is high. The effect of the acetaldehyde is remarkable, since neither ethyl alcohol nor acetic acid has any appreciable influence on the metabolism of the diabetic dog. Propyl alcohol and propionic acid possess the power of gluconeogenesis, but do not affect the nitrogen metabolism or the acidosis to the extent that propaldehyde does.

A remarkable fact is that the very large amount of extra dextrose eliminated is more than would be obtained if the whole of the acetaldehyde injected were converted into sugar. Thus apparently acetaldehyde possesses the power of converting some substance in the animal metabolism that is non-glucogenetic into one that is glucogenetic, and the substance so formed possesses a greater number of carbon atoms than does acetaldehyde. The same is true for propaldehyde, but to a less extent. The authors suggest that the aldehyde may combine with a substance such as  $\beta$ -hydroxy-

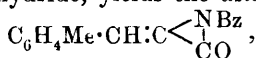
butyric acid, giving methyl-lævulic acid, which would be converted into lævulic acid, and this into dextrose.

Similar experiments were attempted with formaldehyde, but all failed on account of the toxicity of this aldehyde, the animal usually dying within twelve hours of administration. W. G.

**Decomposition of Amino-acids and Formation of Glycine.** F. KNOOP (*Zeitsch. physiol. Chem.*, 1914, **89**, 151—156. Compare this vol., i, 229).—Administration of  $\beta$ -phenylserine to dogs leads to the appearance of hippuric acid in the urine, so that the substitution of oxygen at the  $\beta$ -carbon atom of  $\alpha$ -amino-acids changes the point at which oxidation begins. The administration of  $\epsilon$ -phenyl- $\alpha$ -aminohexoxic acid yields hippuric acid in the urine, no phenacetic acid being formed. R. V. S.

**The Decomposition of *m*-Tolylalanine in the Organism.** I. LUDWIG BÖHM (*Zeitsch. physiol. Chem.*, 1914, **89**, 101—112).—*m*-Tolylalanine was given to dogs subcutaneously, and the urine examined; it is more completely burnt in the body than Dakin showed to be the case with the para-compound. This supports the view that the methyl group in the nucleus is not destroyed; quinol is an intermediate product.

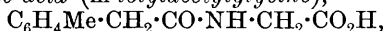
*m*-Tolualdehyde, when heated with hippuric acid, sodium acetate, and acetic anhydride, yields the *azlactone*,



crystallising in yellow needles. This, when dissolved in sodium hydroxide and treated with hydrochloric acid, yields  $\alpha$ -benzoyl-amino-*m*-methylcinnamic acid,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}:\text{C}(\text{NHBz})\cdot\text{CO}_2\text{H}$ , nearly colourless needles, m. p.  $204.5^\circ$ . By reduction in aqueous solution with sodium amalgam, this is converted into benzoyl-*m*-tolylalanine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{NHBz})\cdot\text{CO}_2\text{H}$ , lustrous, colourless plates, m. p.  $195^\circ$ , which by heating for twelve to twenty-four hours with a large excess of 20% hydrochloric acid yields *m*-tolylalanine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , which crystallises in slender needles, m. p.  $245^\circ$ . W. D. H.

**The Decomposition of *m*-Tolylalanine in the Organism.** II. K. FROMHERZ and L. HERMANN (*Zeitsch. physiol. Chem.*, 1914, **89**, 113—120).—The chief quantity of the unburnt excreted residue of this acid cannot be extracted from the urine by ether; the substance isolated from that fluid is *m*-tolylacetic acid; in round figures, about two-thirds of the *m*-tolylalanine given is burnt in the body.

*m*-Tolylacetic acid (*m*-tolylacetyl-glycine),



m. p.  $149^\circ$ , colourless, prismatic crystals, is obtained by the action of glycine on *m*-tolylacetyl chloride, an oil of penetrating odour, b. p.  $136^\circ/15$  mm. W. D. H.

**Adrenaline (Suprarenine) as the Physiological Antagonist of Morphine.** A. GUBER (*Arch. expt. Path. Pharm.*, 1914, **75**, 333—346).—The present experiments on rabbits confirm observa-



tions made by Lichatschov and by Schaternikova, that adrenaline antagonises the depressive and fatal effect of morphine. The observations made in the present research mainly relate to respiration.

W. D. H.

**Hyperglycæmia Produced by Pituitrin and Adrenaline.** THOR STENSTRÖM (*Biochem. Zeitsch.*, 1914, 58, 472—482).—Intravenous injection of pituitrin causes no change in the content in sugar of either the blood or the urine. The intravenous injection of relatively large doses causes a marked, but very transient, hyperglycæmia, and in certain cases, glycosuria. Some of the fractions of pituitary substances, isolated by Fühner's method, exert the same action. When pituitrin is administered subcutaneously, it exerts an inhibitory action on adrenaline, in that, in sufficient doses, it can entirely stop the hyperglycæmia produced by the last-named substance. It can also diminish the *piqûre* hyperglycæmia, and the hyperglycæmia due to diuretin, psychical excitation, and venesection.

S. B. S.

**The Relative Intolerance of the Sheep to Subcutaneous Administration of Dextrose.** ANDREW HUNTER and REUBEN L. HILL (*J. Biol. Chem.*, 1914, 17, 61—63).—The sheep's capacity to deal with subcutaneously administered dextrose is greatly inferior to that of the dog; the latter can dispose of doses of 5, or even 7, grams per kilo. of body-weight; the sheep has difficulty in retaining as small a dose as 0.5 gram. Whether the sheep is readily liable to alimentary glycosuria has not yet been tested. This result is unexpected when the natural diets of dog and sheep are compared. The pig and sheep are very much alike in their intolerance to subcutaneously administered dextrose.

W. D. H.

**The Action of Digitalis in Therapeutics.** A. R. CUSHNY, H. F. MARRIS, and M. D. SILBERBERG (*Heart*, 1912, 4, 33—58).—The digitalis group slow the pulse in a certain number of cases, and, as a rule, this slowing is removed by atropine, and is therefore inhibitory. In other cases atropine has no effect, and there is then a direct action of the drug on the conducting fibres between the pacemaker (sinus region) and the rest of the heart. In auricular fibrillation, digitalis and its allies slow the heart by direct action, for atropine has no effect. The inhibitory stimulation does not play any part in the beneficial action of the drug, which is to be ascribed to its direct action on the cardiac muscle solely.

W. D. H.

**The Action of Egg-yolk Emulsions on Animals.** G. HANSCHMIDT (*Biochem. Zeitsch.*, 1914, 59, 281—297).—The intraperitoneal injection of emulsions of coagulated egg-yolk causes the death of animals (rabbits, guinea-pigs). The egg-yolk is for the most part absorbed, and there is a great emigration of leucocytes into the peritoneal cavity. If the two chief constituents of the yolk are injected separately, the lipoids are found to be resorbed, but not

the proteins, which remain encapsulated in the peritoneum, and no leucocyte emigration is observed. If the two are injected simultaneously, however, the proteins are absorbed, and death of the animals results. Uncoagulated egg-yolk can be injected in very large quantities without injury to the animals. Liquid white of egg is also harmless, even when injected simultaneously with lipoids. If, however, it is coagulated, it causes also, when injected with lipoids, the death of the animal. Lycopodium is partly absorbed when injected with lipoids, but not when injected alone. It appears from these experiments that the toxicity is dependent on three factors, viz., coagulated proteins, lipoids, and leucocytes. The migration of leucocytes is due to the lipoids. When the latter are present, the former can cause the resorption of coagulated proteins from the peritoneal cavity. They are then carried to the blood stream, and cause the death of the animal by production of embolisms.

S. B. S.

**Degradation of Fatty Acids in the Animal Body.** LEO HERMANN (Biochem. Zeitsch., 1914, 59, 333—336).—A discussion and criticism of certain results obtained by the author and by E. Friedmann (A., 1913, i, 1276).

S. B. S.

**Intestinal Autointoxication. I. The Influence of *p*-Hydroxyphenylethylamine on the Blood of Guinea-pigs.** TOKU IWAO (Biochem. Zeitsch., 1914, 59, 436—443).—Repeated injection of *p*-hydroxyphenylethylamine into guinea-pigs lead to severe anæmia of pernicious character. The author gives a detailed description of the blood and differential blood-counts. These results are produced by much larger doses than are necessary to obtain results of therapeutic value.

S. B. S.

**Pharmacology of the Respiratory Centre.** ARTHUR R. CUSHNY (J. Pharmacol. expt. Ther., 1913, 4, 363—398).—Morphine, chloral, urethane, caffeine, and strychnine affect the frequency rather than the depth of respiration, and, as a rule, frequency and depth vary inversely. Morphine, chloral, and urethane retard and deepen respiration; strychnine and caffeine quicken it, and make it shallower. That the respiratory centre is normally dependent on carbon dioxide acting as a hormone receives support from these experiments, for the drugs mentioned vary the reaction of the centre to this gas. The part played by nervous control is also discussed, but changes in nervous control fail to account for all the features observed; drugs act primarily on the rhythmic process, which both nervous and chemical stimuli control.

W. D. H.

**The Behaviour of Neosalvarsan and Salvarsan in the Organism.** J. ABELIN (Arch. expt. Path. Pharm., 1914, 75, 317—332).—After intravenous injection of neosalvarsan, the urine during the first hour contains formaldehyde, which can be detected by the reaction with phenylhydrazine, potassium ferricyanide, and hydrochloric acid. The sterile condition of the urine indicates that

the formaldehyde is either free or in a loosely bound condition. The urine also gives the diazo-reaction; this is true also for salvarsan injection, but after intra-muscular injection it is not present.

W. D. H.

**The Behaviour of Pyridine in the Frog's Organism.** KANAÉ MAYEDA and MASAJIRO OGATA (*Zeitsch. physiol. Chem.*, 1914, **89**, 251—252).—His and others showed that after giving pyridine to hens, goats, and pigs, the urine contains pyridylmethylammonium hydroxide. Abderhalden and his colleagues showed that rabbits are not able to methylate pyridine. The present research shows that frogs in this respect, agree with the animals investigated by His.

W. D. H.

**[Physiological] Action of Strophanthin.** WALTHER STRAUB (*Biochem. Zeitsch.*, 1914, **59**, 496—497).—The author corrects a statement made in a former paper (A., 1910, ii, 1094), in which he gives the toxic solution of *Gratus strophanthin* as 1:400,000, whereas Heffter and Sachs give 1:25,000 as the toxic dose (A., A., 1912, i, 482). He now finds that his own figures are due to an error, as he worked, not with the *Gratus*, but with the Kombé strophanthin. The differences in the toxicity of this preparation as determined now by the author and by Heffter and Sachs may be ascribed to the differences of temperature at which the experiments were performed.

S. B. S.

**Action of the Serum on Ureases (Specific Auxoureases).** MARGARETE FALK (*Biochem. Zeitsch.*, 1914, **59**, 298—315).—When soja urease, in not too large quantity, is mixed with serum, a marked increase in the urease action can be detected. The amount of urease present must, of course, be smaller than that necessary for the production of maximal decomposition of urea. The substance in serum which stimulates the urease action is designated auxourease. This auxourease is not, apparently, a ferment which is activated by the addition of soja-bean extract, as the latter contains a very active urease by itself; furthermore, although the auxo-substance is not dialysable, it can be boiled for two minutes without losing its properties. Sera of rabbits which have been immunised against soja urease still contain the auxo-substance. The soja auxourease is without action on the *Robinia* urease.

S. B. S.

**The Fate of the Soja Urease in Normal and Treated Animals.** MARGARETE FALK (*Biochem. Zeitsch.*, 1914, **59**, 316—325).—Normal sera contain no urease. The ferment can be detected, however, in the sera of animals within four to forty-eight hours after injection of soja extract. After the longer interval, the amount commences to diminish. If the animal has received several injections of soja extract beforehand, smaller amounts than normal of circulating urease can be found in the serum after injection. In the case of an animal which had received previously only

one injection, the amount of urease in the serum after the second injection was much larger than normal. The amount of circulating urease due to soja injection was smaller than normal when the animal had received injections previously of the *Robinia* urease.

S. B. S.

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## Chemistry of Vegetable Physiology and Agriculture.

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**The Biochemical Changes of Protein Hydrolysis Products Produced by Bacteria. I. The Behaviour of Tyrosine towards *B. coli communis*. A Simple Biochemical Method for the Preparation of *p*-Hydroxyphenylethylamine.** TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1914, 59, 429—435).—*p*-Hydroxyphenylethylamine, in a yield of up to 78·7%, was obtained from tyrosine by the action of *B. coli* growing in the following medium: sodium chloride, 5 grams; monopotassium hydrogen phosphate; magnesium sulphate, 0·1 gram; ammonium carbonate, 1 gram; glycerol, 20 c.c.; water, 1000 c.c. Two grams of tyrosine were introduced into 800 c.c. of this solution. S. B. S.

**Action of Colloidal Uranium on the Pyocyanic Bacillus.** H. AGULHON and (Mlle.) TH. ROBERT (*Compt. rend.*, 1914, 158, 349—352).—Colloidal uranium prepared by the electrical method has a much greater effect in increasing the activity of the pyocyanic bacillus than has powdered uranium (compare A., 1913, i, 322), the increases being much greater with cultures on Gessard's medium than on bouillon. The effect is most marked on sowings already somewhat fatigued by several successive passages on synthetic media.

Although colloidal uranium is capable of accelerating the formation of pyocyanin for a race, which produces it normally, it is incapable of producing the chromogenic function in cultures of races which are devoid of this function.

The concentration of the colloidal uranium used was from 1·2 in 10,000,000 to 6 in 100,000. W. G.

**Decomposition of Sugar by Alcoholic Fermentation.** P. BOYSEN-JENSEN (*Biochem. Zeitsch.*, 1914, 58, 451—466).—The author claims to show that dihydroxyacetone can be isolated as an intermediate product of yeast fermentation. Minute quantities of a phenylmethylhydrazone were obtained, similar to that yielded by dihydroxyacetone when the fermentation was allowed to proceed in the presence of the correct amounts of hydroxylamine hydrochloride, which is stated to inhibit the action of yeast on the supposed intermediate product. When crude dihydroxyacetone produced by the oxidation of glycerol with hydrogen peroxide is

treated with charcoal, small amounts of carbon dioxide, and a volatile substance of lower specific gravity than water (alcohol?), are produced. Solutions of the pure crystalline substance, prepared from glycerol by Bertrand's bacillus, do not yield these substances when treated with animal charcoal unless previously treated with hydrogen peroxide (or an iron salt). The author is of the opinion that his experiments indicate that dihydroxyacetone is converted into a labile modification, which is then changed into carbon dioxide and alcohol.

S. B. S.

#### Formation of Lactic Acid during Alcoholic Fermentation.

MAX OPPENHEIMER (*Zeitsch. physiol. Chem.*, 1914, 89, 45—62).—Experiments with yeast-juice, under conditions securing the exclusion of bacterial action, showed a formation of lactic acid as a by-product of alcoholic fermentation. The production of acid is increased by an addition of sugar to the yeast-juice, and still further increased when glyceraldehyde or dihydroxyacetone is supplied. The fact that glyceraldehyde is much more readily decomposed than dihydroxyacetone is regarded as indicating the former to be the intermediate product in the formation of lactic acid during alcoholic fermentation. In contradistinction from results obtained with the animal organism, pyruvic acid does not appear to be of importance as a source of lactic acid during this fermentation.

H. B. H.

#### The Formation of Glycerol during Alcoholic Fermentation.

MAX OPPENHEIMER (*Zeitsch. physiol. Chem.*, 1914, 89, 63—77).—The experiments confirmed earlier observations as to the production of glycerol from dextrose by yeast-juice. It was also found that during alcoholic fermentation by yeast-juice, dihydroxyacetone and glyceraldehyde act as contributory compounds in the production of glycerol, although the former may be regarded as the chief source. The formation of glycerol, as also of lactic acid, appears to depend largely on the fermentative power of the yeast or yeast-juice; the lower the fermentative power, the greater is the production of these by-products.

H. B. H.

**Reduction Processes in the Yeast Cell. The Conversion of *iso*Butaldehyde into *iso*Butyl Alcohol and of Heptaldehyde into *n*-Heptyl Alcohol.** КОНСИ ОНТА (*Biochem. Zeitsch.*, 1914, 59, 183—187).—By slow addition to yeast fermentations of the above aldehydes, they can be converted into the corresponding alcohols. *iso*Butaldehyde was found to yield about 28%, and heptaldehyde about 50%, of the alcohol, the latter giving rise to other by-products.

S. B. S.

#### Formation of Higher Alcohols from Aldehydes by Yeast.

II. The Formation of Amyl Alcohol from Valeraldehyde and the Enzymatic Nature of the Reaction. C. NEUBERG and H. STEENBOCK (*Biochem. Zeitsch.*, 1914, 59, 188—192).—The authors show that amyl alcohol is produced from valeraldehyde when

the latter is added to a yeast suspension in water without the addition of sugar and the production of rapid fermentation. The yield (17%) is, however, smaller than when the aldehyde is added to an ordinary fermentation mixture. They have also succeeded in producing the alcohol by the addition of the aldehyde to a fermentation mixture of sugar and maceration juice. The reduction is therefore an enzymatic process, independent of the existence of living yeast cells. S. B. S.

**Formation of Invertase by Yeast.** HANS EULER and HARALD CRAMÉR (*Biochem. Zeitsch.*, 1914, 58, 467—469).—It has been shown by Euler and others that the treatment of yeast with sucrose or its products of inversion increases the invertase content of the organism. It is now shown that the same result can be produced in quite a marked manner when the yeast is treated with mannose. S. B. S.

**Lanthanum in its Physiological-chemical Relations.** TH. BOKORNY (*Chem. Zeit.*, 1914, 38, 153—154).—The fermenting power of yeast is destroyed by 5% solutions of lanthanum nitrate, but not by the same amount of calcium nitrate. With 0.1% solutions of lanthanum nitrate the yeast retained its activity, but in a less degree than with calcium nitrate. Further experiments with *Spirogyra* showed that lanthanum is unable to take the place of calcium, and that the plants are killed in a short time by 1% solutions of the nitrate. N. H. J. M.

**Fermentation Equilibria. Recommencement of Hydrolysis or Synthesis by Reason of Changes brought about in the Composition of the Mixtures.** EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1914, 158, 206—209; *J. Pharm. Chim.*, 1914, [vii], 9, 104—109).—In the hydrolysis of glucosides by emulsin if, when equilibrium is reached and hydrolysis can proceed no further, a yeast is added which will destroy the dextrose formed, hydrolysis recommences and will proceed until the whole of the glucoside is destroyed. Conversely if, instead of adding the yeast, dextrose is added, synthesis will take place. In the living organism the part played by the yeast would be performed by the cell. W. G.

**A Cause of Error in the Study of the Biological Action of Chemical Elements; the Presence of Traces of Zinc in the Glass.** M. JAVILLIER (*Compt. rend.*, 1914, 158, 140—143).—The author has grown *Aspergillus niger* on Raulin's liquid carefully freed from zinc in vessels of quartz, Bohemian and Jena glass, and under similar conditions with zinc added to the liquid. The addition of zinc causes marked increase in the dry weight of the crop grown in quartz or Bohemian glass vessels, but none where it is grown in Jena glass vessels, the growth being at the same maximum in these vessels without addition of zinc as in the others after addition of zinc. Jena glass vessels, heated in an autoclave with

water acidified to the same degree as Raulin's liquid, yield zinc, precipitable as calcium zinc oxide to the extent of 0.00005 mg. *Aspergillus niger* is thus a very delicate reagent in testing for zinc, and the presence of this metal in the glass is a grave source of error in the study of the biological action of chemical elements. W. G.

**The Action of Milk-mould on Phenylaminoacetic Acid.** HANS HORSTERS (*Biochem. Zeitsch.*, 1914, 59, 444—450).—In a medium containing phenylaminoacetic acid with either invert sugar or dextrose together with monopotassium hydrogen phosphate, magnesium sulphate, and traces of sodium and ferric chlorides, *Oidium lactis* produced the following products: benzyl alcohol, very small traces of phenylglyoxylic acid, benzoic acid, traces of formic acid, and also an appreciable quantity of *l*-mandelic acid. The author suggests formulæ to represent the various changes the phenylaminoacetic acid undergoes. S. B. S.

**Sterilisation of Water by Filtration.** K. CHARITSCHOFF (*Chem. Zeit.*, 1914, 38, 222).—The author has found that all porous substances, in the presence of water, give rise to hydrogen peroxide (A., 1910, ii, 1054). Sterilisation of water consequently occurs when it is allowed to flow through such substances as pumice stone, asbestos, etc. T. S. P.

**Photochemical Studies on the Assimilation of Nitrites and Nitrates.** OSKAR BAUDISCH and ERWIN MAYER (*Zeitsch. physiol. Chem.*, 1914, 89, 175—222).—Both nitrites and nitrates give up oxygen in presence of light, the action of which is mainly due to ultraviolet rays. In solutions of potassium nitrite in alcohol or in aldehyde, the corresponding hydroxamic acids are produced. By prolonged action of light, amino-compounds, and probably nitrogenous *cyclo*-compounds, are formed after the disappearance of the nitrite and the hydroxamic acid. This is the first instance of the conversion of nitrites and nitrates into organic nitrogen compounds by the action of light, and it is considered probable that plants can effect similar changes since the three factors, nitrates, formaldehyde, and light are at their disposal. N. H. J. M.

**Action of Some Ammonium Bases and of Sparteine on the Cell.** W. RUHLAND (*Ber. Deut. bot. Ges.*, 1913, 31, 578—580).—Tetramethyl- and tetraethyl-ammonium hydroxides behave similarly to potassium hydroxide, which, as previously shown (*Jahrb. wiss. Bot.*, 1912, 51, 376), penetrates living cells when suitably diluted, without injurious action. Similar results were obtained with corresponding aromatic bases such as methylene-blue and methylene-green.

As regards sparteine to which reference was previously made, it is now shown that it is a relatively strong tertiary, and not a quaternary, base. N. H. J. M.

**Diffusion and Localisation of the Ions in Vegetable Organisms. Experiments with Cerium.** C. ACQUA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 594—598).—Experiments on the



influence of very dilute solutions of cerium chloride on the growth of *Triticum sativum*, *Zea mais*, and *Phaseolus vulgaris* give results similar to those obtained with manganese, uranium (this vol., i, 124), and lead. Yellow deposits are found in the plant subsequently, and these are situated exclusively in the root. R. V. S.

**The Origin of Purines in Plants.** TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1914, **36**, 337—345).—From the fact that almost all syntheses of purine compounds involve the formation of an iminazole ring in an already-formed pyrimidine derivative, the author regards pyrimidine compounds as the probable precursors of purines in plant growth. The results obtained by Ritthausen (A., 1896, i, 668, 696; 1899, i, 715) as to the nature of the nitrogenous substances, vicine and convicine, obtained from vetch seeds, are discussed from this point of view. D. F. T.

**The Presence, in Leaves and Flowers not Forming Anthocyanin, of Yellow Pigments Capable of being Transformed into Anthocyanin.** RAOUL COMBES (*Compt. rend.*, 1914, **158**, 272—274. Compare this vol., i, 121, 240).—The presence of a yellow pigment in the green leaves of *Ampelopsis hederacea*, capable of conversion by reduction into anthocyanin, is not peculiar to this plant, a similar result having been obtained with the green leaves of *Ligustrum vulgare*, which plant sheds red leaves in winter. The leaves of a variety of vine, *Chasselas doré*, which does not naturally produce a red pigment, and the yellow flowers of *Narcissus incomparabilis*, also contain a yellow pigment, which on reduction yields a red pigment, having the properties of anthocyanin. W. G.

**Chemical Interpretation of Some Mendelian Factors for Flower-colour.** M. WHELDAL and H. LL. BASSETT (*Proc. Roy. Soc.*, 1914, [B], **87**, 300—311).—The yellow *Antirrhinum* pigment is shown to be luteolin. Whilst the ivory variety has the power of forming aepiginin throughout the tissues of the flower, the yellow variety forms luteolin, probably instead of, rather than in addition to, apigenin in the upper epidermis of the lips. The different flavones synthesised seem to indicate fundamental differences in structure in the two varieties which may result in the production of different hydroxybenzoic acids from which the flavones may be synthesised. The white variety failed to yield any flavone, and the conclusion is drawn that either the power of synthesis is wanting, or else the materials. N. H. J. M.

**Oil of Argemone Mexicana.** KSHITIBHUSHAN BHADURI (*Amer. J. Pharm.*, 1914, **86**, 49—54. Compare Crossley and Le Sueur, A., 1899, ii, 324).—The seeds yielded 22·3% of olive-green oil,  $D_{25}^{20}$  0·9117,  $D_{100}^{20}$  0·9007,  $n_D^{20}$  1·46552, having saponification number 185·5, acetyl number 27·9, acid number 146, bromine value 102·2, iodine value 106·7, Reichert-Meissl number 0·61, Hehner number 94·02, and unsaponifiable matter 2·29%. The "mixed fatty acids"

had  $D^{28}$  0.9065,  $D^{100}$  0.8889, iodine value 147.4, and titre test  $22^{\circ}$ , and contained 8.14% of lauric acid, no stearic acid, and 77% of liquid fatty acids.  
T. A. H.

**Action of Individual Nitrates in the Period of Germination of *Avena sativa*.** F. PLATE (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 598—603).—The paper records the results of experiments on the influence of solutions of lithium, sodium, potassium, caesium, rubidium, and ammonium nitrates (taken one at a time) on the growth of this plant.  
R. V. S.

**Action of Individual Nitrates in the Period of Germination of *Avena sativa*.** II. F. PLATE (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 728—733. Compare preceding abstract).—Silver nitrate produces diminution in the weight of *Avena sativa* in degree increasing with the concentration of the salt, but much less than those observed with more concentrated solutions (*loc. cit.*) of alkali nitrates. With copper nitrate, the decreases are intermediate between those given by silver nitrate and by the nitrates of the alkali metals.

Similar experiments with the nitrates of the metals of group II give the following series in which the growth is greatest with the nitrate of the first metal and least with that of the last. Root growth: strontium, calcium, zinc, barium, magnesium, cadmium, mercury; acrospire growth: calcium, barium, zinc, strontium, magnesium, cadmium, mercury; total development: strontium, calcium, zinc, barium, magnesium, cadmium, mercury.

Hence, none of these elements act in accordance with their chemical properties, each having specific biological properties.

T. H. P.

**Percentage in Linseed of Carbohydrates Soluble in Water.** G. B. VAN KAMPEN (*Chem. Weekblad*, 1914, 11, 142—146).—The sugar content of various samples of linseed is between 2 and 2.5%, whilst the corresponding cake contains 3—4%. An explanation of the discrepancy is lacking, but the author is of opinion that it is not to be found in the presence in the seeds of glucosides such as amygdalin and linamarin, and their decomposition with formation of dextrose during the manufacture of the cake.

A. J. W.

**Respiration and Metabolism of Ruminants. A Correction.** N. ZUNTZ (*Landw. Versuchs-Stat.*, 1913, 83, 283—284. Compare A., 1913, i, 577).—Four corrections in results of estimations of the heat of combustion of faeces. The errors, due to an alteration made in the apparatus, do not affect the conclusions drawn.

N. H. J. M.

**Cyanogenesis under Digestive Conditions.** S. J. M. AULD (*J. Agric. Sci.*, 1913, 5, 409—417).—Under digestive conditions cyanogenesis is likely to be inhibited by acids and alkalis, digestive

juices, cellulose, dextrose, molasses, salt, and other substances. The chief cause of the innocuous character of linseed cake is the time the food remains in the digestive tract and the alkaline character of the salivary juices.

In the case of sheep fed with linseed cake shortly before being killed, small amounts of hydrocyanic acid were found, chiefly in the rumen. Poisonous effects are most likely to occur when the cyanogenetic substances are consumed along with foods which contain, or produce, acid; or when hydrocyanic acid is pre-formed, as in the case of linseed gruel improperly made. N. H. J. M.

**Weathering of Silicates and Rocks with Especial Reference to the Influence of Humus.** HANS NIKLAS (*Bied. Zentr.*, 1913, **42**, 803—804; from *Verlag Fachlit. Berlin*, 1912. Compare A., 1913, i, 812).—The results of experiments in which peat and silicates were mixed showed no direct action of the peat on silicates. When, however, the mixture was subjected to electrolysis there was an immediate production of soluble salts.

With reference to the production of kaolin from felspar, the hydrolysis theory of Ramann seems to be the most probable, at any rate, in the case of tropical soils. In the production of laterite, carbon dioxide is probably only of secondary importance.

The action of salt solutions is very different in arid and humid regions, since it is only in the former that readily soluble salts can be available. N. H. J. M.

**The Nature of Humus and its Relation to Plant Life.** S. L. JODIDI (*Biochem. Bull.*, 1913, **3**, 17—22).—Mainly a review of previous work. The underlying idea of the paper is that humification is a means of utilising organic remains of living structures, and that their decomposition makes them available for new generations of plants. W. D. H.

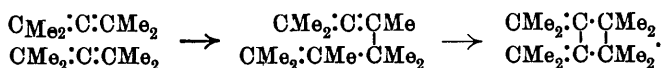
**The Organic Nitrogen of Hawaiian Soils. I. The Products of Acid Hydrolysis.** W. P. KELLEY (*J. Amer. Chem. Soc.*, 1914, **36**, 429—434).—Various samples of Hawaiian soils have been examined, and it is found that the ammonia content is as a rule considerably greater than the nitrate content. The organic nitrogen was investigated by the Osborne-Harris method (A., 1903, i, 585); the quantities of amide nitrogen, basic nitrogen (probably mainly diamino-acids), and non-basic nitrogen (probably largely monoamino-acids), varied considerably, but averaged approximately 24%, 10%, and 65% of the total nitrogen dissolved by boiling hydrochloric acid. D. F. T.

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## Organic Chemistry.

**Tetramethylallene, its Polymerisation and Isomerisation.** B. K. MERESHKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1940—1974).—By prolonged heating with alcoholic potassium hydroxide of the mixture of chlorides resulting from the action of phosphorus pentachloride on isobutyron (diisopropyl ketone), Henry (*Ber.*, 1875, 8, 400) obtained a small yield of a hydrocarbon,  $C_7H_{12}$ , b. p. about  $70^\circ$ , which he described as tetramethylallene,  $CM_e_2:C:CM_e_2$ ; the formation of this compound was regarded as due to the removal of 2 mols. of hydrogen chloride from  $\gamma\gamma$ -dichloro- $\beta\delta$ -dimethylpentane. Vaubel (A., 1891, 996) stated that this compound gives, with mercuric chloride, the white, crystalline precipitate characteristic of all allene hydrocarbons, but Bukont (*J. Russ. Phys. Chem. Soc.*, 1897, 29, 77), repeating Henry's work on a large scale, obtained very little hydrocarbon, b. p.  $70$ — $80^\circ$ . Favorski's results (A., 1913, i, 12) show, however, that Henry could not have obtained  $\gamma\gamma$ -dichloro- $\beta\delta$ -dimethylpentane or tetramethylallene. The author's work now indicates that the removal of hydrogen chloride by prolonged heating with alcoholic potassium hydroxide precludes the possibility of obtaining an individual product.

The author has prepared tetramethylallene and finds that, in accordance with the views advanced by Lebedev and Mereshkovski (A., 1913, i, 1285), it yields only a single dimeride. Lebedev has shown that the views of Harries (A., 1911, i, 798), Kondakov ("Synthetic Caoutchouc, its Homologues and Analogues," Yuriev, 1912), and Ostromislenski ("Caoutchouc and its Analogues," Moscow, 1913), according to which the formation of di- and poly-meric forms of hydrocarbons takes place by way of intermediate aliphatic compounds, are not applicable to hydrocarbons of the butadiene type. These considerations should, however, be valid in the case of allene hydrocarbons, but with tetramethylallene, in which there is no hydrogen atom adjacent to the double linkings, the formation of the dimeride would necessitate the migration of two methyl groups to a non-contiguous carbon atom:



Such an explanation seems improbable.

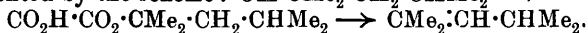
In general, the tetrasubstituted allenes exhibit the properties of their mono-, di-, and tri-substituted analogues, but they show also certain peculiarities, such as readiness to undergo isomeric change into hydrocarbons with conjugated linkings.

According to Lebedev (A., 1913, i, 1285), the lower the number of hydrogen atoms at the central carbon of the allene system, the more marked will be the unsaturated character, and hence also the capability

of reacting, of the hydrocarbon. In comparison with di- and trimethylallenes, tetramethylallene should then undergo isomeric change into the butadiene derivative,  $\alpha\alpha$ -dimethylisoprene, with great readiness, whilst the isomeric *as*-diethylallene should isomerise with much less ease. These conclusions are contradicted by the author's results, since the conditions under which tetramethylallene is obtained pure, result in the formation of an *as*-diethylallene mixed with  $\alpha$ -methyl- $\beta$ -ethylbutadiene, as is shown by the magnitude of its optical exaltation, namely,  $+0.56^\circ$ . Further contradiction is afforded by comparison of the velocities of polymerisation of isomeric allenes, since it is found that the velocity is not constitutive in character, that is, not dependent on the positions of the substituent radicles relative to the central carbon atom of the system, but has similar values for allene hydrocarbons of equal molecular weights.

Tetramethylallene was synthesised as follows: dimethylisobutylcarbinol was converted by dehydration with oxalic acid into the corresponding heptene,  $\beta\delta$ -dimethyl- $\Delta^\beta$ -pentene, and the latter into  $\beta\gamma$ -dibromo- $\beta\delta$ -dimethylpentane, which may also be obtained, but in diminished yield, by direct bromination of the above tertiary alcohol. By removal of successive molecules of hydrogen bromide from the dibromo-derivative, an unsaturated monobromo-compound and tetramethylallene are obtained.

The  $\beta\delta$ -dimethyl- $\Delta^\beta$ -pentene obtained in the above manner is found to be accompanied by an acid ester of oxalic acid and dimethylisobutylcarbinol, b. p. above  $100^\circ$ , so that the course of the reaction is represented by the scheme:  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}_2 \rightarrow$



The action of the oxalic acid is, therefore, not merely one of dehydration, but is similar to that which it exerts on menthol (compare Zelikov, A., 1903, i, 184).

$\beta\gamma$ -Dibromo- $\beta\delta$ -dimethylpentane,  $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{CHMe}_2$ , is a liquid, b. p.  $88^\circ/17$  mm.,  $97^\circ/23$  mm.,  $105^\circ/33$  mm.,  $D_4^{20}$  1.5675,  $D_4^{25}$  1.5431,  $n_D^{25}$  1.50920, and is highly caustic to the taste when prepared by bromination of dimethylisobutylcarbinol, but only slightly so when obtained from  $\beta\delta$ -dimethyl- $\Delta^\beta$ -pentene. When heated with lead oxide and water in a sealed tube at  $145$ – $150^\circ$ , it is converted into isobutyron. The dibromo-compound is accompanied by (1)  $\beta\gamma\delta$ -tribromo- $\beta\delta$ -dimethylpentane,  $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{CMe}_2\text{Br}$ , b. p.  $136$ – $137^\circ/20$  mm.,  $D_4^{20}$  1.8833,  $D_4^{25}$  1.8487,  $n_D^{25}$  1.54654, the constitution of which is settled by Pogorshelski's results (A., 1905, i, 315), and by the fact that the action of 10% potassium hydroxide solution gives, not isobutyryldimethylcarbinol (compare Favorski, A., 1913, i, 12), but the unsaturated bromo-alcohol,  $\text{CMe}_2\cdot\text{CBr}\cdot\text{CMe}_2\cdot\text{OH}$ , the latter remaining unchanged when heated with dilute sulphuric acid. The formation of this tribromo-derivative shows that, on successive replacement of the hydrogen atoms of an organic compound by halogens, these tend to assume positions at carbon atoms formerly free from halogen. (2)  $\beta$ -Bromo- $\beta\delta$ -dimethylpentane,  $\text{CMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{CHMe}_2$ , b. p.  $85^\circ/150$  mm.,  $D_4^{20}$  1.1677,  $D_4^{25}$  1.1415,  $n_D^{25}$  1.44831, which yields dimethylisobutylcarbinol on hydrolysis with water at the ordinary temperature. The percentage yields of the three bromo-derivatives, and of those

similarly obtained by Pogorshelski (*loc. cit.*) from *isobutylene*, are as follows:

	$\beta\delta$ -Dimethyl- $\Delta^{\beta}$ -pentene.	<i>isoButylene</i> .
Monobromo-compound .....	31.3	6.0
Dibromo-compound .....	58.5	72.4
Tribromo-compound .....	10.2	21.6

It is uncertain whether these different results depend on the structure or on the magnitude of the molecule of the unsaturated hydrocarbon.

$\gamma$ -Bromo- $\beta\delta$ -dimethyl- $\Delta^{\beta}$ -pentene,  $\text{CMe}_2\cdot\text{CBr}\cdot\text{CHMe}_2$ , obtained by the action of methyl alcoholic potassium hydroxide on  $\beta\gamma$ -dibromo- $\beta\delta$ -dimethylpentane at  $120^\circ$ , is a liquid, b. p.  $90-91^\circ/100$  mm.,  $D_4^{20}$  1.1915,  $D_4^{21.8}$  1.1681,  $n_D^{21.8}$  1.46823. In this case, as in others, replacement of ethyl by methyl alcohol is advantageous, since the boiling point of the unsaturated bromo-compound and that of the corresponding unsaturated ethyl ether (in this instance,  $\text{CMe}_2\cdot\text{C}(\text{OEt})\cdot\text{CHMe}_2$ ) also formed in the reaction, often differ but slightly and render separation difficult.

Tetramethylallene ( $\beta\delta$ -dimethyl- $\Delta^{\beta\gamma}$ -pentadiene),  $\text{CMe}_2\cdot\text{C}:\text{CMe}_2$ , b. p.  $86.5^\circ/763$  mm.,  $D_4^{20}$  0.7343,  $D_4^{22}$  0.7149,  $n_D^{22}$  1.42473, has an odour similar to that of its homologues, and with tetranitromethane gives a dark cinnamon-red coloration and with mercuric chloride an oily compound which gradually solidifies. It is obtained by the action of alcoholic potassium hydroxide on  $\gamma$ -bromo- $\beta\delta$ -dimethyl- $\Delta^{\beta}$ -pentene in an autoclave at  $130^\circ$  and is accompanied by the unsaturated ether,  $\text{CMe}_2\cdot\text{C}(\text{OEt})\cdot\text{CHMe}_2$ , b. p.  $86^\circ/100$  mm.,  $D_4^{20}$  0.8214,  $D_4^{17.4}$  0.8060,  $n_D^{17.4}$  1.42412. When hydrogenated in alcoholic solution and in presence of platinum black it yields  $\beta\delta$ -dimethylpentane.

The velocities of polymerisation were determined by Lebedev's method (A., 1913, i, 1285) for tetramethylallene, *as*-diethylallene and *aa*-dimethylisoprene ( $\beta\delta$ -dimethyl- $\Delta^{\beta\delta}$ -pentadiene), into which tetramethylallene changes on isomerisation (see below). Comparison of the results obtained with those given by Lebedev (*loc. cit.*) for allene and its di- and tri-methyl derivatives shows that increase in the mass of the substituent entering homologous allene hydrocarbons results in increased velocity of polymerisation at corresponding temperatures.

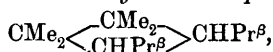
The products of polymerisation of tetramethylallene contain, after removal of the monomeride (see below), 9% of polymeride, the rest consisting of the pure dimeride, 1:1:2:2-tetramethyl-3:4-di-*iso*-

propenylcyclobutane,  $\text{CMe}_2\cdot\text{C}:\text{CMe}_2$ , which is a colourless, mobile

liquid, with a characteristic aromatic odour, b. p.  $87^\circ/9$  mm.,  $D_4^{20}$  0.8563,  $D_4^{25.6}$  0.8457,  $n_D^{25.6}$  1.49535, optical exaltation 2.596; such a high exaltation is explained by the presence of conjugated linkings and of a four-membered ring and by the semicyclic character of the double linking. In spite of its conjugated linkings, the compound gives only a yellow coloration with aqueous sulphur dioxide; with tetranitromethane it yields a dark cinnamon-brown coloration. On oxidation with permanganate in aqueous acetone, it gives successively (1) 1:1:2:2-

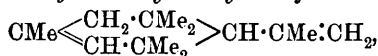
tetramethyl-3-isopropenylcyclobutan-4-one,  $\text{CMe}_2\cdot\text{C}(\text{C}(\text{Me}_2)=\text{CH}_2)\cdot\text{CO}$ , b. p.

104—105°/20 mm., the *semicarbazone* of which has m. p. 229—230° (decomp.); (2) tetramethylsuccinic acid. Hydrogenation in alcoholic solution at a pressure of 67 atmos. and in presence of palladium chloride yields 1 : 1 : 2 : 2-tetramethyl-3 : 4-diisopropylcyclobutane,



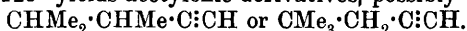
b. p. 106—107°/27 mm.,  $D_4^0$  0.8181,  $D_4^{17}$  0.8035,  $n_D^{17}$  1.44580.

$\beta\delta$ -Dimethyl- $\Delta^{\delta\delta}$ -pentadiene or  $\alpha\alpha$ -dimethylisoprene, which is the monomeride into which tetramethylallene undergoes isomerisation, has been obtained by several investigators, but uncertainty exists as to its physical constants, which the author finds to be: b. p. 93°/759 mm.,  $D_4^0$  0.7515,  $D_4^{23}$  0.7343,  $n_D^{23}$  1.43904, optical exaltation 1.544. On polymerisation, this hydrocarbon gives (1) 75.9% of the dimeride, 1 : 3 : 3 : 5-pentamethyl-4-methylethenyl- $\Delta^1$ -cyclohexene,



which is a mobile liquid, b. p. 122—123°/29 mm.,  $D_4^0$  0.8799,  $D_4^{17}$  0.8696,  $n_D^{17}$  1.48767, and differs in properties from the dimeride obtained by Grignard (A., 1902, i, 142) by the action of sulphuric acid at 0°; (2) 24.1% of polymeride, which is a transparent, gelatinous mass, partly soluble and partly insoluble.

Polymerisation of tetramethylallene in presence of sodium or potassium at 125° yields acetylenic derivatives, possibly



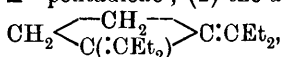
The ease with which tetramethylallene undergoes isomerisation into butadiene derivatives, and the fact that it also, although with difficulty, yields acetylene derivatives with a different carbon skeleton, indicate a condition of considerable tension in the molecule which contains three carbon atoms united by two double linkings and possessing no hydrogen atoms.

$\gamma\delta$ -Dibromo- $\gamma$ -ethylpentane,  $\text{CEt}_2\text{Br} \cdot \text{CHMeBr}$ , prepared by brominating triethylcarbinol at 80—85°, has b. p. 98—99°/21 mm.,  $D_4^0$  1.5489,  $D_4^{23.7}$  1.5211,  $n_D^{23.7}$  1.50957. Ipatiev (A., 1906, i, 401) gives a high value for the boiling point of this compound, namely, 106—109°/20 mm., and for the homologous bromides,  $\text{C}_5\text{H}_{10}\text{Br}_2$  and  $\text{C}_6\text{H}_{12}\text{Br}_2$ .

$\delta$ -Bromo- $\gamma$ -ethyl- $\Delta\gamma$ -pentene,  $\text{CEt}_2 \cdot \text{CMeBr}$ , obtained by the action of methyl alcoholic potassium hydroxide on the above dibromo-compound, has b. p. 94°/100 mm.,  $D_4^0$  1.1912,  $D_4^{22.5}$  1.1661,  $n_D^{22.5}$  1.46980. When heated at 130° with alcoholic potassium hydroxide, it yields *as*-Diethylallene,  $\text{CEt}_2 \cdot \text{C} \equiv \text{CH}_2$ , b. p. 97°/754 mm.,  $D_4^0$  0.7560,  $D_4^{23.9}$  0.7355 (Ipatiev gave  $D_0^0$  0.7475),  $n_D^{23.9}$  1.43683, optical exaltation 0.564, which undergoes isomeric change into the corresponding acetylene derivative,  $\text{CHEt}_2 \cdot \text{C} \equiv \text{CH}$ , in presence of sodium, whilst, when heated, it polymerises and isomerises into 1-methyl-2-ethylbutadiene or  $\gamma$ -ethyl- $\Delta^{\delta\delta}$ -pentadiene,  $\text{CHMe} \cdot \text{CEt} \cdot \text{CH} \cdot \text{CH}_2$ . These observations not only disagree with Lebedev's views (*vide supra*), but contradict Ipatiev's results ("Allene Hydrocarbons," St. Petersburg, 1898, p. 25), on which the author casts doubt.

When subjected to Lebedev's polymerisation conditions, *as*-diethyl-

allene gives (1)  $\gamma$ -ethyl- $\Delta^{85}$ -pentadiene; (2) the *dimeride*,

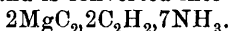


b. p. 102—104°/10 mm.,  $D_4^{16.5}$  0.8569,  $n_D^{16.5}$  1.48643, which gives diethyl ketone and succinic acid on oxidation by means of 1% permanganate solution at 0°.

T. H. P.

**Some Reactions of Liquid Anhydrous Ammonia and Acetylene.** F. G. COTTRELL (*J. Physical Chem.*, 1914, 18, 85—100).

—Mixtures of liquid ammonia and acetylene react with metallic magnesium at the ordinary temperature and on evaporation of the solution, the crystalline compound,  $\text{MgC}_2, 2\text{C}_2\text{H}_2, 5\text{NH}_3$ , is obtained together with ethylene and a small quantity of ethane. At atmospheric pressure, this compound loses a portion of its ammonia, when the temperature reaches 2°, and is converted into the compound



The latter is stable up to 60°, at which temperature acetylene and ammonia are given off, leaving a residue consisting of magnesium amide and nitride together with a little carbide. By the removal of ammonia from the original compound at low temperatures, magnesium carbide is obtained in nearly pure condition.

The electrical conductivity of mixtures of liquid ammonia and acetylene is very much smaller than that of mixtures in which an alkali metal has been dissolved, and from this observation the author draws the conclusion that there is no formation of ammonium carbide or acetylides. These mixtures have no action on zinc, aluminium or copper at the ordinary temperature.

Anhydrous liquid ammonia dissolves metallic magnesium to a slight extent with the formation of a faintly blue solution, which gradually decomposes with the production of magnesiumamide and hydrogen. This reaction is similar to that given by the alkali and alkaline earth metals.

H. M. D.

**Action of Acetylene Hydrocarbons on Organo-zinc and Organo-magnesium Compounds. Bromo- and Di-iodo-acetylenes.**

SH. I. IOCHITSCH (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1545—1551).—The author discusses the views concerning the structure of acetylene and its derivatives advanced by Nef (A., 1898, i, 102), who regards the halogen-substituted acetylenes as derived from the acetylidene modification  $\text{CH}_2:\text{C}$ .

The two cases of bromoacetylene and di-iodoacetylene are considered, and it is shown that, if these have the structures  $\text{CHBr}:\text{C}$  and  $\text{CI}_2:\text{C}$ , treatment of them with an organo-magnesium haloid should give a product yielding compounds containing an ethylene linking, and a halogen atom under the action of either water, or carbon dioxide, or an aldehyde or a ketone. On the other hand, if the true constitutions of these halogenated acetylenes are represented by  $\text{CH}:\text{CBr}$  and  $\text{CI}:\text{CI}$ , the final products obtained as described above should contain an acetylene linking and no halogen.

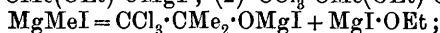
The product obtained from bromoacetylene and magnesium ethyl



bromide gives: (1) with water, acetylene; (2) with carbon dioxide, acetylenedicarboxylic acid; (3) with acetone,  $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol, m. p. 94—96°, b. p. 205—206°; (4) with methylcyclohexanone, the glycol,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 & \text{---} & \text{CH}_2 \\ \text{CHMe} & & \text{CH}_2 \end{smallmatrix} \text{C(OH)C:C} \cdot \text{C(OH)} \begin{smallmatrix} \text{CH}_2 & \text{---} & \text{CH}_2 \\ \text{CH}_2 & & \text{CHMe} \end{smallmatrix} \text{CH}_2$ , m. p. 83—85°. Hence the structure of bromoacetylene must be  $\text{CH}:\text{CBr}$ , its reaction with magnesium ethyl bromide being represented thus:  $\text{CH}:\text{CBr} + 2\text{MgEtBr} = \text{MgBr} \cdot \text{C}:\text{C} \cdot \text{MgBr} + \text{C}_2\text{H}_6 + \text{EtBr}$ .

Similarly, the product obtained from di-iodoacetylene and magnesium methyl iodide gives: (1) with water, acetylene; (2) with carbon dioxide, acetylenedicarboxylic acid; (3) with acetone,  $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol. Hence the structure of di-iodoacetylene must be represented by  $\text{CI}:\text{CI}$ , and its reaction with magnesium methyl iodide by:  $\text{CI}:\text{CI} + 2\text{MgMeI} = \text{MgI} \cdot \text{C}:\text{C} \cdot \text{MgI} + 2\text{MeI}$ . T. H. P.

**Synthesis of Trihalogenated Alcohols.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 553—554).—Dimethyltrichloromethylcarbinol (compare Willgerodt, A., 1882, 491; 1883, 1079; Iocitsch, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 353) may be readily obtained by the action of magnesium methyl iodide on ethyl trichloroacetate, followed by decomposition of the product with water: (1)  $\text{CCl}_3 \cdot \text{CO}_2\text{Et} + \text{MgMeI} = \text{CCl}_3 \cdot \text{CMe}(\text{OEt}) \cdot \text{OMgI}$ ; (2)  $\text{CCl}_3 \cdot \text{CMe}(\text{OEt}) \cdot \text{OMgI} +$



(3)  $\text{CCl}_3 \cdot \text{CMe}_2 \cdot \text{OMgI} + \text{H}_2\text{O} \rightarrow \text{CCl}_3 \cdot \text{CMe}_2 \cdot \text{OH}$ . T. H. P.

**Action of Zinc on Halogen Derivatives of Alcohols and their Acetic Ethers. Synthesis of Mono- and Di-chloro-alcohols.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1551—1553).—The author has previously shown (preceding abstract) that, when the product of the interaction of ethyl trichloroacetate and magnesium methyl iodide is treated with water, dimethyltrichloromethylcarbinol results. It is now found that similar reactions occur with ethyl chloro- and dichloro-acetates.

With ethyl chloroacetate, the reaction is expressed by the following equations:  $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{Et} + 2\text{MgMeI} = \text{CH}_2\text{Cl} \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{MgI} + \text{MgI} \cdot \text{OEt}$  and  $\text{CH}_2\text{Cl} \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{MgI} + \text{H}_2\text{O} = \text{CH}_2\text{Cl} \cdot \text{CMe}_2 \cdot \text{OH} + \text{MgI} \cdot \text{OH}$ . Dimethylchloromethylcarbinol, thus obtained, has b. p. 127—129°, m. p. about -20°,  $D_0^\circ$  1.0892,  $D_{20}^\circ$  1.0668 (compare Krasuski, A., 1901, i, 246; Tiffeneau, A., 1902, i, 449); its *acetyl* derivative,  $\text{CH}_2\text{Cl} \cdot \text{CMe}_2 \cdot \text{OAc}$ , b. p. 149—151°,  $D_0^\circ$  1.0839,  $D_{20}^\circ$  1.0634, was prepared. Under ordinary conditions, zinc reacts neither with this alcohol nor with its acetyl compound.

Similarly, ethyl dichloroacetate gives: (1) *as*-dichloroacetone and (2) dimethyldichloromethylcarbinol, b. p. 149.5—150°/740 mm., m. p. -8°,  $D_0^\circ$  1.2692,  $D_{20}^\circ$  1.2474 (Oeconomides, A., 1881, 793, gave b. p. 143.5° and  $D_0^\circ$  1.0335), the acetyl derivative of which,  $\text{CHCl}_2 \cdot \text{CMe}_2 \cdot \text{OAc}$ , has b. p. 171.5—172.5°/745 mm.,  $D_0^\circ$  1.2237,  $D_{20}^\circ$  1.2017. In this case the reactions are expressed as follows:  $\text{CHCl}_2 \cdot \text{CO}_2\text{Et} + \text{MgMeI} = \text{CHCl}_2 \cdot \text{CMe}(\text{OEt}) \cdot \text{O} \cdot \text{MgI} \rightarrow \text{CHCl}_2 \cdot \text{COMe}$  and  $\text{CHCl}_2 \cdot \text{CO}_2\text{Et} + 2\text{MgMeI} = \text{MgI} \cdot \text{OEt} + \text{CHCl}_2 \cdot \text{CMe}_2 \cdot \text{OMgI} \rightarrow \text{CHCl}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ . Neither

this alcohol nor its acetyl derivative reacts appreciably with zinc under ordinary conditions. T. H. P.

**Synthesis of Halogen Derivatives of Alcohols by means of Organo-magnesium Compounds.** SH. I. IocITSCH (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 443—446).—The action of chloral on an ethereal solution of magnesium ethyl bromide yields ethylene and a product which forms trichloroethyl alcohol when decomposed with ice:  $\text{CCl}_3 \cdot \text{CHO} + \text{MgEtBr} = \text{C}_2\text{H}_4 + \text{CCl}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{MgBr} \rightarrow \text{CCl}_3 \cdot \text{CH}_2 \cdot \text{OH}$ .

The action of chloral on an ethereal solution of magnesium amyl bromide yields  $\beta$ -methyl- $\Delta\gamma$ -butene and a product which is decomposed by ice, forming trichloroethyl alcohol and about 10% of an alcohol, b. p. 104—106°/15 mm., possibly trichloromethylisobutylcarbinol:  $\text{CCl}_3 \cdot \text{CHO} + \text{CH}_2\text{Pr}^\beta \cdot \text{CH}_2 \cdot \text{MgBr} = \text{CHPr}^\beta \cdot \text{CH}_2 + \text{CCl}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{MgBr} \rightarrow \text{CCl}_3 \cdot \text{CH}_2 \cdot \text{OH}$ . T. H. P.

**Action of Organo-magnesium Compounds on Epichlorohydrin and Epibromohydrin.** SH. I. IocITSCH (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 6—8. Compare this vol., 403; also Kling, A., 1904, i, 2).—The action of magnesium ethyl bromide on epichlorohydrin yields  $\alpha$ -chloro- $\gamma$ -bromopropan- $\beta$ -ol, b. p. 190—191°/765 mm., and  $\beta$ -chloromethylbutan- $\alpha$ -ol,  $\text{CH}_2\text{Cl} \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{OH}$ , b. p. 162—164°/765 mm. From magnesium ethyl bromide and epibromohydrin,  $\alpha\gamma$ -dibromopropan- $\beta$ -ol,  $\text{CH}_2\text{Br} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Br}$ , b. p. 89—91°/15 mm., was obtained.

The interaction of magnesium phenyl bromide and epichlorohydrin yields  $\alpha$ -chloro- $\gamma$ -bromopropan- $\beta$ -ol (*vide supra*),  $\alpha$ -chloro- $\gamma$ -phenylpropan- $\beta$ -ol,  $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Ph}$ , b. p. 256—257°, and diphenyl.

These reactions are represented as follows:  $\text{CH}_2\text{Cl} \cdot \text{CH} \begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{O} \end{smallmatrix} + \text{MgRX} = \text{CH}_2\text{R} \cdot \text{CH}(\text{O} \cdot \text{MgX}) \cdot \text{CH}_2\text{Cl}$  or  $\text{MgX} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CHR} \cdot \text{CH}_2\text{Cl}$ , and this  $+ \text{H}_2\text{O} = \text{CH}_2\text{R} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$  or  $\text{OH} \cdot \text{CH}_2 \cdot \text{CHR} \cdot \text{CH}_2\text{Cl}$  (compare Grignard, A., 1901, i, 679). T. H. P.

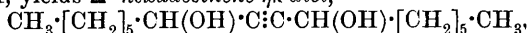
**Action of Acetylene and its Monosubstituted Derivatives on Organo-metallic Compounds of Magnesium and Zinc.** SH. I. IocITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 430—431).—Treatment of dimagnesium acetylene dibromide with acetaldehyde and decomposition of the complex formed by means of water proceed according to the equations:  $\text{MgBr} \cdot \text{C} \equiv \text{C} \cdot \text{MgBr} + 2\text{CH}_3 \cdot \text{CHO} = \text{MgBr} \cdot \text{O} \cdot \text{CHMe} \cdot \text{C} \equiv \text{C} \cdot \text{CHMe} \cdot \text{O} \cdot \text{MgBr} \rightarrow + 2\text{H}_2\text{O} = \text{OH} \cdot \text{CHMe} \cdot \text{C} \equiv \text{C} \cdot \text{CHMe} \cdot \text{OH} + 2\text{MgBr} \cdot \text{OH}$ .

$\Delta\gamma$ -Hexinene- $\beta\epsilon$ -diol, thus obtained, is a viscous, glycerol-like liquid, b. p. 116—116.5°/9 mm.,  $D_4^{20}$  1.0344,  $D_4^{20}$  1.0210, sparingly soluble in water. Bromine (2 atoms) and iodine combine with it, forming crystalline compounds. T. H. P.

**Syntheses by means of Magnesium-acetylene and Magnesium-diacetylene Compounds.** SH. I. IocITSCH (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 656—659).—In order to illustrate the general

character of the preparation of  $\gamma$ -glycols and homologues of propargyl alcohol by means of magnesium acetylene haloids, the following syntheses have been effected.

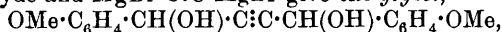
Heptaldehyde, when treated with  $\text{MgI} \cdot \text{C} \equiv \text{C} \cdot \text{MgI}$ , containing  $\text{CH}_3 \cdot \text{C} \cdot \text{MgI}$ , yields  $\Delta^8$ -hexadecinene- $\eta\kappa$ -diol,



m. p.  $51^\circ$ , and a liquid, probably  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OH}) \cdot \text{C} \equiv \text{CH}$ , giving metallic precipitates with ammoniacal cuprous chloride and alcoholic silver nitrate solutions.

Bromal and  $\text{MgBr} \cdot \text{C} \equiv \text{C} \cdot \text{MgBr}$  give  $\alpha\alpha\zeta\zeta\zeta$ -hexabromo- $\Delta^7$ -hexinene- $\beta\epsilon$ -diol,  $\text{CBr}_3 \cdot \text{CH}(\text{OH}) \cdot \text{C} \equiv \text{C} \cdot \text{CH}(\text{OH}) \cdot \text{CBr}_3$ , m. p.  $244-245^\circ$ ; the corresponding acetyl derivative, m. p.  $127^\circ$ , was prepared.

Anisaldehyde and  $\text{MgBr} \cdot \text{C} \equiv \text{C} \cdot \text{MgBr}$  give the glycol,



m. p.  $121-123^\circ$ .

Diethyl ketone and  $\text{MgI} \cdot \text{C} \equiv \text{C} \cdot \text{MgI}$  give  $\gamma\zeta$ -diethyl- $\Delta^8$ -octinene- $\gamma\zeta$ -diol,  $\text{OH} \cdot \text{C} \cdot \text{Et}_2 \cdot \text{C} \equiv \text{C} \cdot \text{C} \cdot \text{Et}_2 \cdot \text{OH}$ , which forms tabular crystals, m. p.  $73^\circ$ , b. p.  $140-141^\circ/20$  mm.,  $242-244^\circ/762$  mm.

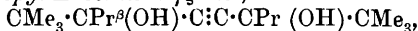
Methyl butyl ketone and the same reagent give  $\epsilon\theta$ -dimethyl- $\Delta^5$ -dodecinene- $\epsilon\theta$ -diol,  $\text{CH}_3 \cdot [\text{CH}_2]_3 \cdot \text{CMe}(\text{OH}) \cdot \text{C} \equiv \text{C} \cdot \text{CMe}(\text{OH}) \cdot [\text{CH}_2]_3 \cdot \text{CH}_3$ , which forms crystals, m. p.  $66-68^\circ$ .

Diisopropyl ketone and the same reagent give  $\beta\eta$ -dimethyl- $\gamma\zeta$ -diisopropyl- $\Delta^8$ -octinene- $\gamma\zeta$ -diol,  $\text{OH} \cdot \text{CPr}^\beta \cdot \text{C} \equiv \text{C} \cdot \text{CPr}^\beta \cdot \text{OH}$ , crystals, m. p.  $106-107^\circ$ .

Methyl hexyl ketone and the same reagent give  $\eta\mu$ -dimethyl- $\Delta^4$ -octadecinene- $\theta\lambda$ -diol,  $\text{C}_6\text{H}_{13} \cdot \text{CHMe} \cdot \text{C}(\text{OH}) \cdot \text{C} \equiv \text{C} \cdot \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{C}_6\text{H}_{13}$ , crystals, m. p.  $87-88^\circ$ .

Mesityl oxide and the same reagent give  $\beta\delta\eta$ -tetramethyldeca- $\Delta^{\beta\theta}$ -dien- $\Delta^4$ -inene- $\delta\eta$ -diol,  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CMe}(\text{OH}) \cdot \text{C} \equiv \text{C} \cdot \text{CMe}(\text{OH}) \cdot \text{CH} \cdot \text{CMe}_2$ , crystals, m. p.  $102^\circ$ .

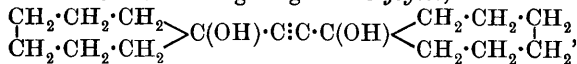
isoButyl tert.-butyl ketone and the same reagent give  $\beta\beta\eta\eta$ -tetramethyl- $\gamma\zeta$ -diisopropyl- $\Delta^8$ -octinene- $\gamma\zeta$ -diol,



crystals, m. p. about  $136^\circ$ .

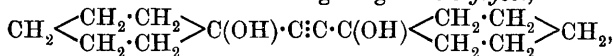
Acetophenone and the same reagent give  $\beta\epsilon$ -diphenyl- $\Delta^7$ -hexinene- $\beta\epsilon$ -diol,  $\text{OH} \cdot \text{CMePh} \cdot \text{C} \equiv \text{C} \cdot \text{CMePh} \cdot \text{OH}$ , crystals, m. p.  $156-158^\circ$ .

Suberone and the same reagent give the glycol,



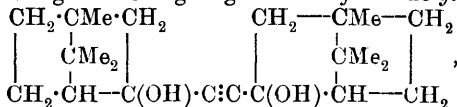
crystals, m. p.  $76-78^\circ$ .

cycloHexanone and the same reagent give the glycol,



crystals, m. p.  $102^\circ$ .

Camphor and  $\text{MgBr} \cdot \text{C} \equiv \text{C} \cdot \text{MgBr}$  give the crystalline glycol,



m. p.  $204-206^\circ$ .

Chloral and dimagnesium dipropargyl dibromide give *ααακκκ-hexachloro-Δ<sup>77</sup>-decadi-inens-βθ-diol*,

$\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{C} \equiv \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \equiv \text{C} \cdot \text{CH}(\text{OH}) \cdot \text{CCl}_3$ ,  
crystals, m. p. 105—107°.

The above results give justification for stating that organo-magnesium compounds with an acetylene linking react with all organic and inorganic compounds with which organo-magnesium compounds containing saturated radicles enter into reaction. The fact that dimagnesium acetylene di-iodide may be kept unchanged for years in ordinary glass vessels, and the readiness with which it reacts with aliphatic aldehydes and ketones, render it an excellent reagent for the detection of the carbonyl group.

T. H. P.

**Basic Function of Methoxyl.** Remarks on the Communication of Kauffmann and Kieser. BERNHARD FLÜRSCHHEIM (*Ber.*, 1914, 47, 590).—The author indicates that the views of Kauffmann and Kieser (this vol., i, 54) and of others on the distribution of valency are substantially those which he advanced in T., 1910, 97, 91.

J. C. W.

**Hydrolecithin.** FRIEDRICH RITTER (*Ber.*, 1914, 47, 530—532).—Hitherto, a pure specimen of hydrolecithin has not been obtained. Paal and Oehme (*A.*, 1913, i, 584), for example, found that their product yielded on hydrolysis a number of acids besides stearic acid. A purified lecithin has now been obtained by extracting the air-dried yolks of fresh eggs with light petroleum and ether, and then extracting the residue left on evaporating the solution by methyl alcohol, all the operations being performed, as far as possible, in absence of air, light and moisture. This material was then reduced by Paal's method and the product was repeatedly precipitated from the chloroform solution by methyl acetate. Pure *distearyl-lecithin*,  $\text{C}_{44}\text{H}_{90}\text{O}_9\text{NP}$ , was thus obtained, the only acid which could be isolated from the hydrolysis product being stearic acid. It is thus proved that there are egg-lecithins in which the acids are exclusively those of the stearic acid series, but whether it is the rule that an unsaturated member always enters into the composition of the molecule or that individual, saturated lecithins do exist in the egg has yet to be determined.

J. C. W.

**Iodine Values of Lecithins.** J. CRUICKSHANK (*J. Path. Bact.*, 1914, 18, 428—431).—Previous authors dealing with lecithins of various origins and prepared in different ways give the iodine values as varying between 48 and 100. In the present research, lecithins were prepared from tissues (heart, liver, spleen, pancreas, etc.) by the author's method, and the iodine values varied from 37 to 117. The same tissue yields lecithins of varying iodine value in successive extractions, being highest in the latest extracts.

W. D. H.

**Catalytic Synthesis of Formic Acid under Pressure.** G. BREDIG and S. R. CARTER (*Ber.*, 1914, 47, 541—545).—All the methods for the reduction of carbon dioxide or metallic hydrogen carbonates to formic acid or its salts have hitherto required agents of greater

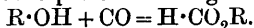
activity than gaseous hydrogen, such as alkali metals, alkali hydrides, amalgams, hydrogen evolved under high cathode potential, or hydrogen under the influence of the silent discharge. It is known that catalysts like the platinum metals speedily bring about the decomposition of free formic acid, but not of formates (compare Blackadder, A., 1912, ii, 36). Still, Kleinstück (A., 1910, ii, 715) reduced an alkaline carbonate by hydrogen in presence of palladium-alumina under ordinary pressures, and Wieland (A., 1912, ii, 347) detected a trace of formic acid in the product obtained by shaking a saturated solution of carbon dioxide with hydrogen and palladium-black.

From a consideration of the law of mass action, it appeared that if the partial pressure due to the formic acid were reduced by the addition of carbonates or salts of other weak acids, the reduction would proceed farther. This was found to be the case, and the application of a catalyst and high pressure in addition were found to hasten the reaction. Thus, a solution of potassium hydrogen carbonate at 70°, with hydrogen under 60 atmospheres pressure, gave in twenty-four hours a 0.6% yield of the formate, and with spongy palladium in addition, nearly a 75% yield, calculated on the salt used. Sodium carbonate, however, under the latter conditions gave only a 0.4% yield in seven hours, from which it follows that the partial pressure due to carbon dioxide is of paramount importance. Calcium carbonate with hydrogen (50 atm.) and carbon dioxide (20 atm.) at 70°, with the catalyst, gave a 100% yield in four and a-half hours. Borax was also effective.

The bomb used was an improved form of that described by Stuckert and Enderli (A., 1913, ii, 1038). The process has already been notified for a patent, but the recent notices of Bach (this vol., i, 15) and of F. Fischer and Prziza (this vol., ii, 198) have called for the present communication, although the whole study of the equilibria, kinetics, and catalysis of the formation of formic acid is the real aim of the authors.

J. C. W.

**Reactions Under High Pressures. II. The Addition of Carbon Monoxide to Alcohols.** ARTHUR STÄHLER (*Ber.*, 1914, 47, 580—590).—Many attempts have been made to prepare aliphatic acids by the addition of carbon monoxide to the sodium compounds of alcohols, according to the scheme  $R\cdot OH + CO = R\cdot CO_2H$ , a synthesis which finds a place in the text-books. Some authors have met with no success and none have obtained more than traces of the expected acids, whilst it seems that it has not occurred to any of these workers that an addition might take place according to the scheme :



The author has now made use of compressed carbon monoxide in this connexion, instead of working under ordinary pressures, in order to arrive more quickly at some definite result.

In the first place, pure dry sodium ethoxide was treated at 180° with dry carbon monoxide under 300 atmospheres pressure until no more gas was absorbed. The volatile acids were titrated, boiled with mercuric oxide, which was weighed, filtered from mercury, and treated with hydrogen sulphide, which deposited the merest traces of mercuric sulphide. Formic acid was therefore the main product.

Sodium methoxide, *isobutyloxyde*, and *isoamlyloxyde* also gave no more than traces of the next highest fatty acids. The various results obtained by previous workers are explained by assuming that, during the days or weeks that the experiments had lasted, the sodium alkylloxides themselves had undergone decomposition. In presence of a trace of moisture, sodium phenoxide gave phenol and sodium formate, a reaction which has been notified for a patent.

These unsuccessful experiments were then modified. To begin with, dry sodium ethoxide was treated with compressed carbon monoxide at lower temperatures, when a small quantity of ethyl formate was obtained. This implies the liberation of alcohol during the reaction and leads to the assumption that an intermediate compound is formed. Methyl iodide, however, failed to indicate the existence of such a compound and no explanation is as yet forthcoming. At any rate, the conclusion is drawn that some intermediate additive compound is formed with which alcohol reacts with the production of ethyl formate and the re-formation of sodium ethoxide. In other words, sodium ethoxide should behave as a catalyst in the synthesis of ethyl formate. This was found to be the case. Sodium and excess of alcohol were treated with compressed carbon monoxide at ordinary temperatures, heat having a bad effect, and high yields of the ester were obtained.

For example, 23 grams of sodium and 625 grams of ethyl alcohol gave in fourteen days, 423.5 grams of pure ethyl formate, another 68.5 grams being dissolved in the water with which the crude distillate was washed. The free alkali left still amounted to 60% of the original. Similarly, 15 grams of sodium and 500 c.c. of methyl alcohol yielded in eleven days, 590 grams of methyl formate, but by this time the alkali was also destroyed. *isoAmyl* alcohol reacted in the same way, but with much less success. The idea that the reaction could be carried over to syntheses involving ethyl formate was also fulfilled, for 18 grams of the sodium compound of hydroxymethyleneacetophenone were obtained by treating 25 grams of acetophenone with carbon monoxide under 150 atmospheres in the presence of 10 grams of sodium dissolved in 200 grams of alcohol.

J. C. W.

**Esterification of Glycerol by Acetic Acid in Presence of Catalysts.** J. B. SENDERENS and JEAN ABOULENC (*Compt. rend.*, 1914, 158, 581—583. Compare Böttiger, A., 1891, 1183).—The three catalysts tried in the esterification of monohydric alcohols (compare A., 1911, i, 600, 637; ii, 1080; 1912, i, 694; 1913, i, 41, 42, 700) are also effective as catalysts for esterification of glycerol. With a mixture of glycerol (1 mol.) and glacial acetic acid (3 mols.) boiled for one hour, the amount of acid converted into ester is increased from  $\frac{2}{5}$  mol. without a catalyst to  $1\frac{1}{5}$  mol., using potassium hydrogen sulphate, to  $1\frac{1}{3}$  mol. using anhydrous aluminium sulphate, and to  $1\frac{1}{2}$  mol. using 1% sulphuric acid. Prolonging the time of reaction causes no further esterification in the presence of the catalysts, but in the case of sulphuric acid if the proportion of acetic acid is increased to 12 mols. then the whole of the glycerol is converted into triacetin. Potassium hydrogen sulphate is not a satisfactory catalyst, since on

cooling at the end of the reaction it forms a hard mass from which it is difficult to separate the ester formed. W. G.

**The Composition of Paint Vapours.** HENRY A. GARDNER (*J. Ind. Eng. Chem.*, 1914, 6, 91—95. Compare Armstrong and Klein, A., 1913, i, 587).—Purified air was drawn through cylinders of galvanised sheet iron or large glass bottles, previously coated with the paint or oil to be investigated, and then through a series of bottles containing absorbents. The first bottle contained either sulphuric acid ("66°") or fuming sulphuric acid, and the succeeding bottles, a solution of barium hydroxide. In some cases a heated glass tube was interposed between the painted cylinders and the sulphuric acid bottle. Carbon monoxide was estimated by the iodine pentoxide method. Experiments were made (1) using oils alone, namely, raw linseed oil, soja bean oil, tung oil and menhaden oil; (2) using paints mixed with raw linseed oil, no turpentine or drier being added, the paints being basic carbonate-white lead, basic sulphate-white lead, zinc oxide, and lithopone; (3) using paints containing turpentine.

The conclusions arrived at are as follows: When linseed oil or similar drying oils are spread in thin layers, the absorption of oxygen which takes place is accompanied by the evolution of considerable amounts of carbon dioxide and organic substances. Carbon monoxide is also evolved in small amount.

Oil paints containing lead or zinc pigments do not emit volatile compounds of metallic nature.

Drying paints evolve acid substances soluble in water, such as formic acid, as well as acid substances which are apparently of a fatty nature. Carbon dioxide and carbon monoxide are also present in the vapours from the drying paint. The type of pigment used in the paint may directly affect the amount and character of the volatile substances produced. Basic pigments apparently stimulate the evolution of such products.

Aldehydic substances are present in the vapours from drying oil paints; they probably have a marked bactericidal effect on pathogenic bacteria, and this would account for the sanitary value ascribed to oil-pigment paints. T. S. P.

**Strongly Unsaturated Higher Fatty Acids in Sardine Oil.** RIKÔ MAJIMA and TEPPEI OKADA (*Sci. Reports Tohoku Imp. Univ.*, 1914, 3, 1—18).—The investigation was primarily undertaken with the object of preparing pure cluepanodonic acid (compare Isujimoto, *Chem. Zentr.*, 1909, i, 1491, 1616) and determining its constitution. This hope has not been realised, but the existence of unsaturated fatty acids of the series  $C_nH_{2n-8}O_2$  and  $C_nH_{n-10}O_2$ , and particularly of such in which  $n=20$  and 22 has been established.

The oil, which had an iodine number 182.8, acid number 1.605, saponification number 198.3, was purified by agitating its solution in light petroleum with 10% potassium hydroxide solution at a temperature below 10°. The purified oil had D 0.910, iodine number 185. It is readily saponified by potassium hydroxide in cold aqueous alcoholic solution, or by shaking its solution in light petroleum with

aqueous potassium hydroxide and alcohol. The fatty acids are distilled under diminished pressure in an atmosphere of carbon dioxide and have the iodine number 189.

Bromination of the fatty acids is effected in glacial acetic acid, or, better, in ethereal solution. The bromo-acids darken from about 100°, and have m. p. about 220° (decomp.). The analytical results agree with those required by the formula  $C_{18}H_{23}O_2Br_8$ .

Debromination of the polybromo-acids is best effected by warming with zinc dust in glacial acetic acid solution, whereby, however, a slight alteration of the fatty acids formed is unavoidable. The high molecular weight (338) and the iodine number (380) of the acid obtained render the formula  $C_{18}H_{28}O_2$  untenable.

Attempts to separate the polybromo-fatty acids by means of acetone were unsuccessful; in a series of experiments, the soluble portions were progressively poorer in bromine, but, on the other hand, the bromine content of the residue did not greatly increase, so that the soluble polybromo-fatty acid is possibly altered by loss of hydrobromic acid. The results obtained, however, show the lack of uniformity in the material.

Catalytic reduction of the debrominated fatty acids in ethereal solution by Willstätter's method gives a saturated fatty acid, m. p. 75°, mol. wt. 349. The unsaturated fatty acids must, therefore, be derived from the higher homologues of stearic acid, such as  $C_{20}H_{40}O_2$  or  $C_{22}H_{44}O_2$ , or the corresponding unsaturated acids.

Attempts to separate the fatty acids by fractional solidification are also described. The liquid portion obtained after cooling first with ice and salt and then with solid carbon dioxide and ether is very highly unsaturated, and, on catalytic reduction, yields saturated acids of high molecular weight which are closely related to those described in the preceding paragraph.

The fatty acids of the liquid portion were converted into the corresponding methyl esters by neutralisation with potassium hydroxide and action of methyl sulphate. Attempts to separate them by fractional distillation under greatly reduced pressure were fruitless on account of polymerisation.

The portion of the fatty acids which remains liquid after cooling with ice and salt has been oxidised with potassium permanganate. Two isomeric dihydroxypalmitic acids have been thereby obtained, m. p. 125° and 112—114° respectively; in addition, very small quantities of a compound, m. p. 215—218°, which has the composition of decahydroxybehenic acid,  $C_{22}H_{44}O_2(OH)_{10}$ , are produced. The presence of tetrahydroxy- or hexahydroxy-stearic acid could not be established.

H. W.

**Methylcarbonato-derivatives of Hydroxy-acids. II. Derivatives of Glycollic and Lactic Acids.** EMIL FISCHER and HERMANN O. L. FISCHER (*Ber.*, 1914, 47, 768—780. Compare A., 1913, i, 1194).—In continuation of their previous investigation, the authors describe the preparation of *methylcarbonato-acetic acid* in the pure state. The substance is readily converted into the *chloride*, which on treatment with aniline is transformed into the corresponding *anilide*. The



latter is converted by dilute aqueous alkali into the phenylurethane of glycollic acid. Probably, diketophenyltetrahydro-oxazole (annexed formula) is first formed by loss of methyl alcohol, which, according to Lambling (A., 1902, i, 537), is readily converted into the urethane of glycollic acid. A somewhat similar change is shown to occur with the anilide of methylcarbonatomandelic acid (described in the previous paper as the aniline compound of methylcarbonatomandelic acid). The scope of this method of preparing urethanes or oxalole derivatives has not yet been determined, but it cannot be applied in the case of secondary bases in which the possibility of the formation of oxalole derivatives is excluded.

Methylcarbonatoacetyl chloride reacts readily with benzene in the presence of aluminium chloride. The *methylcarbonato*-derivative of *benzoylcarbinol* is thereby formed, from which the latter substance is obtained by means of alkali. Analogous experiments with acetoxyacetyl chloride have been described by Anschütz and Förster (A., 1909, i, 715).

The behaviour of lactic acid is similar to that of glycollic acid.

A suspension of glycollic acid in chloroform is treated with three portions of dimethylaniline and methyl chloroformate; after removal of the base, the solution, is evaporated in a vacuum, the residue dissolved in acetone, and gradually treated with a 25% aqueous solution of potassium hydrogen carbonate. After removal of by-products with ether, the solution is acidified with hydrochloric acid, whereby methylcarbonatoacetic acid, b. p. ca.  $112^{\circ}/0.6$  mm., m. p.  $33-34^{\circ}$ , is obtained in 40% yield. The *ammonium* salt, colourless leaflets, *silver* salt, microscopic needles, and *lead* salt, microscopic plates, are described.

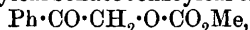
*Methylcarbonatoacetyl chloride*, b. p. ca.  $47^{\circ}/0.75$  mm., is prepared by the action of thionyl chloride on the acid. It is only slowly decomposed by cold water; with dry pyridine, it gives a red to brown solution, with quinoline, the coloration is pale red.

*Methylcarbonatoacetomethylanilide*,  $\text{NMePh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}_2\text{Me}$ , prisms or plates, m. p.  $82-83^{\circ}$  after slight softening, is prepared by mixing methylaniline and methylcarbonatoacetyl chloride in ethereal solution. When treated with *N*-sodium hydroxide solution and subsequently with hydrochloric acid, it gives the *methylanilide* of *glycollic acid*, m. p.  $52.5-53^{\circ}$ .

Methylcarbonatoacetanilide, m. p.  $101-102^{\circ}$ , is prepared in the same manner as the corresponding methylanilide. When treated with *N*-sodium hydroxide solution at the ordinary temperature and then acidified, an evolution of carbon dioxide is not observed and the phenylurethane of glycollic acid is almost quantitatively precipitated. Diazomethane converts the latter substance into the corresponding *methyl ester*, colourless rods, m. p.  $73.5-74^{\circ}$ , the constitution of which follows from its identity with the product obtained from methylglycolate and phenylcarbimide according to Lambling's method (A., 1899, i, 52).

When aluminium chloride is added in small portions to a well-cooled solution of methylcarbonatoacetyl chloride in benzene, a feeble evolution of hydrogen chloride is finally observed and the solution

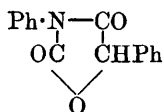
deposits a crystalline *product* containing aluminium, chlorine, and organic matter. If the solution is decomposed with ice and dilute hydrochloric acid, methylcarbonatobenzoylcarbinol,



m. p. 48—49°, is obtained, from which benzoylcarbinol, identical with the product described by Zincke (*Annalen*, 1883, 216, 306), is prepared by the action of *N*-sodium hydroxide solution at the ordinary temperature.

For the preparation of derivatives of lactic acid, a commercial specimen of the latter was employed as starting point; since this contains a certain proportion of the optically active acids (compare McKenzie, T., 1905, 87, 1375), the products are not uniform. The applicability of the process to lactic acid is, however, established. *α*-Methylcarbonatopropionic acid is obtained as a colourless, viscous oil, which becomes partly crystalline when preserved, and which is strongly dextrorotatory in aqueous solution, when lactic acid is treated in the manner described for glycollic acid (see above). Thionyl chloride transforms it into the corresponding *chloride*, b. p. about 47—48°/0.2—0.3 mm.,  $D_{20}^{25}$  1.249.

When methylcarbonatomandelanilide is dissolved in warm methyl alcohol, the solution quickly cooled, treated with 10*N*-sodium hydroxide (about 3 mols.), and, after two minutes, largely diluted with water, mandelanilide, m. p. 151—152° (corr.), is precipitated (compare Bischoff and Walden, A., 1894, i, 525); the filtrate, after extraction with ether to remove dissolved mandelanilide, is acidified with hydrochloric acid, when the phenylurethane of mandelic acid, m. p. 147—149° (corr. decomp.), is obtained (compare Lambling, A., 1899, i, 52). The formation of the former substance is most readily explained on the supposition that the ester group is first saponified, and that



carbon dioxide is then lost either directly or on acidification. It is, however, possible that diketo-diphenyltetrahydro-oxazole (annexed formula) is first produced, which is subsequently decomposed by the addition of water, whereby, on the one hand, the phenylurethane of mandelic acid is formed as main product, whilst on the other hand the anilide of mandelic acid is produced by loss of carbon dioxide. The latter hypothesis is supported by Lambling's observation that both the phenylurethane and the anilide of mandelic acid are formed by the saponification of the phenylurethane of ethyl mandelate.

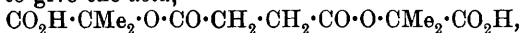
H. W.

**Action of Zinc on an Alcoholic Solution of the Acetyl Derivative of Ethyl Trichlorolactate.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 428—430).—The *ethyl* ester of the *acetyl* derivative of *ββ*-trichlorolactic acid,  $\text{CCl}_3 \cdot \text{CH}(\text{OAc}) \cdot \text{CO}_2\text{Et}$ , is a liquid, b. p. 121—121.5°/16 mm.,  $D_{20}^{20}$  1.3917,  $D_{20}^{20}$  1.367, and on reduction in alcoholic solution, by means of zinc, yields ethyl *ββ*-dichloroacrylate:  $\text{CCl}_3 \cdot \text{CH}(\text{OAc}) \cdot \text{CO}_2\text{Et} + \text{Zn} = \text{ZnCl} \cdot \text{CCl}_2 \cdot \text{CH}(\text{OAc}) \cdot \text{CO}_2\text{Et} = \text{CCl}_2 \cdot \text{CH} \cdot \text{CO}_2\text{Et} + \text{ZnCl} \cdot \text{OAc}$ .  
T. H. P.

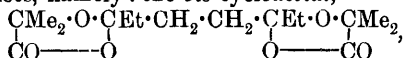
**A New Method of Preparation of Tricarballic Acid.** H. GAULT (*Compt. rend.*, 1914, 158, 632—634).—The lactone (annexed formula) obtained by the action of potassium acetate or of ammonia on ethyl oxalacetate (compare Claisen, A., 1891, 425, and Wislicenus and Beckh, A., 1895, i, 335; 1897, i, 397) does not distil unchanged at 210—216°/30 mm. as stated by Wislicenus and Beckh (*loc. cit.*). Either at this or lower pressures decomposition commences at 130—150°, carbon dioxide is evolved and ethyl propane- $\alpha\beta\gamma$ -tetracarboxylate is formed, which can be converted into tricarballic acid by the action of dilute mineral acids. At the same time a part of the lactone must decompose with elimination of alcohol, which reacts with more of the lactone to give the above reaction. W. G.

**Syntheses by means of Mixed Organo-metallic Derivatives of Zinc  $\alpha\delta$ -Acyclic Diketones.** E. E. BLAISE (*Compt. rend.*, 1914, 158, 504—506).—The interaction of chlorides of acids of the succinic series with zinc alkyl iodides does not give the required diketones, but products having constitutions of the type  $\begin{array}{c} \text{CH}_2 \cdot \text{CR}_2 \\ | \\ \text{CH}_2 - \text{CO} \end{array} > \text{O}$ .

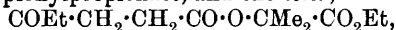
The difficulty can be overcome by the use of mixed *cyclo*acetals, and in this way the author has prepared *s*-dipropionylethane. Succinyl chloride condenses with  $\alpha$ -hydroxyisobutyric acid when warmed on a water-bath to give the *acid*,



m. p. 195°, which with phosphorus pentachloride gives the corresponding *acid dichloride*, m. p. 62°, yielding with aniline a *dianilide*, m. p. 144—145°. The dichloride condenses with zinc ethyl iodide, giving a mixture of products, namely: the *bis*-cycloacetal,



m. p. 129—130°, b. p. 197°/17 mm.; a neutral liquid which on saponification gives  $\alpha$ -hydroxyisobutyric acid,  $\beta$ -propionylpropionic acid, and ethyl  $\alpha$ -hydroxyisopropyl ketone; an acid liquid which on esterification gives ethyl  $\beta$ -propionylpropionate, and the *ester*,



b. p. 160—161°.

The *bis*-cycloacetal by treatment with methyl alcohol containing a little hydrochloric acid by Haller's method yields *s*-dipropionylethane, b. p. 98°/14 mm., m. p. 34—35°, which readily yields cyclic derivatives under the influence of alkalis, an excellent yield of methylethylcyclopentenone being obtained. W. G.

**Some Complex Compounds of Ethylenethioglycollic [Ethylenedithiolacetic] Acid.** LUDWIG RAMBERG and ÅKE TIBERG (*Ber.*, 1914, 47, 730—737).—*Ethylenedithiolacetic acid*,

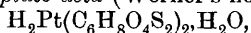


is readily obtained by adding gradually ethylene dibromide (0.2 mol.) to a solution of thiolacetic acid (0.4 mol.) and 95% sodium hydroxide

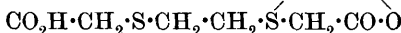
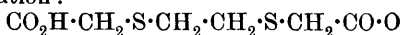
(1.2 mols.) boiling under reflux. When the reaction is complete the contents of the flask are dissolved in water and the acid precipitated by the addition of sulphuric acid. Recrystallisation from water gives colourless prisms, m. p. 108—109°.

In this acid sulphur is linked to an  $\alpha$ -carbon atom, and it should therefore give rise to internal complex salts (compare Ramberg, A., 1913, i, 952; Tschugaev, *ibid.*, i, 1149); this is found to be the case.

*Bis-ethylenethiolacetatoplato-acid* (Werner's nomenclature),

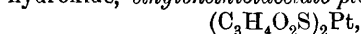
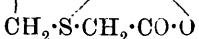
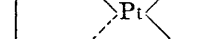
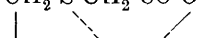


separates as almost colourless, microscopic prisms when potassium platinochloride (1/200-mol.) is added to a hot solution of ethylenethiolacetic acid (1.1/100-mol.). It is practically insoluble in water. It also results when sodium platinichloride (1 mol.) is treated with sodium ethylenethiolacetate (3 mols.), the platinichloride being first reduced to the platinous condition. It corresponds with the analogous compound of thiodiacetic acid (A., 1906, i, 791), and probably, therefore, has the constitution:



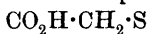
It is at the same time a salt and a dibasic acid; the *sodium salt*,  $\text{Na}_2\text{Pt}(\text{C}_6\text{H}_8\text{O}_4\text{S}_2)_2 \cdot 10\text{H}_2\text{O}$ , forms large, colourless, flat prisms.

*Dichloroethylenethiolacetatoplato-acid* results from the interaction of potassium platinochloride (1/100 mol.) and ethylenedithiolacetic acid (1/100 mol.) when heated in aqueous solution on the water-bath. It forms yellow, wart-shaped crystals, m. p. 242°. The constitution is probably given by the annexed formula. As a dibasic acid it gives the *potassium salt*,  $\text{K}_2\text{Pt}(\text{C}_3\text{H}_4\text{O}_2\text{S})_2 \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$ , which crystallises in yellow, microscopic needles or prisms. When treated with silver acetate, and the precipitated silver chloride removed with ammonium hydroxide, *ethylenethiolacetato-platinum*,

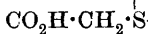


is obtained as a colourless, microcrystalline powder insoluble in all solvents. It is an internal complex salt of the annexed constitution.

Cuprous oxide is readily dissolved by a boiling dilute solution of ethylenethiolacetic acid. From the solution, colourless prismatic crystals of a *cuprous salt*,  $\text{CuH} \cdot \text{C}_6\text{H}_8\text{O}_4\text{S}_2 \cdot \text{C}_6\text{H}_{10}\text{O}_4\text{S}_2$ , separate, in which the cuprous copper is co-ordinatively saturated, the constitution



being:



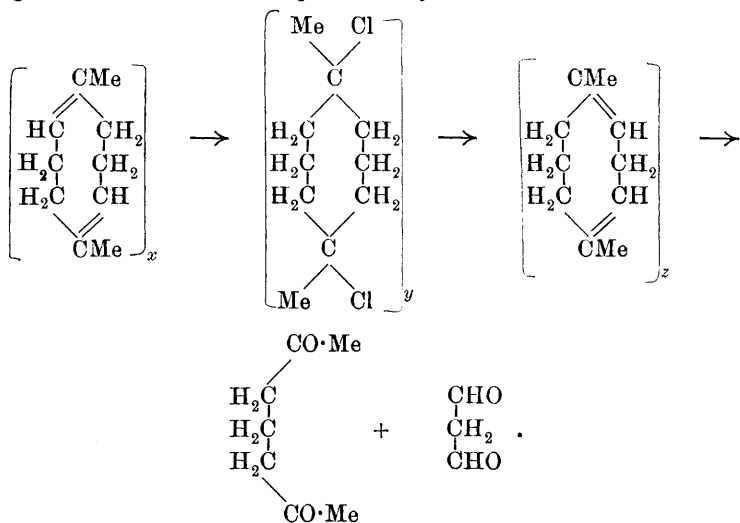
**Autoxidisable Substances and Systems of Physiological Interest. III. Some Auto-oxidisable Thio-compounds.** TORSTEN THUNBERG (*Chem. Zentr.*, 1914, i, 458—459; from *Skand. Arch. Physiol.*, 1913, 30, 285—298. Compare A., 1911, ii, 33).—The absorption of oxygen by neutralised 1% solutions of thiolacetic,  $\alpha$ -thiolpropionic and  $\alpha$ -amino- $\beta$ -thiolpropionic acids has been studied. The latter acid (cysteine) has the quickest action, and the solution becomes red, and altered in alkalinity. The temperature-coefficient for the absorption by thiolacetic acid agrees with that of vital oxygen uptake, but in the case of the thiolpropionic acid it is much higher. The velocity of the absorption is nearly proportional to the square-root of the oxygen pressure.

The influence of catalysts was marked. Manganese salts in the dilution one-millionth mol. per litre doubled the speed in the case of thiolpropionic acid and quadrupled it in the case of thiolacetic acid, whereas Mathews and Walker found that the oxidation of cysteine was unaffected by manganese (A., 1909, i, 698). J. C. W.

**Crystalline Paraformaldehyde.** FRITZ POLLAK (*Chem. Zentr.*, 1914, i, 123; from *Farbenzeit.*, 1913, 19, 371—372).—Amorphous paraformaldehyde is dissolved in sulphuric acid of different concentrations. The solutions are filtered from undissolved particles, allowed to crystallise gradually, and the crystals washed with water until neutral. According to the concentration of the acid, different crystalline polyoxymethylenes are obtained; with 25% acid the  $\alpha$ -variety, with 40—50% acid the  $\beta$ -variety, and with 70—80% acid the  $\gamma$ -form (insoluble in sodium sulphite) is formed. The products are identical with those described by Auerbach and Barschall (A., 1908, i, 131). When sulphuric acid is replaced by hydrochloric acid or other strong acids, undesirable by-products are formed. H. W.

**Diacetylpropane [Heptane- $\beta\zeta$ -dione] from Caoutchouc.** C. HARRIES (*Ber.*, 1914, 47, 784—791).—In a previous paper (A., 1913, i, 1211) the author has described the degradation of Para caoutchouc to a crystalline diketone which from its properties and from the constitution of its disemicarbazone was considered to be *cyclo-octane-1:5-dione*. The experiments have been repeated with larger quantities of material with the result that the product is shown to be *heptane- $\beta\zeta$ -dione*,  $\text{CH}_3\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{CH}_3$ . The error in the previous paper is due to the ease with which this substance loses water with the formation of 1-methyl- $\Delta^1$ -*cyclohexen-3-one*,  $\text{C}_7\text{H}_{10}\text{O}$ , so that the crude product of the reaction invariably consists of a mixture of the diketone and its dehydration product, the boiling points of which under diminished pressure lie close together. In these mixtures the carbon content is increased to such an extent that the analytical figures closely correspond to those required by a substance,  $\text{C}_8\text{H}_{12}\text{O}_2$ . Further, it has now been found impossible to prepare the pure disemicarbazone even from the pure ketone; partial ring closure always occurs, and a uniform product cannot be obtained by repeated crystallisation. The substance behaves in a similar manner towards nitrophenylhydrazine acetate, but under suitable conditions readily yields

a crystalline *dioxime*. The formation of heptane- $\beta\zeta$ -dione from regenerated caoutchouc is represented by the scheme :



From this scheme, the dialdehyde or semialdehyde of malonic acid or the latter substance itself should also be found among the decomposition products; up to the present, none of the substances has been identified. Under the experimental conditions used in decomposing the diozonide with water, the semi-aldehyde acid would be decomposed into acetaldehyde and carbon dioxide, and the presence of these substances has been observed. Possibly, the malonic acid may be contained in the mixture of calcium salts obtained by neutralising the decomposition products of the ozonide with calcium carbonate, but these have not yet been sufficiently accurately investigated.

The ozonisation of the caoutchouc and decomposition of the ozonide by water are effected in much the same manner as previously described (*loc. cit.*). On fractionation under 10 mm. pressure, the following products are obtained: (1) b. p. 60–70°, containing chiefly lævulin-aldehyde; (ii), b. p. 75–90°, containing methylcyclohexenone; (iii) b. p. 90–110°, containing heptane- $\beta\zeta$ -dione, and (iv), b. p. 110°, etc. The third fraction is purified by repeated solidification and filtration, crystallisation from light petroleum, distillation in a vacuum, and subsequent crystallisation. In this manner, heptane- $\beta\zeta$ -dione, m. p. 33–34°, b. p. 221–222°/764 mm. (slight decomp.), 96·5–97°/10–11 mm.,  $D_4^{20}$  0·94986,  $n_D^{20}$  1·42767,  $n_a$  1·42610,  $n_b$  1·43430, is obtained in the pure state and can be preserved indefinitely. In the presence of traces of impurities, it rapidly sinters together, and becomes yellow and opaque. It reduces hot Fehling's solution and ammoniacal silver solution, does not give the pyrrole test, and does not yield a coloration with ferric chloride. The corresponding *dioxime*, stout, glassy prisms, m. p. 87°, is best prepared by adding an aqueous solution of the calculated quantity of hydroxylamine hydrochloride,

previously neutralised with sodium carbonate, to an aqueous solution of the diketone. The *bisnitrophenylhydrazone*, golden-yellow needles, m. p. 182—183°, is precipitated when alcoholic solutions of the diketone and nitrophenylhydrazine are mixed. The disemicarbazone, prepared according to Bouveault's method (A., 1905, i, 178), is not a uniform product. Repeated crystallisation raises the m. p. to 214° (instead of 185·5° previously recorded), but it is still indistinct. The *bisphenylhydrazone* could not be obtained in the crystalline state.

When diacetylpropane is dissolved in water and the solution treated with a few drops of 40% sodium hydroxide solution, 1-methyl- $\Delta^1$ -cyclohexen-3-one, b. p. 194—196°,  $D_4^{21}$  0·9738,  $n_D^{21}$  1·49299,  $n_a$  1·48909,  $n_\beta$  1·50360,  $n_\gamma$  1·51320, is obtained. This is identified by comparison with a specimen of the ketone prepared by the hydrolysis of methylenediacetoacetic ester with sulphuric acid, and further by preparation of the corresponding semicarbazone, m. p. 199—200° (compare Vorländer and Gaertner, A., 1899, i, 259). When heptane- $\beta\zeta$ -dione is boiled with ammonia, with or without addition of acetic acid, methylcyclohexenone is also obtained, together with a small amount of a substance which is probably a lutidine base.

The sensitiveness of heptane- $\beta\zeta$ -dione to alkali explains its non-production from ethyl acetoacetate and formaldehyde or methylene iodide according to the methods of Knoevenagel and Hagemann.

H. W.

**The Pentose of the Nucleic Acids, *d*-Ribose.** W. ALBERDA VAN EKENSTEIN and J. J. BLANKSMA (*Chem. Weekblad*, 1914, 11, 182—184. Compare A., 1913, i, 1044; Levene and Jacobs, A., 1909, i, 858).—The synthetic *d*-ribose prepared by the authors is identical with that isolated from nucleic acids by Levene and Jacobs. Both substances and their mixture have m. p. 95°. From both substances a *p*-bromophenylhydrazone, m. p. 165°, is obtained, and a mixture of the products has the same m. p. *i*-Ribose has been prepared by crystallising a mixture of equimolecular proportions of the two optical isomerides, and forms crystals, m. p. 83—84°.

A. J. W.

***l*-Lyxose.** W. ALBERDA VAN EKENSTEIN and J. J. BLANKSMA (*Chem. Weekblad*, 1914, 11, 189—191).—A description of the preparation of *l*-lyxose and some of its derivatives. For the preparation of the sugar the *i*-galactose formed by oxidation of dulcitol with hydrogen peroxide is fermented, and the residual *l*-galactose oxidised to *l*-galactonic acid by means of bromine water. Hydrogen peroxide converts calcium *l*-galactonate into *l*-lyxose, colourless, hygroscopic crystals of sweet taste, m. p. 105°. It exhibits mutarotation, having  $[\alpha]_D +5\cdot8^\circ$  immediately after solution, and later  $[\alpha]_D +13\cdot5^\circ$ . With *p*-bromophenylhydrazine it yields *l*-lyxose-*p*-bromophenylhydrazone, colourless crystals, m. p. 157°. The corresponding *d*-lyxose-*p*-bromophenylhydrazone is prepared similarly, and melts at the same temperature, but a mixture of the two substances in equimolecular proportions has m. p. 145°. With *p*-nitrophenylhydrazine, *l*-lyxose yields *l*-lyxose-*p*-nitrophenylhydrazone, m. p. 172°. A mixture with the dextrorotatory isomeride in equimolecular proportions has m. p. 160°.

*i-Lyxose* is obtained as a syrup by evaporating an aqueous solution of the two optical isomerides in equimolecular proportions. A similar mixture of the two solid isomerides has m. p.  $95^{\circ}$ . A. J. W.

**The Mechanism of Oxidation Processes.** G. BREIDIG (*Ber.*, 1914, 47, 546—548).—In connexion with the publications of Wieland on the mechanism of oxidation processes (A., 1913, i, 1304), the author calls attention to the various papers on inorganic ferments, etc., which have been issued from his laboratories, and deal to a large extent with the same subject. T. S. P.

**Identity of Galactitol and  $\alpha$ -Ethylgalactoside.** EMIL FISCHER (*Ber.*, 1914, 47, 456—459).—An examination of the substance described by Ritthausen as galactitol,  $C_9H_{18}O_7$  (A., 1896, i, 405), indicates that the composition is in reality  $C_8H_{16}O_6$ , the substance, indeed, being identical with the  $\alpha$ -ethylgalactoside of Fischer and Beensch (A., 1894, i, 565). Contrary to its earlier description, the substance is dextrorotatory,  $[\alpha]_D + 186^{\circ}$ , this value suggesting that the galactitol is, indeed, purer than the samples of  $\alpha$ -ethylgalactoside obtained earlier, this view being supported by the somewhat higher m. p.  $141^{\circ}$ , instead of  $138$ — $139^{\circ}$ . The impurity in the  $\alpha$ -ethylgalactoside described earlier is probably the  $\beta$ -stereoisomeride.

The  $\alpha$ -ethylgalactoside is, in all probability, not present as such in the lupines from which Ritthausen obtained it; it is probably produced from galactose or some galactose polysaccharide during the rather lengthy process of extraction by alcohol. D. F. T.

**Some New Compounds of Iridium and Rhodium.** OSKAR VON FRAENKEL (*Monatsh.*, 1914, 35, 119—135).—The author has prepared a number of different compounds of iridium and rhodium chlorides with various substituted ammonium chlorides. They were obtained directly by mixing aqueous or alcoholic solutions of the respective chlorides, aqueous solutions being used when the compounds obtained were insoluble in alcohol.

*Tetramethylammonium iridichloride*,  $(NMe_4)_2IrCl_6$ , is a crystalline, brownish-red powder. *Ethylammonium iridichloride*,  $(NH_3Et)_2IrCl_6$ , forms small, brownish-red tablets. *Diethylammonium iridichloride*,  $(NH_2Et)_2IrCl_6$ , crystallises in dark red, monoclinic double pyramids. *Triethylammonium iridichloride*,  $(NEt_3)_2IrCl_6 \cdot 2H_2O$ , forms transparent, brown scales, which lose  $2H_2O$  at  $85^{\circ}$ . *Tetraethylammonium iridichloride*,  $(NEt_4)_2IrCl_6$ , is a brownish-red, crystalline powder, but can be obtained as transparent, brown needles.

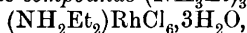
On mixing alcoholic solutions of hydrogen rhodichloride and methylamine hydrochloride, a rose-red, microcrystalline precipitate of the compound,  $(NH_3Me)_2RhCl_5$ , is obtained. It can be considered as the anhydrous compound belonging to the type  $[Rh^{Cl}_5OH_2]H_2$ . Recrystallised from alcohol it gives small, four-sided prisms, but it is decomposed by water with the partial separation of rhodium; from the aqueous solution the compound  $(NH_3Me)_4RhCl_7$  is obtained (compare Vincent, A., 1885, 1116; 1886, 311), belonging to the type  $[Rh^{Cl}_2(HCl)_4]Cl$ . The



dimethyl- and trimethyl-ammonium rhodichlorides were also obtained, their composition agreeing with those given by Vincent (*loc. cit.*).

Tetramethylammonium chloride and hydrogen rhodichloride give a purple-red, aqueous solution, from which brown, six-sided tablets of the compound  $(\text{NMe}_4)_4\text{Rh}_2\text{Cl}_9$  are obtained; the compound is the acid salt of the hexabasic acid,  $[\text{Rh}(\text{HCl})_6]\text{Cl}_3$ , three hydrogens being replaced by  $\text{Rh}^{+++}$ .

Ethylamine, diethylamine, and triethylamine hydrochlorides give garnet-red crystals of the compounds  $(\text{NH}_3\text{Et})_3\text{RhCl}_6$ ,



and  $(\text{NH}_2\text{Et}_3)\text{RhCl}_6 \cdot 9\text{H}_2\text{O}$  respectively; the latter salts lose  $3\text{H}_2\text{O}$  and  $9\text{H}_2\text{O}$  respectively at  $100^\circ$ .

Alcoholic solutions of tetraethylammonium chloride and hydrogen rhodichloride give brown crystals of the compound  $(\text{NEt}_4)_4\text{RhCl}_7$ ; on recrystallisation from water, six-sided, light brown plates of the compound  $(\text{NEt}_4)_3\text{Rh}_2\text{Cl}_9$  are obtained.

T. S. P.

**Isolation of Betaine Hydrochloride from Residues Containing Nitrates.** H. STOLTZENBERG (*Chem. Zentr.*, 1914, i, 22; from *Zentr. Zuckerind.*, 1913, 22, No. 4).—The author gives an account of the treatment of large quantities of sugar residues from the year 1912 according to his method with hydrogen chloride (A., 1912, i, 680). In these experiments, ethyl alcohol was also replaced by methyl alcohol for the dilution of the concentrated filtrates. Ethyl alcohol denatured with methyl alcohol is very suitable for the precipitation of betaine hydrochloride.

H. W.

**Isolation of Betaine Hydrochloride from Molasses Residues.** H. STOLTZENBERG (*Chem. Zentr.*, 1914, i, 22; from *Zentr. Zuckerind.*, 1913, 22, No. 5. Compare A., 1912, i, 680; 1913, i, 345).—Urban's method of preparing betaine from molasses residue (A., 1913, i, 449) is criticised with regard to the quantity of hydrochloric acid added, the use of animal charcoal, and the omission of alcohol. Since the solubilities of betaine hydrochloride, glutamic acid hydrochloride and potassium chloride in water are practically identical, the evaporation of a solution of a mixture of these substances cannot yield an individual product. A method for the preparation of pure glutamic acid cannot be based on this procedure.

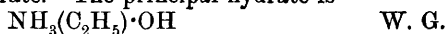
The isolation of betaine hydrochloride from fermentation molasses residue is also described.

H. W.

**The Formation of Glycine from Oxalic Acid.** WALTHER LÖB (*Biochem. Zeitsch.*, 1914, 60, 159—170).—The author confirms an earlier observation that glycine is formed from ammonia, carbon dioxide, and water under the influence of the silent discharge, isolating the former substance in the form of its naphthalenesulphonyl compound. As oxamic acid is regarded as an intermediate product in the reaction, experiments were carried out to reduce this acid by direct chemical means. This succeeded by electrolytic methods in sulphuric acid solution, under conditions in which scission of the amide groups readily takes place. Oxalic acid itself was therefore reduced in the presence of sulphuric acid and ammonia, and under certain conditions

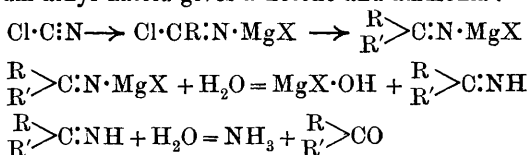
glycine was also obtained. Glyoxylic acid was the chief product. It is assumed that ammonia forms with this substance hydroxylaminoacetic acid, which, by the action of hydrogen, yields glycine. Under similar conditions of reduction as those applied to oxalic acid, malonic acid does not give rise to an amino-acid, whilst succinic acid yields  $\gamma$ -aminobutyric acid. The experimental conditions for the production of amino-acids by the reduction of dibasic acids in the presence of ammonia are difficult to attain, but full details of the methods employed are given by the author. S. B. S.

**Calorimetric Study of the System Water-Monomethylamine.** E. BAUD, F. DUCCELLIEZ, and L. GAY (*Compt. rend.*, 1914, 158, 629—631).—An application of the calorimetric method already described for ammonia (compare A., 1909, ii, 558) to ethylamine to determine its hydrates. The maximum heat of formation for a mixture of the base with water corresponds with the molecular mixture which yields a hydrate. The principal hydrate is



**The Constitution of the Gaseous and Liquid Cyanogen Chlorides.** V. GRIGNARD and E. BELLET (*Compt. rend.*, 1914, 158, 457—461).—The authors favour the nitrile form  $\text{N}\equiv\text{C}\cdot\text{Cl}$  for the liquid chloride and the isonitrile  $\text{C}\equiv\text{N}\cdot\text{Cl}$  for the gaseous chloride, and in support of this view give the following facts. The difference between the boiling points of these two chlorides is of the same order as that between the boiling points of the first terms of the nitriles and corresponding isonitriles.

Cyanogen iodide with organomagnesium compounds always gives the alkyl iodide. Gaseous cyanogen chloride, on the contrary, reacts with aliphatic or aromatic organomagnesium compounds giving principally the corresponding nitrile, whilst with cyclic compounds of the type of magnesium *cyclohexyl* bromide it gives principally the alkyl chloride, with a very small amount of the nitrile. Further the intermediate complex formed in the first reaction of cyanogen chloride is very stable, and by controlled hydrolysis gives a ketimine (compare Moureu and Mignonac, A., 1913, i, 873), which with another molecule of magnesium alkyl haloid gives a ketone and ammonia :



The authors draw the conclusion that gaseous cyanogen chloride reacts as a nitrile to give nitriles and as isonitrile to give chlorides, the tautomeric change being controlled by the magnesium alkyl haloid with which it is reacting, the isomerisation being rapid with aliphatic and aromatic magnesium haloids and slow with the cyclic compounds.

This view is confirmed by determining the relative amounts of chlorocyclohexane and cyclohexanecarboxylonitrile produced from gaseous and liquid cyanogen chloride respectively when operating under the same conditions. W. G.

The Platinum Compounds of the *iso*Cyanides [Carbylamines]. L. TSCHUGAEV and P. TEEARU (*Ber.*, 1914, 47, 568—573).—Ramberg (A., 1907, i, 604) described two isomeric compounds which he obtained by the action of platinous chloride on phenylcarbylamine. One was violet and changed into the pale yellow, crystalline form,  $\text{PtCl}_2 \cdot 2\text{CNPh}$ , m. p. 257—258°, on heating to 110—115° or in boiling chloroform. The constitution of the violet compound has now been established. It has the formula  $[\text{Pt}_4\text{CNPh}]\text{PtCl}_4$ , since it reacts with Reiset's chloride,  $[\text{Pt}_4\text{NH}_3]\text{Cl}_2$ , to form Magnus's green salt,  $[\text{Pt}_4\text{NH}_3]\text{PtCl}_4$  (compare A., 1912, i, 70).

The corresponding derivatives of methyl- and *tert.*-butyl-carbylamines have also been studied. When a saturated solution of ammonium or potassium platinochloride is treated with methylcarbylamine in the cold, the compound,  $[\text{Pt}_4\text{Me} \cdot \text{NC}]\text{PtCl}_4$ , separates in flesh-red crystals which are quickly transformed, at 145—150° in a sealed tube into the colourless *isomeride*,  $[\text{Pt}_2\text{Me} \cdot \text{NC}]\text{Cl}_2$ , m. p. 233° (decomp.) The red compound reacts with Reiset's chloride as above, and also with sodium picrate, to form a *picrate*,  $[\text{Pt}_4\text{Me} \cdot \text{NC}][\text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3]_2$ . The colourless salt only gave these reactions after shaking with excess of methylcarbylamine and water, when the necessary ion,  $[\text{Pt}_4\text{Me} \cdot \text{NC}]$ , was established. Similarly, *tert.*-butylcarbylamine forms the deep red compound,  $[\text{Pt}_4\text{Me}_3\text{C} \cdot \text{NC}]\text{PtCl}_4$ , which dissolves on shaking with carbylamine and water to give a colourless solution from which sodium picrate precipitates the unstable picrate. A colourless *isomeride* could not be obtained. An attempt to obtain one by the decomposition of the salt,  $[\text{Pt}_4\text{C}_4\text{H}_9\text{NC}]\text{Cl}_2$ , contained in the above solution, led to other and interesting products.

Soluble picrates are recommended as precipitants for salts containing co-ordinated, saturated anions.

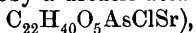
J. C. W.

New Class of Aliphatic Arsenic Compounds. EMIL FISCHER (*Annalen*, 1914, 403, 106—117).—Behenolic acid and arsenic trichloride ( $1\frac{1}{4}$  parts), heated for six hours at 140°, yield an additive compound which probably contains the group  $\cdot\text{C}(\text{AsCl}_2) \cdot \text{CCl}$ . It is converted by water or by cold dilute alkalis into an *acid* which contains the group  $\cdot\text{C}(\text{AsO}) \cdot \text{CCl}$ , and is therefore called *chloroarsinosobehenolic acid*. The acid has not been freed completely from behenolic acid, but it certainly contains arsenic and chlorine in atomic proportions and probably has the formula  $\text{C}_{22}\text{H}_{40}\text{O}_3\text{AsCl}$ . The purest specimen has been obtained as a faintly brownish-red oil. The alkali salts are stable in neutral solution, but are decomposed, rapidly by warming, by an excess of alkali, an alkali arsenite being formed. The salts of the alkaline earths are amorphous, almost colourless, and insoluble in water; the *strontium* salt is employed medicinally under the name *elaron*.

By heating with aqueous alcoholic potassium hydroxide and subsequently acidifying, chloroarsinosobehenolic acid yields behenolic acid.

Chloroarsinosobehenolic acid, methyl alcohol, and concentrated sulphuric acid yield the *methyl* ester; this reacts additively with about 1 mol. of bromine in carbon disulphide to form a *substance*

which is decomposed by water into hydrogen bromide and a monobasic acid, *methyl chlorobenzenolatearsinic acid*,  $C_{23}H_{44}O_5AsCl$ . This arsinic acid, which probably contains the group  $\cdot CCl \cdot C[AsO(OH)_2] \cdot$ , and is best isolated in the form of the *strontium* salt, is hydrolysed by an excess of 10% methyl-alcoholic potassium hydroxide at the ordinary temperature, yielding thereby a dibasic acid (*strontium* salt

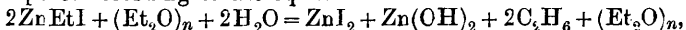


which is much more stable than chloroarsinosobenzenic acid to alkalis.

Stearolic acid and arsenic trichloride react at  $140^\circ$  in a similar manner and yield an oil from which again only amorphous derivatives have been obtained. Phenylpropionic acid and arsenic trichloride yield crystalline products; these, however, belong to a different class of arsenic compounds and are to be described later. C. S.

**Action of Allylene on Magnesium Ethyl Bromide.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 431—432).—When allylene is passed into an ethereal solution of magnesium ethyl bromide, ethane is liberated and magnesium allylene bromide formed:  $MgEtBr + CMe:CH = CMe:C \cdot MgBr + C_2H_6$ . The magnesium allylene bromide is obtained as a double compound with ether in the form of a viscous, glycerol-like liquid, which is only slightly soluble in ether and gradually separates in long, stout crystals. With carbon dioxide, magnesium allylene bromide yields the compound,  $CMe:C \cdot CO_2 \cdot MgBr$ , which is decomposed by water, giving tetrolic acid,  $CMe:C \cdot CO_2H$ , m. p.  $77-78^\circ$ , b. p.  $99-100^\circ/18$  mm. This acid inflames readily, and with bromine under the influence of electric light yields dibromocrotonic acid, m. p.  $96-97^\circ$ . T. H. P.

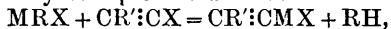
**Action of Mono-substituted Acetylenic Hydrocarbons on Organo-zinc and Organo-magnesium Compounds.** New General Method of Obtaining Alcohols with Acetylene Linkings. SHIVON I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 239—341).—Treatment of zinc and iodine with ether in a reflux apparatus on a water-bath for eight hours under a pressure of 150 mm. yields a transparent ethereal solution of zinc ethyl iodide, which is identical in properties with magnesium ethyl iodide (compare Grignard, A., 1900, i, 382). Thus, it does not inflame in the air and can be safely poured from one vessel into another. With water it decomposes according to the equation:



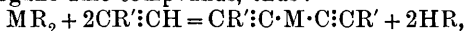
whilst with phenylacetylene it gives zinc phenylacetylene iodide, thus:  $ZnEtI + CPh:CH = I \cdot Zn \cdot C:CPh + C_2H_6$ . Zinc phenylacetylene iodide gives with methylcyclohexanone the same tertiary alcohol as is formed from magnesium phenylacetylene iodide and methylcyclohexanone (see this vol., i, 401).

Zinc ethyl and phenylacetylene react at the ordinary temperature, giving the complex  $CPh:C \cdot Zn \cdot C:CPh$ , which does not inflame in the air, is decomposed when heated with water, yielding phenylacetylene and zinc hydroxide, and with methylcyclohexanone forms the tertiary alcohol referred to above.

Hence, the action of mono-substituted acetylenes on magnesium or zinc alkyl haloids may be represented thus :



and that on organo-zinc compounds, thus :



where R and R' represent alkyl radicles, X bromine or iodine, and M zinc or magnesium.

T. H. P.

**Preparation of Zinc Alkyl Haloids and Syntheses by means of them.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 251—252).—In some cases zinc alkyl haloids react differently from magnesium alkyl haloids. Thus, with chloroanhydrides of acids the latter give only tertiary alcohols, whilst the former give either ketones or tertiary alcohols, as desired. Again, with carbonylic compounds, zinc alkyl haloids react readily, whilst magnesium alkyl haloids do not react.

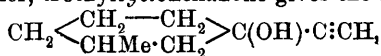
Until now zinc alkyl haloids have not been obtained in the free state, and as their reaction with organic compounds proceeds simultaneously with their formation in presence of a large excess of zinc, syntheses with compounds which are not indifferent towards zinc cannot be effected.

The author has previously described (preceding abstract) the preparation of an ethereal solution of zinc ethyl iodide, and he has now obtained similar solutions of zinc methyl, isopropyl, amyl and allyl iodides. The procedure is as follows: To the zinc dust (1 atom), previously treated with iodine under the conditions employed by von Baeyer for the activation of magnesium (A., 1905, i, 766) and placed in a round flask, the alkyl haloid (1 mol.) diluted with double its volume of dry ether is gradually added. The flask is then fitted with a condenser and with a stirrer passing through a mercury seal, and is heated on a water-bath for two to five days.

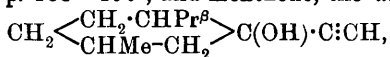
By means of zinc methyl iodide, the following compounds have been synthesised: acetone, in 70% yield, from chloroacetic anhydride; acetophenone, in 65% yield, from benzoyl chloride; and *α*-chloro-*β*-ethoxypropane,  $\text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{OEt}$ , b. p. 116—117.5°, from *as*-dichloroethylene. Zinc ethyl iodide yields: with acetyl chloride, methyl ethyl ketone; with benzoyl chloride, phenyl ethyl ketone; with *as*-dichloroethyl ether, *α*-chloro-*β*-ethoxypropane,  $\text{CH}_2\text{Cl}\cdot\text{CHEt}\cdot\text{OEt}$ , b. p. 140—141°. T. H. P.

**Preparation of Monomagnesiumacetylene and Syntheses by means of it.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 252—253).—In order to obtain compounds of the type  $\text{CH}\text{:C}\cdot\text{MgX}$ , and not  $\text{MgX}\cdot\text{C}\text{:C}\cdot\text{MgX}$ , it is necessary to keep a current of acetylene passing through the reacting compounds, and to keep the product in an atmosphere of the same gas.

When the product of the interaction of trioxymethylene and magnesium acetylene haloid is treated with water, propargyl alcohol and  $\Delta^2$ -butinene- $\alpha\delta$ -diol,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}\text{:C}\cdot\text{CH}_2\cdot\text{OH}$ , m. p. 58°, are obtained. In a similar manner, methylcyclohexanone gives the alcohol,



m. p. 50—51°, b. p. 188—190°, and menthone, the *alcohol*,



b. p. 96—98°/12 mm.

T. H. P.

*cyclo*Mercuripentamethylene. J. VON BRAUN (*Ber.*, 1914, **47**, 490—492. Compare A., 1913, i, 719).—Comparison of the boiling points of the pentamethylene series of compounds,  $(\text{CH}_2)_5 > \text{R}$ , with those of the series, Et-R-Et, where R may be O, CH<sub>2</sub>, NH, S, or Hg, indicates that *cyclo*mercuripentamethylene should have a boiling point of about 210°; it should distil without decomposition under diminished pressure, and probably without decomposition under ordinary pressure. The substance described by Hilpert and Grüttner (this vol., i, 261) as *cyclo*mercuripentamethylene is probably a polymeride of this compound, since it has a melting point of 120°. T. S. P.

**Chemical Action of Light. IV. Autoxidations.** HERMANN SUIDA (*Ber.*, 1914, **47**, 467—472. Compare A., 1913, i, 28, 52).—The author has already shown (A., 1913, i, 28) that the autoxidation of xylene under the influence of light gives rise to larger quantities of peroxide substances when a small quantity of an aromatic nitro-compound is added. This effect of the nitro-compound is found to be due to its influence in increasing the relative stability of the less stable intermediate products, so that whilst smaller quantities of carboxylic acid substances are obtained, relatively larger quantities of peroxides and aldehydes accumulate in the liquid. The effect is likened to that of a yellow screen in making prints from a flat photographic negative.

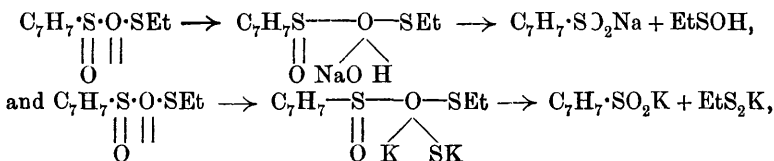
Experiments were made with *o*-, *m*-, and *p*-nitrotoluene, and only in the case of the first was the nitro-compound itself appreciably altered.

For the purpose of comparison, terephthalaldehyde was converted into its phenylhydrazones; *phenylhydrazone*, orange-yellow needles, m. p. 152—154°; *bisphenylhydrazone*, lemon-yellow scales, m. p. 276—278° (decomp.).

By exposing benzaldehyde in solution in light petroleum to the light of a quartz lamp, the solution being surrounded by a mixture of ether and solid carbon dioxide, a white deposit was slowly obtained which had strong oxidising properties and a pungent odour; benzaldehyde was also present in the deposit, and the peroxide substance present could not be isolated on account of the rapid conversion into benzoic acid. At the same temperature, but with exclusion of light, no indications of oxidation were observable. D. F. T.

**The Action of Alkaline Reducing Agents on Disulphoxides and Sulphoxides.** A. GUTMANN (*Ber.*, 1914, **47**, 635—639).—When ethyl *p*-toluenethiosulphonate in alcoholic solution is heated with an aqueous alkaline solution of sodium arsenite in a closed flask at 100°, reduction occurs with formation of *p*-toluenesulphinic acid, ethyl mercaptan and sodium arsenate. In a similar manner the ester reacts with a mixture of potassium cyanide and potassium sulphide in alcoholic solution producing *p*-toluenesulphonic acid, ethyl mercaptan, and potassium thiocyanate.

These results are interpreted as favouring the unsymmetrical formula  $R \cdot SO_2 \cdot SR$  as opposed to the symmetrical formula  $R \cdot S : O \cdot SR : O$  for substances of this class (compare Hinsberg, A., 1909, i, 6). The reactivity is attributed to the presence of a reactive oxygen atom (compare Gutmann, A., 1912, i, 397), and the above chemical changes are explained by the formulæ:



the last substance in each of these schemes then undergoing reduction with formation of ethyl mercaptan with sodium arsenate and potassium thiocyanate respectively.

Dibenzyl sulphoxide,  $(CH_2Ph)_2S : O$ , when treated with alkaline sodium arsenite solution, and with a mixture of potassium sulphide and potassium cyanide left these reagents unaffected, thus enabling a decision in favour of the structure  $R_2S : O$  as opposed to  $RS \cdot OR$ . Ethyl *p*-toluenesulphonate, ethyl sulphite, methyl sulphate, sodium ethyl sulphate, *p*-tolyl ethyl sulphone, and *p*-tolyl benzyl sulphone do not oxidise sodium arsenite, and so are regarded as containing no "reactive" oxygen or sulphur (compare A., 1909, i, 144).

D. F. T.

#### Action of Magnesium Phenylacetylene on Nitrobenzene.

SH. I. IOCHITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 555).—The action of magnesium phenylacetylene bromide on nitrobenzene in ethereal solution yields a crystalline compound which is decomposed by water into a compound, which has the empirical composition,  $C_{16}H_{10}$ , and forms crystals, m. p. 87—88.5°.

T. H. P.

#### Addition of Metals at Multiple Linkings.

W. SCHLENK, J. APPENRODT, A. MICHAEL, and A. THAL (*Ber.*, 1914, 47, 473—490).—As a consequence of the power of the carbonyl group to form additive compounds with alkali metals as evidenced in the metal ketyls (Schlenk and Thal, A., 1913, i, 1205), the authors have commenced a systematic investigation of the additive power of various multiple linkings towards the alkali metals, and in this communication describe results obtained with the groups  $C : C$ ,  $C : N$ ,  $N : N$ , and  $C : O$ .

The experimental procedure is to agitate in a sealed vessel containing an atmosphere of nitrogen, a mixture of powdered sodium with the unsaturated compound and ether. Ether is more suitable than benzene, as it causes a higher velocity of reaction. The reaction is allowed to proceed at the ordinary temperature, and the product, if soluble in ether, can be afterwards submitted to analysis. In cases where the product is insoluble and is obtained mixed with free sodium, the composition can be proved by the nature of the various products obtainable by suitable chemical treatment of the mixture. Aromatic compounds

have been chosen hitherto for the investigation, as with them the additive properties of the multiple linkings appear to be more marked.

When 3 grams of stilbene were shaken with 250 c.c. of ether and 10 grams of sodium powder, the first appearance of reaction occurred after curiously varying periods in different cases, the first indication being a yellow coloration of the liquid. The liquid then darkened and deposited a brownish-violet powder; for the entire conversion of the stilbene into this compound, continuous shaking for several days was necessary. This substance is a *disodium* derivative,  $\text{CHPhNa} \cdot \text{CHPhNa}$ , of stilbene, as shown by the following changes. Water converts it into *s*-diphenylethane and sodium hydroxide. Carbon dioxide gives *s*-diphenylsuccinic acid, whilst oxygen, towards which the sodium compound is remarkably sensitive, removes sodium regenerating stilbene. Treatment with methyl iodide or bromobenzene yields only a mixture of stilbene with ethane or diphenyl respectively.

Styrene under conditions similar to the preceding soon gave indications of formation of a sodium derivative, but the reaction did not proceed to any extent on account of the polymerisation of the hydrocarbon, under the influence of the sodium, with production of metastyrene which does not possess this additive power.

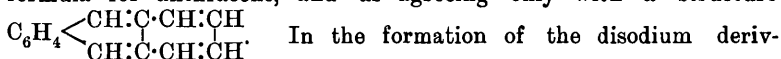
*s*-Tetraphenylethylene reacted rapidly with sodium, giving a yellowish-red ethereal solution. The product is evidently a *disodium* derivative, because the action of water converts it into *s*-tetraphenylethane. This result is especially noteworthy, as the hydrocarbon shows but little tendency to form additive compounds with the halogens.

*as*-Diphenylethylene reacts readily, and after several days a brick-red deposit, sometimes in prismatic crystals, of a *disodium* derivative,  $\text{CPh}_2\text{Na} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CPh}_2\text{Na}$ , is obtained. The formation of a compound of this structure is attributed to the greater reactivity of the  $\text{CPh}_2$ -carbon atom, so that the primary product is  $\text{CPh}_2\text{Na} \cdot \text{CH}_2$ -; these groups then undergo condensation in pairs. The final disodium compound yields *aa* $\delta\delta$ -tetraphenylbutane with water, and on treatment with carbon dioxide gives rise to the sodium salt of *aa* $\delta\delta$ -tetraphenyladipic acid,  $\text{CO}_2\text{H} \cdot \text{CPh}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$ . As the sodium atoms are not adjacent in this disodium derivative, the action of methyl iodide might be expected to follow a different course from that experienced with the disodium derivative of stilbene, and actually  $\beta\beta\epsilon\epsilon$ -tetraphenylhexane,  $\text{CPh}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CPh}_2\text{Me}$ , is obtained as flat prisms, m. p.  $110^\circ$ .

Anthracene is found to give a *disodium* derivative,



this result being described as incompatible with the usual diagonal formula for anthracene, and as agreeing only with a structure



In the formation of the disodium derivative a blue coloration is first observed in the solution, which subsequently changes to a violet. Spectroscopic examination shows these colours to be quite distinct, and the blue colour first obtained is believed to be due to the transient presence of a monosodium deriv-

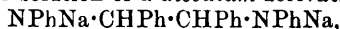


ative containing tervalent carbon, namely,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CHNa} \\ \text{C} \cdot \text{H} \end{smallmatrix} \text{C}_6\text{H}_4$ . The disodium derivative, which in the solid state has a deep blue colour, on treatment with water gave dihydroanthracene. Carbon dioxide gives *dihydroanthracenecarboxylic acid*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}(\text{CO}_2\text{H}) \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_4$ , needles, m. p. 208—210°, or *dihydroanthracenedicarboxylic acid*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}(\text{CO}_2\text{H}) \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} \text{C}_6\text{H}_4$ , needles, m. p. 287—288° (decomp.), according to the period of treatment with the gas.

The *o*-quinonoid structure favoured by the authors for anthracene (above) is confirmed by the behaviour of diphenylbis(diphenyl)quinodimethane,  $\text{C}_6\text{H}_4\text{Ph} \cdot \text{CPh} : \text{C}_6\text{H}_4 : \text{CPh} \cdot \text{C}_6\text{H}_4\text{Ph}$ , which gives a deep blue solution of a *disodium* derivative, the crystals of which have a metallic lustre. The structure  $\text{C}_6\text{H}_4\text{Ph} \cdot \text{CPhNa} \cdot \text{C}_6\text{H}_4 : \text{CPhNa} \cdot \text{C}_6\text{H}_4\text{Ph}$  is demonstrated by the action of carbon dioxide, which yielded *diphenylbis(diphenyl)-p-xylylenedicarboxylic acid*, a substance sparingly soluble in the usual organic solvents.

In spite of the strong colour of these sodium derivatives of the hydrocarbons, the structure is believed to be normal and not due to any rearrangement to quinonoid configuration.

As examples of substances containing the C:N grouping, benzophenoneanil and benzylideneaniline were taken. The former gave a *disodium* derivative,  $\text{CPh}_2\text{Na} \cdot \text{NPhNa}$ , as a deep red powder which is immediately decomposed by the air. With water it yields diphenylmethylaniline,  $\text{NPh} \cdot \text{CHPh}_2$ , whilst with carbon dioxide the sodium salt of a dicarboxylic acid,  $\text{CO}_2\text{Na} \cdot \text{CPh}_2 \cdot \text{NPh} \cdot \text{CO}_2\text{Na}$ , is obtained; this is decomposed by water or by dilute sulphuric acid, giving anilino-diphenylacetic acid. Benzylideneaniline and sodium in the presence of ether gave a clear solution of a *disodium* derivative,



which can be precipitated as an almost colourless powder by the addition of light petroleum. The product undergoes decomposition in the air, gives *s*-dianilinodiphenylethane on treatment with water, whilst carbon dioxide converts it into the sodium salt of a dicarboxylic acid,  $\text{CO}_2\text{Na} \cdot \text{NPh} \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{NPh} \cdot \text{CO}_2\text{Na}$ ; this is rapidly decomposed by water or by dilute acid, giving carbon dioxide and dianilinodiphenylethane.

Azobenzene was chosen as a type of the substances containing the N:N group. The violet-brown reaction product was not merely a sodium additive derivative, for treatment with water regenerated some azobenzene. A metallic derivative was therefore prepared also by the interaction of the potassium ketyl of phenyl diphenyl ketone with azobenzene, when it was found by analysis to be an additive compound of equimolecular quantities of azobenzene and the *dipotassium* derivative,  $\text{NPhK} \cdot \text{NPhK}$ . This rapidly oxidises in the air, giving azobenzene, whilst the action of water produces hydrazobenzene and azobenzene in equimolecular proportion. The action of carbon dioxide on an ethereal suspension of the metallic derivative gave rise to the potassium salt of *hydrazobenzene-NN'-dicarboxylic acid*,  $\text{CO}_2\text{K} \cdot \text{NPh} \cdot \text{NPh} \cdot \text{CO}_2\text{K}$ , a colourless powder, which is slowly

decomposed by water and immediately by dilute hydrochloric acid, yielding hydrazobenzene.

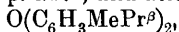
The action of sodium or potassium in pieces of fair size on compounds containing a carbonyl group has already been shown to yield metal ketyls in which the alkali metal has been added at only the oxygen side of the double bond, so that tervalent carbon is simultaneously produced (Schlenk and Thal, *loc. cit.*). Experiment has now shown that with sodium powder, addition of two atoms of the metal takes place as in the case of the preceding groups. Benzophenone in ethereal solution with sodium powder thus first gives rise to the well known blue coloration due to sodium benzophenone,  $\text{CPh}_2\cdot\text{C}\begin{smallmatrix} \nearrow \\ \text{ONa} \end{smallmatrix}$ , which

after several hours' further treatment changes to a violet-red coloration of a disodium additive product, namely, *disodiobenzhydrol*,  $\text{ONa}\cdot\text{CPh}_2\cdot\text{Na}$ , which separates as a powder. In a similar manner phenyl diphenyl ketone and bisdiphenyl ketone give first the bluish-green and yellowish-green colorations due to their respective metal ketyl derivatives, these colours then being replaced by the deep blue of the *disodium* derivatives. When these sodium derivatives are submitted to the action of air or of iodine, it is the sodium atom directly attached to carbon which is first removed and the colour due to the metal ketyl as an intermediate stage in the oxidation to ketone is easily perceptible. This observation constitutes the first in which tervalent carbon has been found as a result of an oxidation process. These disodium derivatives behave like the others already described in the preceding, towards water and carbon dioxide; the action of the former gives rise to the corresponding hydrogen derivatives, for example, the disodium derivative of phenyl diphenyl ketone,  $\text{C}_6\text{H}_5\text{Ph}\cdot\text{CPhNa}\cdot\text{ONa}$ , yields phenyldiphenylcarbinol; the action of carbon dioxide on the same sodium compound gives rise to the *sodium* salt,  $\text{C}_6\text{H}_5\text{Ph}\cdot\text{CPh}(\text{CO}_2\text{Na})\cdot\text{O}\cdot\text{CO}_2\text{Na}$ , which rapidly decomposes in aqueous solution with formation of the *sodium* salt of *phenyldiphenylglycollic acid*,  $\text{C}_6\text{H}_5\text{Ph}\cdot\text{CPh}(\text{OH})\cdot\text{CO}_2\text{H}$ , m. p.  $164^\circ$ . When treated with carbon dioxide the metal ketyl derived from phenyl diphenyl ketone and potassium (containing one atom of potassium and tervalent carbon) also gives phenyldiphenylglycollic acid together with phenyl diphenyl ketone in which case the change must be accompanied by some rearrangement. With the sodium derivatives of bisdiphenyl ketone the results are similar; the metal ketyl produces an equimolecular mixture of bisdiphenylglycollic acid and bisdiphenyl ketone, whilst the disodium derivative gives only *bisdiphenylglycollic acid*,  $(\text{C}_6\text{H}_5\text{Ph})_2\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ ; the disodium derivative of benzophenone,  $\text{CPh}_2\cdot\text{Na}\cdot\text{ONa}$ , likewise produces exclusively benzoic acid.

The red coloration obtained on the addition of concentrated sulphuric acid to benzoic acid has its analogues in the blue and green colorations formed by phenyldiphenylglycollic acid and bisdiphenylglycollic acid respectively under similar treatment. Attention is also drawn to the enormous chromophoric power of tervalent carbon in the metal ketyls; the conversion of these into the corresponding disodium compounds is accompanied by a brightening in colour.

D. F. T.

**The Ether-oxides of Carvacrol.** PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1914, 158, 608—612. Compare A., 1910, i, 668, 669).—The dehydration of carvacrol in the state of vapour by means of thorium oxide at 400—500° did not proceed satisfactorily, a mixture of dicarvacryl and dicarvacrylene oxides being obtained, which could not be separated by fractional distillation. A mixture of the vapours of methyl alcohol and carvacrol passed over thorium oxide at 420—450° yielded the methyl ether, b. p. 217°, and *dicarvacryl oxide*,



small prisms, m. p. 109—110°. If in this reaction the temperature rose to 480°, there was obtained in addition *dicarvacrylene oxide*,  $\text{C}_6\text{H}_2\text{MePr}^\beta > \text{O}$ , yellowish-white, fluorescent prisms, m. p. 150°. A mixture of ethyl alcohol and carvacrol vapours passed over the catalyst at 400—500° gave a small quantity of the ethyl ether, a liquid distilling at 300°, which did not crystallise, and probably was a mixture of the two oxides described above.

An equimolecular mixture of phenol and carvacrol vapours passed over thorium oxide at 470—480° yielded *phenyl carvacryl oxide*, a colourless liquid with an agreeable odour, b. p. 296°, and dicarvacryl and dicarvacrylene oxides, but no diphenyl or diphenylene oxides.

*p*-Cresol and carvacrol at 440—450° gave a certain proportion of *p*-tolyl carvacryl oxide, a colourless liquid, b. p. 300°, and *p*-tolyl oxide but no carvacryl oxide. At 480° the mixture behaved as though it were *p*-cresol alone.

W. G.

**Preparation of Tribromocresorcinol or 3 : 5 : 6-Tribromo-2 : 4-dihydroxy-1-methylbenzene.** J. J. BLANKSMA (*Chem. Weekblad*, 1914, 11, 185—189).—Several derivatives of 6-nitro-*o*-toluidine have been prepared. Bromination converts it into 3 : 5-dibromo-6-nitro-*o*-toluidine, m. p. 105°, converted by diazotisation into 3 : 5 : 6-tribromo-2-nitrotoluene, colourless crystals, m. p. 93°. Nitration transforms this substance into 3 : 5 : 6-tribromo-2 : 4-dinitrotoluene, colourless crystals, m. p. 208°, reduced by acetic acid and iron-powder to 3 : 5 : 6-tribromo-2 : 4-tolylenediamine, colourless crystals, m. p. 180°. The amino-groups of this substance cannot be replaced by hydroxyl by the diazotisation method.

Reduction with acetic acid and iron-powder of 3 : 5 : 6-tribromo-2-nitrotoluene yields 3 : 5 : 6-tribromo-*o*-toluidine, colourless crystals, m. p. 87°, also formed by bromination of 6-bromo-*o*-toluidine. Acetic anhydride converts the product into aceto-3 : 5 : 6-tribromo-*o*-toluidide, colourless crystals, m. p. 218°, transformed by nitration into aceto-3 : 5 : 6-tribromo-4-nitro-*o*-toluidide, colourless crystals, m. p. 275°, which hydrolyses to 3 : 5 : 6-tribromo-4-nitro-*o*-toluidine, light brown crystals, m. p. 203°. Reduction of the substance last mentioned with acetic acid and iron-powder produces 3 : 5 : 6-tribromo-2 : 4-tolylenediamine.

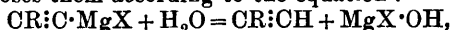
Diazotisation converts 3 : 5 : 6-tribromo-*o*-toluidine into 3 : 5 : 6-tribromo-*o*-cresol, colourless crystals, m. p. 229°, transformed by acetylation into the corresponding acetyl derivative, colourless crystals, m. p. 175°. Nitration of this cresol or its acetyl derivative yields 3 : 5 : 6-tribromo-4-nitro-*o*-cresol, m. p. 212°, reduced by acetic acid and iron-

powder to 3:5:6-tribromo-4-amino-*o*-cresol, colourless crystals, m. p. 234°. Diazotisation transforms the product last mentioned into 3:5:6-tribromo-2:4-dihydroxytoluene, light red crystals, m. p. 227°. It sublimes at 150°.

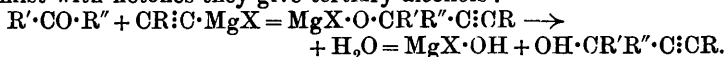
An unsatisfactory yield of 3:5:6-tribromo-4-nitro-*o*-cresol is produced by diazotisation of 3:5:6-tribromo-4-nitro-*o*-toluidine.

A. J. W.

**Magnesium-Acetylene Compounds. New General Method of Obtaining Alcohols with Acetylene Linkings.** SHIVON I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 100—102).—The interaction of magnesium ethyl bromide and a monosubstituted acetylene results in the complete replacement of the alkyl radicle by the acetylene residue:  $\text{CR}:\text{CH} + \text{MgEtBr} = \text{CR}:\text{C}\cdot\text{MgBr} + \text{C}_2\text{H}_6$ . The magnesium acetylene haloids thus obtained do not inflame in the air and may be kept without visible change in ethereal solutions in closed vessels. Water decomposes them according to the equation:

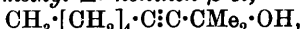


whilst with ketones they give tertiary alcohols:



By this method the following alcohols have been obtained: (1)  $\text{OH}\cdot\text{CMe}_2\cdot\text{C}:\text{CPh}$  (compare Skosarevski, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 652), in 95% yield, from magnesium phenylacetylene haloid;

(2)  $\text{CPh}:\text{C}\cdot\text{C}(\text{OH})\langle\text{CH}_2\cdot\text{CHMe}\rangle\text{CH}_2$  (compare Bertrond, A., 1905, i, 775), in 97% yield, from magnesium phenylacetylene haloid and methylcyclohexanone; (3)  $\beta$ -methyl- $\Delta^7$ -noninen- $\beta$ -ol,



b. p. 94—96°/10 mm., in about 80% yield, from magnesium ethylidene haloid and acetone.

$\alpha$ -Diphenyl- $\gamma$ -methyl- $\Delta^8$ -pentadi-enen- $\gamma$ -ol,  $\text{CPh}:\text{C}\cdot\text{CMe}(\text{OH})\cdot\text{C}:\text{CPh}$ , prepared from magnesium phenylacetylene haloid and ethyl acetate, is a liquid, b. p. 110—110.5°. T. H. P.

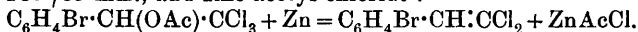
**Action of Magnesium on *p*-Dibromobenzene.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 971).—The action of magnesium on *p*-dibromobenzene yields an organo-magnesium compound which readily reacts with carbon dioxide, giving about 70% of *p*-bromobenzoic acid, so that only one of the bromine atoms of the dibromobenzene reacts with the magnesium. This organo-magnesium compound also reacts well with aldehydes, ketones and esters giving the corresponding alcohols in about 60% yields. Thus, chloral forms bromophenyltrichloromethylcarbinol,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ , m. p. 44°, b. p. 188°/15 mm.; the acetyl compound has m. p. 142°. Acetaldehyde gives bromophenylmethylcarbinol,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHMe}\cdot\text{OH}$ , b. p. 128—130°/13 mm., and acetone, bromophenyldimethylcarbinol,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CMe}_2\cdot\text{OH}$ , m. p. 135—137°/15 mm. T. H. P.

**Action of Magnesium on Ethereal Solutions of *p*-Dibromobenzene and *m*-Dibromoxylene.** SH. I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 8—9. Compare preceding abstract).—The

action of magnesium on an ethereal solution of *p*-dibromobenzene gives magnesium bromophenyl bromide which readily reacts with carbon dioxide, forming *p*-bromobenzoic acid in 70% yield, so that only one bromine atom takes part in this reaction.

The alcohol obtained by the interaction of acetaldehyde and magnesium bromophenyl bromide is a crystalline compound, m. p. 33—34°, b. p. 128—130°/13 mm. Similarly, acetone gives a crystalline alcohol, m. p. 20—22°, b. p. 137°, and chloral, the crystalline *p*-bromophenyltrichloromethylcarbinol,  $C_6H_4Br \cdot CH(OH) \cdot CCl_3$ , m. p. 44—46°, the acetate of which forms crystals, m. p. 144—145°. Each of these alcohols is accompanied by a small proportion of *p*-dibromodiphenyl.

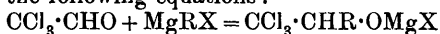
The action of zinc on the above acetyl derivative, m. p. 144—145°, gives *p*-bromodichlorostyrene,  $C_6H_4Br \cdot CH : CCl_2$ , m. p. 23—24°, b. p. 138—140°/15 mm., and zinc acetyl chloride :



The action of magnesium on an ethereal solution of 4:6-dibromo-*m*-xylene gives an organo-magnesium compound, which reacts readily (1) with carbon dioxide, forming 5-bromo-2:4-dimethylbenzoic acid in 70% yield, and (2) with chloral, forming an alcohol, b. p. 197—199°/15 mm.

T. H. P.

**New Method of Preparing Halogen Derivatives of Alcohols.** SHIVON ILBITSCH IOICITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 96—98. Compare *ibid.*, 1898, 30, 920, 998).—The action of chloral and its substituted derivatives on magnesium phenyl bromide and its homologues, and decomposition of the resultant product with water are represented by the following equations :



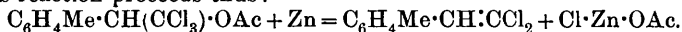
and this  $+ H_2O = CCl_3 \cdot CHR \cdot OH + MgX \cdot OH$ .

Thus chloral and magnesium phenyl bromide in ethereal solution yield phenyltrichloromethylcarbinol, identical with that obtained by the action of potassium hydroxide on a mixture of chloroform and benzaldehyde (compare *J. Russ. Phys. Chem. Soc.*, 1897, 29, 97); its acetyl derivative, m. p. 86—87.5°, yields *aa*-dichlorostyrene on reduction with zinc turnings. Chloral and magnesium *p*-tolyl bromide give *p*-tolyltrichloromethylcarbinol,  $C_6H_4Me \cdot CH(OH) \cdot CCl_3$ , b. p. 61.5—62.5°. Butylchloral and magnesium phenyl bromide yield *α*-phenyl-ββ-trichlorobutan-*α*-ol,  $OH \cdot CHPh \cdot CCl_2 \cdot CHMeCl$ , which is a very viscous liquid, b. p. 180—183°/8 mm.

Epichlorohydrin and magnesium ethyl bromide give the alcohol,  $OH \cdot CH_2 \cdot CHEt \cdot CH_2Cl$  or  $OH \cdot CHPr \cdot CH_2Cl$ , b. p. 87—88°/9 mm.; the acetyl derivative, b. p. 210—214°/778 mm., was prepared (compare Lopatkin, A., 1885, 497).

T. H. P.

**Action of Zinc Turnings on Alcoholic Solution of *o*-Tolyltrichloromethylacetylcarbinol.** SHIVON I. IOICITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 239).—Under the conditions previously employed for the preparation of *aa*-dichloroethylenic hydrocarbons, this reaction proceeds thus :

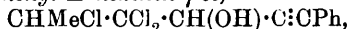


β-*o*-Tolyl-*aa*-dichloroethylene, thus formed in about 80% yield, is a liquid, b. p. 223—225°/769 mm.

T. H. P.

**Action of Magnesium Phenylacetylene on Chlorinated Aldehydes.** SH. I. IocITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 241—242).—The action of magnesium phenylacetylene bromide on an ethereal solution of chloral at 0° gives phenyl- $\beta$ -ethinyl-trichloromethylcarbinol,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{CPh}$ , b. p. 165—166°/6 mm.,  $D_0^{20}$  1.3833,  $D_0^{20}$  1.3639 (compare Moureu and Desmots, A., 1902, i, 289), in 75% yield:  $\text{CCl}_3\cdot\text{CHO} + \text{CPh}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr} = \text{CCl}_3\cdot\text{CH}(\text{OMgBr})\cdot\text{C}\equiv\text{CPh}$  and this  $+ \text{H}_2\text{O} = \text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{CPh} + \text{MgBr}\cdot\text{OH}$ .

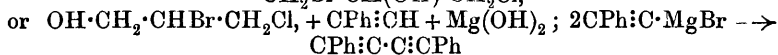
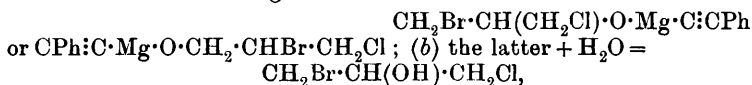
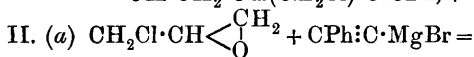
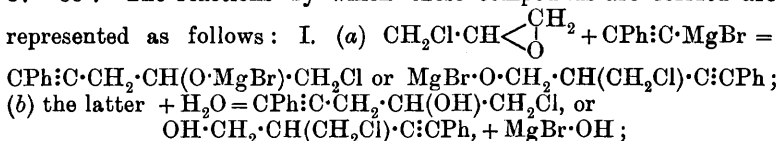
Similarly, butylchloral and magnesium phenylacetylene bromide give  $\delta\delta\epsilon$ -trichloro- $\alpha$ -phenyl- $\Delta^2$ -hexinen- $\gamma$ -ol,



b. p. 187—189°/6 mm.,  $D_0^{20}$  1.3405,  $D_0^{20}$  1.3228, in about 70% yield.

T. H. P.

**Action of Magnesium Phenylacetylene on Epichlorohydrin.** SH. I. IocITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 554—555).—The action of magnesium phenylacetylene bromide on an ethereal solution of epichlorohydrin yields the following products: (1) phenylacetylene; (2) chlorobromohydrin, b. p. 190—191°, or 82—82.5°/15 mm.,  $D_0^{20}$  1.7622,  $D_0^{20}$  1.7335; (3)  $\epsilon$ -chloro- $\alpha$ -phenyl- $\Delta^2$ -pentinen- $\delta$ -ol,  $\text{CPh}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , or  $\alpha$ -phenyl- $\gamma$ -chloromethyl- $\Delta^2$ -butinen- $\delta$ -ol,  $\text{CPh}\cdot\text{C}\cdot\text{CH}(\text{CH}_2\text{Cl})\cdot\text{CH}_2\cdot\text{OH}$ , a viscous liquid, b. p. 166—167°/15 mm.; (4) diphenyldiacetylene,  $\text{CPh}\cdot\text{C}\cdot\text{C}\equiv\text{CPh}$ , m. p. 87—89°. The reactions by which these compounds are formed are represented as follows: I. (a)

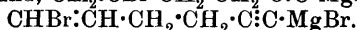


(compare Blaise, A., 1902, i, 357).

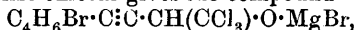
T. H. P.

**Action of Acetylene and Monosubstituted Acetylenes on Organo-zinc and Organo-magnesium Compounds.** SH. I. IocITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1269—1275).—The action of magnesium allylene bromide on pinacolin yields  $\delta\epsilon\epsilon$ -trimethyl- $\Delta^2$ -hexinen- $\delta$ -ol,  $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{C}\equiv\text{CMe}$ , b. p. 173—175°/760 mm.

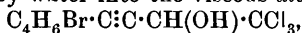
The action of  $\gamma$ -(or  $\delta$ )-bromo- $\Delta^2$ -butenylacetylene on an ethereal solution of magnesium ethyl bromide yields the corresponding magnesium compound,  $\text{CH}_2\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{MgBr}$  or



With the latter, carbon dioxide gives a product which, when decomposed by water acidified with sulphuric acid, yields a crystalline acid, m. p. 84—85°, whilst chloral gives the compound

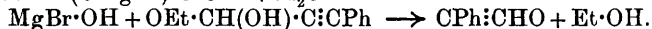
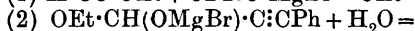
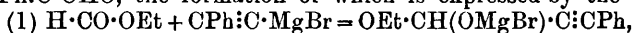


which is decomposed by water into the viscous *alcohol*,

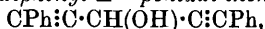


b. p. 176—177°/15 mm.

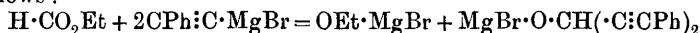
The course taken by the action of magnesium phenylacetylene bromide on ethyl formate varies according to the conditions: with 1 mol. of each reagent mixed at  $-15^\circ$  and left for fifteen minutes, the sole product of subsequent decomposition with water is the aldehyde,  $\text{CPh}:\text{C}\cdot\text{CHO}$ , the formation of which is expressed by the equations:



If, however, 2 mols. of the acetylene derivative and 1 mol. of the ester are left for two hours at the ordinary temperature, the product consists entirely of *ae-diphenyl- $\Delta^{\alpha\delta}$ -pentadi-enen- $\gamma$ -ol*,

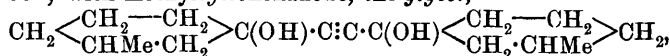


crystallising in prisms, m. p. 69—70°; the reaction then proceeds as follows:—



and this  $+ \text{H}_2\text{O} \longrightarrow \text{CPh}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{C}:\text{CPh}.$

Dimagnesium acetylene dibromide gives, with methyl ethyl ketone,  *$\gamma\zeta$ -dimethyl- $\Delta^8$ -octinene- $\gamma\zeta$ -diol*,  $\text{OH}\cdot\text{CMeEt}\cdot\text{C}:\text{C}\cdot\text{CMeEt}\cdot\text{OH}$ , m. p. 48—49°; with methyl propyl ketone,  *$\delta\eta$ -dimethyl- $\Delta^6$ -decinene- $\delta\eta$ -diol*,  $\text{OH}\cdot\text{CMePr}\cdot\text{C}:\text{C}\cdot\text{CMePr}\cdot\text{OH}$ , m. p. 56—58°; with pinacolin,  *$\beta\beta\eta\eta$ -tetramethyl- $\Delta^8$ -octinene- $\gamma\zeta$ -diol*,  $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{C}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_3$ , m. p. 65—66°; with methylcyclohexanone, the *glycol*,



m. p. 83—85°; with benzaldehyde,  *$\alpha\delta$ -diphenyl- $\Delta\beta$ -butinene- $\alpha\delta$ -diol*,  $\text{OH}\cdot\text{CHPh}\cdot\text{C}:\text{C}\cdot\text{CHPh}\cdot\text{OH}$ , m. p. 138—140°.

The action of bromine on an ethereal solution of dimagnesium acetylene dibromide at  $-20^\circ$  yields tetrabromoethylene and a heavy liquid which inflames in the air and is probably dibromoacetylene (compare Lemoult, A., 1903, i, 595, 673). The action of iodine on the same compound yields di-iodoacetylene (compare von Baeyer, A., 1885, 1198), to which Nef (A., 1898, i, 102) attributes the structure



The action of magnesium phenylacetylene bromide yields bromophenylacetylene, b. p. 88—90°/13 mm., whilst that of iodine gives a crystalline compound, m. p. 99—100°. T. H. P.

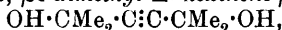
**Benzhydrol:** Preparation of Benzhydrol or of *s*-Tetraphenyl-ethane. PAUL SABATIER and M. MURAT (*Compt. rend.*, 1914, 158, 534—537. Compare this vol., i, 168).—By modifying the method of isolation of the products of reaction, as previously used, the authors have now obtained a newly theoretical yield of benzhydrol from the action of benzaldehyde on magnesium phenyl bromide. After the action has ceased, the crystalline mass is treated with dilute sulphuric acid in the cold, and when solution is complete the liquid is saturated with sodium hydrogen carbonate, and the ethereal layer is decanted and rapidly washed with water. The ether is evaporated on a water-

bath and the liquid allowed to crystallise, giving almost pure benzhydrol. If, however, instead of leaving this liquid to crystallise, it is fractionally distilled, practically no benzhydrol is obtained, but the products are benzophenone and *s*-tetraphenylethane. This decomposition must be effected by the presence of small quantities of impurities produced in the reaction, since benzhydrol can be distilled at 298° under ordinary pressure practically unchanged. The authors have shown that this change can be catalysed by small amounts of acids or salts.

W. G.

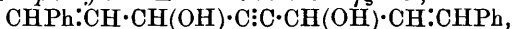
**Action of Acetylene on Organo-metallic Compounds of Magnesium and Zinc. General Method for Obtaining  $\gamma$ -Glycols with Acetylene Linkings.** SH. I. IOCI<sup>TS</sup>CH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 242—244).—When dry, purified acetylene is passed into an ethereal solution of magnesium ethyl bromide, ethane is liberated and dimagnesium acetylene dibromide formed:  $\text{CH}_3\text{CH} + 2\text{MgEtBr} = \text{Br}\cdot\text{Mg}\cdot\text{C}\equiv\text{C}\cdot\text{Mg}\cdot\text{Br} + 2\text{C}_2\text{H}_6$ . This compound, which forms with ether a viscous glycerol-like liquid, does not inflame in the air, is not exploded by shock, and in closed vessels undergoes no visible decomposition. By water it is decomposed according to the equation  $\text{MgBr}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr} + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{MgBr}_2 + \text{Mg}(\text{OH})_2$ , and with carbon dioxide it forms acetylenedicarboxylic acid.

With ketones it yields ditertiary  $\gamma$ -glycols, thus:  $\text{MgBr}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr} + 2\text{R}\cdot\text{COR}^1 = \text{MgBr}\cdot\text{O}\cdot\text{CRR}^1\cdot\text{C}\equiv\text{C}\cdot\text{CRR}^1\cdot\text{O}\cdot\text{MgBr}$ , and the latter  $+ 2\text{H}_2\text{O} = \text{OH}\cdot\text{CRR}^1\cdot\text{C}\equiv\text{C}\cdot\text{CRR}^1\cdot\text{OH} + 2\text{MgBr}\cdot\text{OH}$ . By this method were obtained, from acetone,  *$\beta$* -dimethyl- $\Delta\gamma$ -hexinene- *$\beta$* -diol,



m. p. 94—96°, b. p. 206°/759 mm., in about 80% yield; from pinacolin, a crystalline compound, m. p. 64—66°; from methylcyclohexanone, a crystalline compound, m. p. 83—85°; from menthone, a crystalline compound, m. p. 101—103°; and from carvone, a crystalline compound, m. p. 145—147°.

With aldehydes it forms dissecondary  $\gamma$ -glycols, thus:  $2\text{R}\cdot\text{CHO} + \text{MgBr}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr} = \text{MgBr}\cdot\text{O}\cdot\text{CHR}\cdot\text{C}\equiv\text{C}\cdot\text{CHR}\cdot\text{O}\cdot\text{MgBr}$ . By this method were obtained, from chloral,  *$\alpha\alpha\zeta\zeta$* -hexachloro- $\Delta\gamma$ -hexinene- *$\beta$* -diol,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ , which forms crystals, m. p. 132—134°; from isobutaldehyde,  *$\beta\eta$* -dimethyl- $\Delta^{\delta}$ -octinene- $\gamma\zeta$ -diol,  $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$ , m. p. 67—69°; from cinnamaldehyde,  *$\alpha\theta$* -diphenylocta- $\Delta^{\alpha\eta}$ -diene- $\Delta^{\delta}$ -inene- $\gamma\zeta$ -diol,



m. p. 159—161°.

When acetylene is passed into an ethereal solution of zinc ethyl iodide, ethane is liberated and dizinc acetylene di-iodide,  $\text{I}\cdot\text{Zn}\cdot\text{C}\equiv\text{C}\cdot\text{Zn}\cdot\text{I}$ , formed. The ethereal solution of this compound is a colourless, transparent liquid, which keeps without apparent decomposition, does not inflame in the air and is not exploded by shock. The compound is precipitated from its ethereal solution by addition of benzene or light petroleum as an amorphous, white powder. Water decomposes it as follows:  $\text{ZnI}\cdot\text{C}\equiv\text{C}\cdot\text{ZnI} + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{ZnI}_2 + \text{Zn}(\text{OH})_2$ . T. H. P.

**Crystallography of Mono-substituted Benzoic Acids.** H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1914, **53**, 463—487).—A long



series of crystallographic determinations are given for the ortho-, meta-, and para-chloro-, bromo-, iodo-, hydroxy-, amino-, and nitro-derivatives of benzoic acid.

L. J. S.

**Crystallography of Dinitrobenzoic Acids.** B. GOSSNER (*Zeitsch. Kryst. Min.*, 1914, 53, 488—493).—Four of the six possible isomerides were determined in detail. The 2:4-, 3:4-, and 3:5-dinitro-compounds are monoclinic, whilst the 2:6- is orthorhombic.

L. J. S.

**Benzoperoxide as a Desulphurising Agent.** L. VANINO and A. SCHINNER (*Ber.*, 1914, 47, 699—703).—The sulphur of thiocarbamide is slowly liberated when a mixture with benzoperoxide in alcoholic solution is kept at 35°; cyanoamide, which is already known to be the primary product of desulphurisation by other agents, can be detected in the resulting solution. The reaction is more rapid on a water-bath and is complete in three hours, but on account of the higher temperature the cyanamide undergoes at least partial conversion into dicyanodiamide.

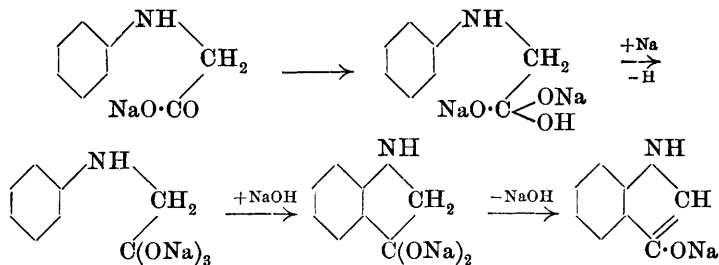
Thiocarbamilide can be successfully desulphurised by benzoperoxide using benzene as a solvent, but allylthiocarbimide failed to respond to this reagent.

In endeavouring to replace the benzoperoxide by hydrogen peroxide, it was discovered that when thiocarbamide is gradually introduced into 30% hydrogen peroxide solution at 5°, a colourless *additive* compound,  $\text{CS}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$ , transparent prisms, m. p. 128—130° (decomp.), is obtained.

D. F. T.

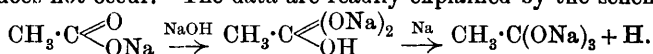
**Reactions in Molten Alkali Hydroxides.** HEINRICH FEUCHTER (*Chem. Zeit.*, 1914, 38, 273—274).—The poor yields of indoxyl obtained by the action of molten potassium hydroxide on the potassium salt of phenylglycine can be greatly improved by the addition of sodium or sodamide and the employment of a mixture of sodium and potassium hydroxides. The mechanism of the reaction is discussed.

Since the formation of the indoxyl ring involves the elimination of a molecule of water which is capable of decomposing the potassium salt of phenylglycine into aniline and potassium acetate, and thus depressing the yield of the indoxyl derivative, the favourable action of sodium may be attributed to its power of immediately decomposing the latter. The author, however, is led to consider that the improvement in the yield is more probably to be attributed to the formation of ortho-salts, and a more ready occurrence of ring formation on



account of their greater reactivity. Reaction is therefore interpreted according to the scheme on p. 406, and thus resembles the Claisen-Wislicenus condensation with sodium ethoxide.

In support of this theory, experiments with sodium acetate and sodium sulphate are quoted. A mixture of sodium and potassium hydroxides is dehydrated by ignition in a nickel vessel, and the last traces of water removed at a lower temperature by gradual addition of sodium until no further evolution of hydrogen occurs, operations being effected in an atmosphere of nitrogen. The molten mass is now maintained at 200—220°, anhydrous sodium acetate is added followed by sodium until the evolution of hydrogen ceases, whereby a white homogeneous fused mass is obtained. Quantitative measurements show that (1) one molecule of hydrogen is evolved from two molecules of sodium acetate, (2) one atom of sodium is required for each molecule of sodium acetate, and (3) the acetic acid recoverable from the fusion is equal to that contained in the sodium acetate used, so that polymerisation does not occur. The data are readily explained by the scheme :

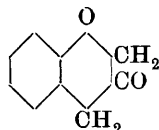


Similar experiments with anhydrous sodium sulphate at about 260° lead to the formation of sodium orthosulphate,  $\text{S}(\text{ONa})_6$ .

*Action of acetylene on molten alkali hydroxides.*—The work described in the previous section in which the addition of sodium hydroxide to the  $\text{C}\equiv\text{O}$  group is discussed, has been extended to other unsaturated substances. Acetylene is readily absorbed by a dehydrated mixture of sodium and potassium hydroxides at about 220°, the volume of hydrogen evolved being one-half that of the acetylene used, whilst acetic acid can be obtained from the fusion in 60% yield. The process appears to consist of the asymmetric addition of two molecules of sodium hydroxide to each molecule of acetylene with the formation of the substance,  $\text{HC}(\text{ONa})_2 \cdot \text{CH}_3$ , which, by further addition of sodium hydroxide and loss of hydrogen, is converted into sodium orthoacetate. If metallic sodium is added to the molten alkali, the reaction takes a different course. Acetylene is readily absorbed without evolution of hydrogen, whilst for the solution of four parts of sodium, one part of acetylene is required. A homogeneous mass with pale grey fracture is obtained, which, on treatment with water, evolves ethane, the volume of the latter being equal to that of the acetylene used. Acetic acid cannot be obtained from the fusion. The course of the reaction has not been definitely elucidated.

H. W.

**Dye Baths.** EFISIO MAMELI (*Chem. Zentr.*, 1914, i, 139; from Pamphlet, 1913, 48 pp.).—A detailed account is given of the different classes of dyes and their technical application in dyeing. The synthesis of chromanone (annexed formula) by ring closure from *o-cresolacetic acid* [*o-tolyloxyacetic acid*] could not be accomplished, but the latter substance and some of its derivatives are described.



*Ethyl o-tolyloxyacetate*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p. 165—166°/20 mm., 258—260°/ordinary pressure, is obtained as a colourless oil of pleasant odour by

heating sodium *o*-tolylxide with ethyl chloroacetate for four hours at 160°. Its solution in concentrated sulphuric acid gradually acquires a pink colour. Hydrolysis with boiling 30% sulphuric acid converts the ester into *o*-tolylxyacetic acid (*o*-tolyl ether of glycollic acid), which is also obtained by the action of metallic sodium or sodium ethoxide. It forms plates, m. p. 153—154°, which dissolve in concentrated sulphuric acid with a cherry-red colour. The following salts are described: *zinc* salt, white, gelatinous precipitate; *copper* salt, blue crystals; *iron* salt, dirty yellow; *cobalt* salt, pink; *lead* salt, white; *barium* salt, white powder containing water of crystallisation, which is lost at 130°; *silver* salt, white prisms, which gradually darken on exposure to light.

When acted on by concentrated sulphuric acid at 80° for six hours, the acid yields a *sulphonic acid*,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , the *barium* salt of which is a white powder. H. W.

**The Action of Methylamine and Ethylamine on Benzoyldehydracetic Acid.** JOH. SCHÖTTLE (*Ber.*, 1914, 47, 688—692. Compare Petrenko-Kritschenko and Schöttle, A., 1911, i, 1020; 1912, i, 128; Schöttle, A., 1912, i, 915).—It has already been shown that the action of various amines on benzoyldehydracetic acid at the ordinary temperature or with gentle warming yields derivatives of the corresponding lactam. A different reaction is found to occur if the acid or its lactam is heated in a sealed tube with an excess of an alcoholic solution of methylamine or ethylamine.

When heated at 135—150° with excess of alcoholic methylamine for three hours, benzoyldehydracetic acid, or, better, its lactam, is converted into a crystalline methylamine *derivative* of the structure

$\text{NHMe}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}(\text{:CPh}\cdot\text{NHMe})\cdot\text{C}(\text{NHMe})_2\cdot\text{OH}$ , m. p. 116—118°, this structure being indicated by treatment with excess of an alcoholic solution of hydroxylamine, the product being a yellow *dioxime*,  $\text{CPh}\cdot\text{CH}(\text{N}(\text{OH})\cdot\text{CO})\cdot\text{CH}\cdot\text{CPh}\cdot\text{NOH}$ , m. p. 151—152°, which produces a deep red coloration with ferric chloride; its *silver* derivative was also analysed. The action of phenylhydrazine hydrochloride on the above substance of m. p. 116—118° yielded a brownish-yellow *substance*,  $\text{CPh}\cdot\text{CH}(\text{N}(\text{NHPh})\cdot\text{CO})\cdot\text{CH}\cdot\text{CPh}\cdot\text{N}\cdot\text{NHPh}$ , m. p. 137—138°.

Ethylamine under similar conditions to the preceding converts benzoyldehydracetic acid and its lactam into the corresponding *ethyl* derivative,  $\text{NHEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}(\text{:CPh}\cdot\text{NHEt})\cdot\text{C}(\text{NHEt})_2\cdot\text{OH}$ , as a crystalline solid, m. p. 92—94°, which gives a dark coloration with ferric chloride. This product when treated with hydroxylamine and phenylhydrazine gives the same compounds as are described above in connexion with the methylamine derivative of benzoyldehydracetic acid.

D. F. T.

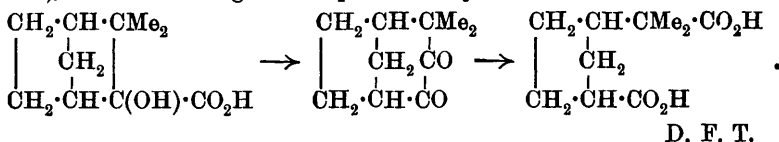
**2:4:6-Trinitro-3-aminophenol.** J. J. BLANKSMA (*Ber.*, 1914, 47, 687).—The substance, decomp. near 240°, obtained by the action of ammonia in alcoholic solution on 2:3:4:6-tetranitrophenol

(Blanksma, A., 1902, i, 442), and which Flürscheim (this vol., i, 270) has recently described as 2:4:6-trinitro-3-aminophenol, is in reality the ammonium salt of this phenol; 2:4:6-trinitro-3-aminophenol, which has m. p. 175°, can also be obtained by the action of ammonia on 3-chloro-2:4:6-trinitrophenol. D. F. T.

**Conversion of Hydroxycamphenilanic Acid (Camphenylic Acid) into Camphenecamphoric Acid.** S. V. HINTIKKA (*Ber.*, 1914, 47, 512—514. Compare Komppa and Hintikka, A., 1908, i, 852).—As Moycho and Zienkowski have observed the formation of a yellow substance in addition to camphenylene and dehydrocamphenylic acid when hydroxycamphenilanic acid is submitted to dry distillation, the author has examined the behaviour of the lead salt of this acid under similar treatment.

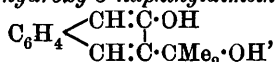
It is found that dry distillation of the lead salt gives a yellow diketone,  $C_{10}H_{14}O_2$ , yellow prisms, m. p. 58—59°, for which the name *carbocamphenilone* is suggested; *dioxime*, m. p. 178—180°. This diketone on oxidation in acetic acid by hydrogen peroxide yields camphenecamphoric acid.

Judging from analogy to the results obtained by Wallach in a similar treatment of fenchocarboxylic acid (A., 1898, i, 486; 1901, i, 331), the above changes are represented by the formulæ:



**The Action of Organo-magnesium Compounds on Methyl 2-Hydroxy-3-naphthoate.** PAUL LAMMER (*Monatsh.*, 1914, 35, 171—188).—Methyl 2-hydroxy-3-naphthoate reacts in the usual manner of carboxylic esters with organo-magnesium compounds with the formation of tertiary alcohols; the products show great similarity to triphenyl- and trinaphthyl-carbinol.

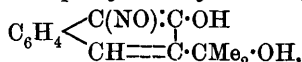
To magnesium methyl iodide in ethereal solution there was added a benzene solution of the above ester, and the mixture was boiled for three hours. The substance obtained after the usual treatment of the reaction product was 2-hydroxy-3-naphthyltrimethylcarbinol,



colourless, microscopic prisms, m. p. 140—141°, which are coloured red by sulphuric acid, and then dissolve to a green colour changed to reddish-brown by a little nitric acid; the substance gives a green coloration with ferric chloride solution. When heated with sodium acetate in acetic anhydride solution for three hours, the preceding carbinol undergoes concurrent acetylation and dehydration with formation of  $\beta$ -2-acetoxy-3-naphthylpropylene,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CH} \cdot \text{C} \cdot \text{OAc} \\ \diagdown \text{CH} \cdot \text{C} \cdot \text{CMe} \cdot \text{CH}_2 \end{array}$ , colourless leaflets, m. p. 68—69°, which on treatment with bromine in

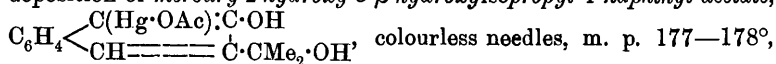
carbon disulphide solution is converted into  $\alpha\beta$ -dibromo- $\beta$ -2-acetoxy-3-naphthylpropane,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}:\text{C}\cdot\text{OAc} \\ | \\ \text{CH}:\text{C}\cdot\text{CMeBr}\cdot\text{CH}_2\text{Br} \end{smallmatrix}$ , colourless crystals, m. p. 104—105°.

1-Nitroso-2-hydroxy-3-naphthyltrimethylcarbinol,



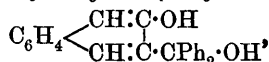
was obtained by the addition of dilute sulphuric acid to a mixture of sodium nitrite and the above hydroxynaphthyltrimethylcarbinol in dilute cold alkaline solution; it forms greenish-yellow, microscopic needles, and gives a deep reddish-brown coloration with ferric chloride, whilst the solution in sulphuric acid is deep brown, changing to red on the addition of a little nitric acid.

When treated in acetic acid solution with a similar solution of mercuric acetate, the hydroxynaphthyltrimethylcarbinol gives a gradual deposition of mercury 2-hydroxy-3- $\beta$ -hydroxyisopropyl-1-naphthyl acetate,



colourless needles, m. p. 177—178°, which gives an intense green coloration with ferric chloride.

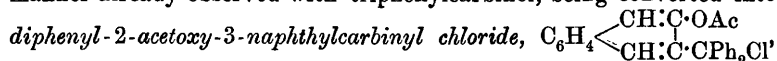
Under similar conditions to the previous, methyl 2-hydroxy-3-naphthoate and magnesium phenyl bromide undergo reaction with production of diphenyl-2-hydroxy-3-naphthylcarbinol,



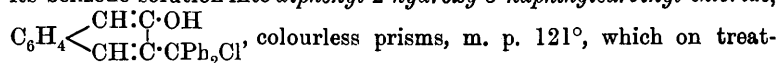
microscopic, hexagonal rhombs, m. p. 175—176°, which gives a very sensitive reaction with sulphuric acid producing a reddish-brown

coloration; acetyl derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}:\text{C}\cdot\text{OAc} \\ | \\ \text{CH}:\text{C}\cdot\text{CPh}_2\cdot\text{OH} \end{smallmatrix}$ , needles, m. p.

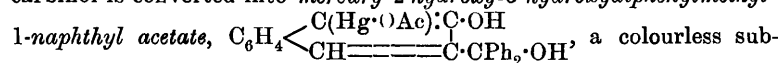
168—169°, which with sulphuric acid gives a green coloration changed to red by a trace of nitric acid. On boiling with acetyl chloride for three hours, the diphenylhydroxynaphthylcarbinol is affected in the manner already observed with triphenylcarbinol, being converted into



colourless prisms, m. p. 110—111°. The diphenylhydroxynaphthylcarbinol is also converted by the action of hydrogen chloride on its benzene solution into diphenyl-2-hydroxy-3-naphthylcarbinyl chloride,



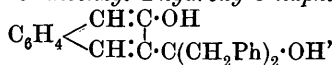
colourless prisms, m. p. 121°, which on treatment in benzene solution with finely divided silver gives a yellow colour due to the formation of diphenyl-2-hydroxy-3-naphthylmethyl, subsequent exposure to the air causing oxidation to a deep red coloration of the corresponding peroxide. When treated with mercuric acetate in acetic acid solution, diphenylhydroxynaphthylcarbinol is converted into mercury-2-hydroxy-3-hydroxydiphenylmethyl-



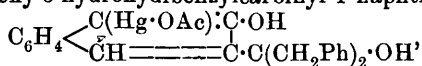
a colourless substance, m. p. 197—198°, which gives an intense green coloration with

ferric chloride. Nitrous acid in the manner described above converts diphenylhydroxynaphthylcarbinol into *diphenyl-1-nitroso-2-hydroxy-3-naphthylcarbinol*,  $C_6H_4 \begin{smallmatrix} C(NO):C \cdot OH \\ | \\ CH= \end{smallmatrix} C \cdot CPh_2 \cdot OH$ , orange-coloured leaflets, m. p. 191—192°, which give a deep red coloration with sulphuric acid, changing to brown on the addition of a trace of nitric acid.

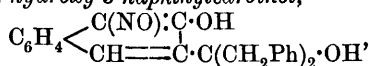
Magnesium benzyl chloride and methyl 2-hydroxy-3-naphthoate react with formation of *dibenzyl-2-hydroxy-3-naphthylcarbinol*,



microscopic, elongated plates, m. p. 161—162°, which gives in sulphuric acid a pale yellow coloration, changing to brown on the addition of nitric acid. This substance reacts with mercuric acetate, producing mercury 2-hydroxy-3-hydroxydibenzylcarbiny-1-naphthyl acetate,

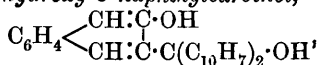


colourless, stout prisms, m. p. 183°, and with nitrous acid, forming *dibenzyl-1-nitroso-2-hydroxy-3-naphthylcarbinol*,

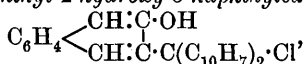


reddish-yellow, microscopic needles, m. p. 155—156°, which give a reddish-brown coloration with ferric chloride.

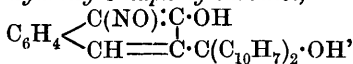
Magnesium  $\alpha$ -naphthyl bromide and methyl 2-hydroxy-3-naphthoate yield *di- $\alpha$ -naphthyl-2-hydroxy-3-naphthylcarbinol*,



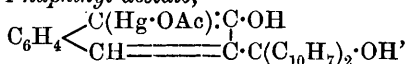
microscopic needles, m. p. 187—188°, which gives an indigo-blue solution in sulphuric acid, passing through violet to brown on the addition of nitric acid; treatment with acetic anhydride and sodium acetate affects only the 2-hydroxy-group, producing the corresponding *acetyl* derivative, prisms, m. p. 220°. The dinaphthylhydroxynaphthylcarbinol is converted by phosphoryl chloride in acetyl chloride solution into *di- $\alpha$ -naphthyl-2-hydroxy-3-naphthylcarbiny-1-naphthyl chloride*,



colourless prisms, m. p. 270—272°, which on treatment with finely-divided silver gives indications of formation of di- $\alpha$ -naphthyl-2-hydroxy-3-naphthylmethyl. Nitrous acid converts the carbinol into *di- $\alpha$ -naphthyl-1-nitroso-2-hydroxy-3-naphthylcarbinol*,



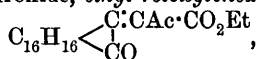
needles, m. p. 185° (decomp.), which gives a deep red coloration with ferric chloride, whilst mercuric acetate reacts in the usual manner with the parent carbinol, producing *mercury 2-hydroxy-3-hydroxy-di- $\alpha$ -naphthylcarbiny-1-naphthyl acetate*,



colourless, microscopic needles, decomp. near 185°; with ferric chloride this gives an intense green coloration.

D. F. T.

**Retene. IV. Condensation of Retenequinone with Ethyl Acetoacetate.** A. HEIDUSCHKA and CH. KHUDADAD (*Arch. Pharm.*, 1913, 251, 682—700).—Retenequinone does not condense with ethyl acetoacetate in the presence of aqueous potassium hydroxide, as does phenanthraquinone (Japp and Streatfeild, T., 1883, 43, 28; Japp and Klingemann, T., 1891, 59, 1). By boiling retenequinone and ethyl acetoacetate with alcohol and a little piperidine or, better, with alcoholic potassium hydroxide, *ethyl retoxyleneacetoacetate*,



m. p. 193°, decomp. 210°, yellow needles or prisms, is obtained. The ester undergoes "acid decomposition" by boiling with dilute sulphuric acid and yields *ethyl retoxyleneacetate*,  $\text{C}_{16}\text{H}_{16} \begin{array}{c} \diagup \text{C}:\text{CH}\cdot\text{CO}_2\text{Et} \\ \diagdown \text{CO} \end{array}$ , m. p.

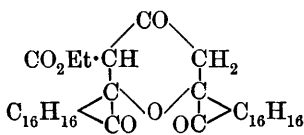
183—184° (decomp.), colourless needles. By boiling with glacial acetic acid, ethyl retoxyleneacetoacetate loses 1 mol. of water and yields two products, *ethyl α-anhydretoxyleneacetoacetate*,  $\text{C}_{24}\text{H}_{22}\text{O}_3$ , m. p. 270°, colourless crystals, and *ethyl β-anhydretoxyleneacetoacetate*,  $\text{C}_{24}\text{H}_{22}\text{O}_3$ , m. p. 220—240°, colourless needles; the former is apparently unchanged by cold concentrated sulphuric acid, but by warming exhibits the same colour changes as does the β-isomeride, which develops a red coloration in the cold, and a dirty blue coloration, changing to green by dilution with water, by warming.

Ethyl retoxyleneacetoacetate is reduced by prolonged boiling with formic acid, D 1.22, and is converted into a *substance*,  $\text{C}_{24}\text{H}_{24}\text{O}_3$ , m. p. 240° (decomp.), brownish-white crystals, which is regarded as *ethyl 2:3-methyl isopropylidiphenylene-4:5-dihydro-Δ<sup>1</sup>-cyclopenten-5-one-1-carboxylate*,  $\text{C}_{16}\text{H}_{16} \begin{array}{c} \diagup \text{C}:\text{C}(\text{CO}_2\text{Et}) \\ \diagdown \text{CH}=\text{CH}_2 \end{array} \text{CO}$ . By heating on the water-bath with formic acid, however, ethyl retoxyleneacetoacetate, like ethyl phenanthroxyleneacetoacetate (Japp and Klingemann, *loc. cit.*), undergoes intramolecular change and is isomerised to *ethyl isoretroxyleneacetoacetate (ethyl 3-hydroxy-2:3-methylisopropylidiphenylene-4:5-dihydro-Δ<sup>1</sup>-cyclopenten-5-one-1-carboxylate)*,  $\text{C}_{16}\text{H}_{16} \begin{array}{c} \diagup \text{C}:\text{C}(\text{CO}_2\text{Et}) \\ \diagdown \text{C}(\text{OH})\cdot\text{CH}_2 \end{array} \text{CO}$ , m. p. 172—174°, faintly yellow crystals, *ethyl isoretroxyleneacetoacetate formate*,  $\text{C}_{25}\text{H}_{24}\text{O}_5$ , m. p. 150° (decomp.), pale yellow crystals, being obtained as a by-product.

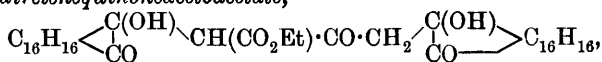
By heating with 50% hydrazine hydrate and alcohol until the latter is completely evaporated, ethyl retoxyleneacetoacetate simultaneously undergoes reduction and hydrazide formation, yielding *ethyl dihydroretroxyleneacetoacetate hydrazide*,  $\text{C}_{24}\text{H}_{28}\text{O}_3\text{N}_2$ , m. p. 180—181°, colourless crystals. Ethyl retoxyleneacetoacetate and 50% hydrazine hydrate in glacial acetic acid on the water-bath yield, like other unsaturated αδ-diketones (Japp and Wood, T., 1905, 87, 707), an *o*-diazine, *ethyl 3:4-methylisopropylidiphenylene-6-methyl-1:2-diazine-5-carboxylate*,  $\text{C}_{16}\text{H}_{16} \begin{array}{c} \diagup \text{C}:\text{C}(\text{CO}_2\text{Et}) \\ \diagdown \text{C}=\text{N}-\text{N} \end{array} \text{CMe}$ , m. p. 200—205° (decomp.), red crystals, which cannot be obtained from ethyl α- or β-anhydro-

retoxyleneacetoacetate. Ethyl retoxyleneacetoacetate and 5% hydrazine hydrate in alcohol at 60° react to form apparently an additive compound,  $C_{24}H_{28}O_4N_2$ , m. p. 215—216°, colourless needles.

The reaction between retenequinone and ethyl acetoacetate in acetic anhydride in the presence of a little concentrated sulphuric acid yields a mixture of several substances from which the following have been isolated: *ethyl diretenequinoneacetoacetate anhydride*,  $C_{42}H_{40}O_8$ , m. p. above 305°, orange-yellow needles,



which is regarded as a tetrahydro- $\gamma$ -pyrone derivative (annexed formula) in consequence of its intense green fluorescence in solution; *ethyl diretenequinoneacetoacetate*,



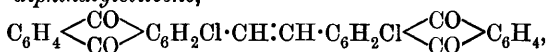
m. p. 235—237°, yellow crystals, which is not fluorescent in solution; a substance, m. p. 225—227°, yellow crystals, which might be, according to the analytical data, *ethyl diretenequinoneacetoacetate diacetate*,  $C_{46}H_{46}O_9$ , or *ethyl anhydroretenequinoneacetoacetate acetate*,  $C_{26}H_{26}O_5$ , the latter being regarded as the more probable formula by analogy with Richards' results of the condensation of phenanthraquinone and ethyl acetoacetate in the presence of acetic anhydride (T., 1910, 97, 1456). C. S.

**2-Chloroanthraquinone-3-carboxylic Acid.** FRITZ ULLMANN and INANENDRA CHANDRA DAS GUPTA (*Ber.*, 1914, 47, 553—568).—In order to prepare the "linear" anthraquinone-2:3-acridone (for the 1:2- and 2:1-isomerides, see A., 1911, i, 468, 489) and similar derivatives of anthraquinone, it was necessary to discover a simple process for the preparation of 2-chloroanthraquinone-3-carboxylic acid. Heller and Schülke (A., 1908, i, 994) obtained a chloromethylantraquinone from *o*-chlorotoluene and oxidised it by means of nitric acid in a sealed tube to an acid. The question of constitution was left open and it is now found that the first product was a mixture containing chiefly 2-chloro-3-methylantraquinone. Various methods for the convenient oxidation of this substance have been tried and almost quantitative yields have been obtained by introducing bromine into the methyl group, hydrolysing the dibromide to 2-chloro-3-aldehydoanthraquinone, and oxidising this.

A 93% yield of 3-chloro-4-methylbenzophenone-2'-carboxylic acid [*p*-2-chlorotoluoyl-*o*-benzoic acid] was obtained by dissolving phthalic anhydride in *o*-chlorotoluene, adding aluminium chloride to the cold mixture, and gradually warming to 90° during three to four hours, with vigorous stirring (*ibid.*). The barium salt,  $\text{Ba}(\text{C}_{15}\text{H}_{10}\text{O}_3\text{Cl})_2$ , was crystallised from hot water, but the barium salt of the product of oxidation by permanganate, namely, chlorobenzophenonedicarboxylic acid [2-chloro-3-carboxybenzoyl-*o*-benzoic acid] (*ibid.*) is freely soluble. The acid was condensed in fuming sulphuric acid (*ibid.*), the crude product representing a yield of 92%. About 80% of this crystallised from hot toluene in colourless, rhombic plates, m. p. 219° (corr.), and



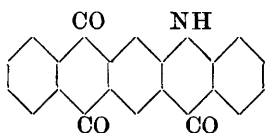
was 2-chloro-3-methylanthraquinone. The mother liquors were concentrated and deposited the isomeride, most probably 2-chloro-1-methylanthraquinone, in long, yellow needles, m. p. 170—171°, which become red in the light. The bromination of the former ketone could be effected in a sealed tube, but the same product, namely, 2-chloro-3-dibromomethylanthraquinone,  $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_2 \begin{smallmatrix} \diagup Cl \\ \diagdown CHBr_2 \end{smallmatrix}$ , was also obtained by slowly adding bromine to the solution in nitrobenzene at 165—170°. The substance was freed from mono- and tri-bromo-derivatives by crystallisation from toluene, and formed shining, hexagonal leaflets, m. p. 210—211° (corr.). When heated with copper powder in nitrobenzene for a few minutes, it deposited 2:2'-dichloro-4:5:4':5'-diphthalylstilbene,



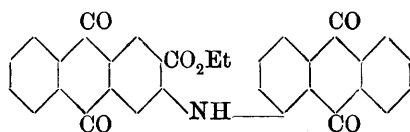
in long, silky, yellow, practically insoluble needles, m. p. above 440°. The hydrolysis of the dibromide was carried out by heating the compound to 130° for an hour, in sulphuric acid containing a little anhydride, a current of air being conducted through the mass. The yield of 2-chloro-3-aldehydoanthraquinone was quantitative. The compound crystallises in pale yellow needles or leaflets, m. p. 237° (corr.), and forms a red phenylhydrazone, m. p. 265—267°, and a yellow oxime, m. p. 272° (decomp.). The crude aldehyde was oxidised by sodium dichromate and acetic acid to 2-chloroanthraquinone-3-carboxylic acid (*ibid.*), a 95% yield being obtained. The ethyl ester, obtained from the acid chloride or by means of sulphuric acid, forms pale yellow needles, m. p. 153—154° (corr.).

When heated with concentrated ammonia and a trace of copper powder in a sealed tube, the acid was converted into 2-aminoanthraquinone-3-carboxylic acid (Willgerodt and Maffezzoli, A., 1910, i, 678). It was also converted into 2-anilinoanthraquinone-3-carboxylic acid by boiling with aniline, potassium acetate, and a little copper acetate.

This forms fiery red needles, m. p. 316—317°, and is condensed by the action of phosphorus pentachloride in toluene to anthraquinone-2:3-acridone [2:3-phthaloylacridone] (annexed formula), which forms yellowish-red needles from nitrobenzene, does not melt below 440°, and, like other acridones derived from 2-aminoanthraquinone, it is an alkali-sensitive, vat dye. Similarly, 2-β-naphthylaminoanthraquinone-3-carboxylic acid was obtained in deep red needles, m. p. 332° (corr.),



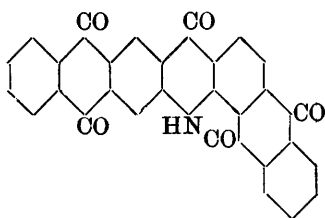
(I.)



(II.)

and condensed to anthraquinone-2:1-naphthacridone [6:7-benzo-2:3-phthaloylacridone], formula I, which forms red needles.

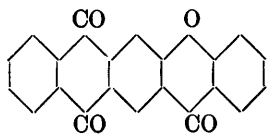
The ethyl ester of the acid was condensed with 1-aminoanthraquinone to ethyl 2:1'-anthraquinonylaminoanthraquinone-3-carboxylate, formula II, which



forms small, deep red needles, m. p. 314° (corr.), and is further condensed in concentrated sulphuric acid at 150° to 1:2-anthraquinonyl-2:3-anthracridone [2:3:8:9-diphthaloylacridone] (annexed formula). This was crystallised from sulphuric acid in small, radiating,

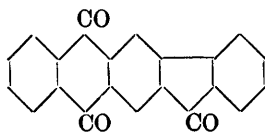
deep red needles.

The acid was also boiled with phenol, potassium carbonate, and copper powder, and converted into 2-phenoxyanthraquinone-3-carboxylic acid. This forms almost colourless needles, m. p. 270° (corr.), and is



condensed by means of phosphorus pentachloride in nitrobenzene to anthraquinone-2:3-xanthone [2:3-phthaloylxanthone] (annexed formula), which crystallises in long, pale, yellow, shining needles, m. p. 357° (corr.).

Finally, the acid was treated with phosphorus pentachloride in benzene, followed by aluminium chloride, and converted into 2-chloro-3-benzoylanthraquinone, which crystallises in almost colourless, rhombic plates, m. p. 199° (corr.). This was heated with ammonia and copper powder at 190—200°, when a 98% yield of 2-amino-3-benzoylanthraquinone was obtained in golden, quadratic



tablets, m. p. 331° (corr.). A poorer yield was obtained by hydrolysing the toluenesulphonylamido-derivative, which forms lemon-yellow needles, m. p. 240°. The amine was treated in strong sulphuric acid with sodium nitrite, and the solution was diluted without allow-

ing the temperature to rise, when the diazo-compound separated as a yellowish-red substance. The mass was then heated with copper powder, and anthraquinone-2:3-fluorenone [2:3-phthaloylfluorenone] (annexed formula) was obtained in pale reddish-yellow needles, m. p. 365° (corr.).

J. C. W.

**The Two Phthaloximes.** Studies on the Absorption Spectra and Constitution. D. S. PRATT and H. D. GIBBS (*Chem. Zentr.*, 1914, i, 539—540; from *Philippine J. Sci.*, 1913, 8, A, 165—189. Compare A., 1912, i, 190).—The isomerisation of the two oximes is due to the arrangement of the hydroxyl and carbonyl groups. The yellow compound is the *syn*-form in which these groups are nearer together than in the *anti*-modification. In the original, the results of spectroscopic examinations are given in a series of curves and photographs. The yellow isomeride exhibits a greater absorption in the visible part of the spectrum. The optical properties on p. 416 may be given.

The methyl ether of the white oxime forms long, colourless needles, m. p. 133°; the methyl ether of the yellow isomeride is pale yellow. Similarly, the benzoates form white and pale yellow columns, m. p.

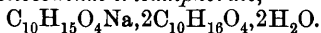
Compound.	Transmitted rays.	Pleochroism.
White oxime .....	White	None
Ethyl ether of white oxime .....	White and pale greenish-yellow	Faint
Yellow oxime .....	White and yellow	Faint
Acid sodium salt of white oxime .....	Pale yellow and orange	Distinct
Ammonium salt of white oxime .....	Straw-yellow and reddish-orange	Strong
Sodium salt of white oxime .....	Pale and deeper purple	Fairly distinct

171.5°. The solubility of the potassium salt in 100 c.c. of absolute alcohol at 30° is 0.05909 grams, of the sodium salt, 0.0076 grams.

J. C. W.

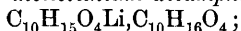
The Acid Salts of Dibasic Acids. The *d*-Camphorates. II. Different Metallic *d*-Camphorates. E. JUNGFLIECH and PH. LANDRIEU (*Compt. rend.*, 1914, 158, 445—450. Compare this vol., i, 13).—The authors have prepared the various *d*-camphorates of a number of metals and determined the conditions of their formation and their decomposition by water, which are shown by curves.

Sodium salts: the following have been obtained crystalline. *Disodium camphorate*,  $C_{10}H_{14}O_4Na_2 \cdot 3H_2O$ ; *monosodium camphorate*,  $C_{10}H_{15}O_4Na$ ; and *monosodium tricamphorate*,



The curve showing the conditions of formation of these salts is different from that for the potassium salts (*loc. cit.*), and shows that the neutral sodium salt is not dissociated by water, whilst the other two salts are ultimately decomposed by it into the neutral salt and the free acid.

Lithium salts: *dilithium camphorate*,  $C_{10}H_{14}O_4Li_2$ ; *monolithium camphorate*,  $C_{10}H_{15}O_4Li$ ; *monolithium dicamphorate*,



and *monolithium tetracamphorate*,  $C_{10}H_{15}O_4 \cdot 3C_{10}H_{16}O_4$ . The series of salts and the curve showing the conditions of formation is similar to that of the potassium salts. The acid salts are decomposed progressively by water giving finally the neutral salt and the free acid.

Ammonium salts: *diammonium camphorate*,  $C_{10}H_{14}O_4(NH_4)_2 \cdot 2H_2O$ ; *monoammonium camphorate*,  $C_{10}H_{15}O_4NH_4 \cdot H_2O$ ; and *monoammonium tricamphorate*,  $C_{10}H_{15}O_4NH_4 \cdot 2C_{10}H_{16}O_4 \cdot 3H_2O$ . This series corresponds with the series of sodium salts.

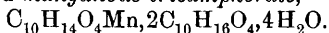
Barium salts: *Barium camphorate*,  $C_{10}H_{14}O_4Ba \cdot 4H_2O$ ; and *barium tetracamphorate*,  $C_{10}H_{14}O_4Ba \cdot 3C_{10}H_{16}O_4$ . The latter salt is so sparingly soluble that it separates from almost all solutions rendered acid.

Strontium salts: *strontium camphorate*,  $C_{10}H_{14}O_4Sr \cdot 4H_2O$ ; and *strontium tetracamphorate*,  $C_{10}H_{14}O_4Sr \cdot 3C_{10}H_{16}O_4$ . These two salts resemble the barium salts in their solubility in water.

*Calcium camphorate*,  $C_{10}H_{14}O_4Ca$ , which has been obtained crystalline with 7 and 4  $H_2O$  and in the anhydrous state. The authors could not succeed in preparing Kemper's acid salt.

*Magnesium camphorate*,  $C_{10}H_{14}O_4Mg$ , crystallising with 5 or 14  $H_2O$ , and resembling the calcium salt in its properties.

Manganese salts : *manganous camphorate*,  $C_{10}H_{14}O_4Mn$ , crystallising with 1 or  $2H_2O$ ; and *manganous tricamphorate*,



The acid salt is decomposed by water into the neutral salt and the free acid.

Cobalt salts : *cobaltous camphorate*,  $C_{10}H_{14}O_4Co$ , blue in the anhydrous state, and pink when crystallising with  $7H_2O$ ; and *cobaltous dicamphorate*,  $C_{10}H_{14}O_4Co, C_{10}H_{16}O_4$ . The acid salt is decomposed by water, giving the neutral salt and the free acid.

Piperidine salts : *dipiperidine camphorate*,  $C_{10}H_{14}O_4(C_5H_{11}N)_2$ ; and *monopiperidine camphorate*,  $C_{10}H_{15}O_4(C_5H_{11}N), H_2O$ . These salts are comparable with the metallic salts.

The readiness with which the acid camphorates are decomposed by water into the neutral salt and the free acid leads to the conclusion that their constitution is similar to that of acid salts of monobasic acids.

W. G.

**Synthesis of *o*-Diorsellinic Acid and Structure of Evernic Acid.** EMIL FISCHER and HERMANN O. L. FISCHER (*Ber.*, 1914, 47, 505—512).—A considerable amount of the matter in this paper has already been published (Fischer, A., 1913, i, 1352; Fischer and Fischer, *ibid.*, i, 732).

The *methyl* ester of the *trimethyl ether* of *o*-diorsellinic acid can be prepared by the action of diazomethane on the acid; it is quite distinct from the corresponding derivative of evernic acid, and has m. p.  $104-105^\circ$  (corr.).

Treatment of evernic acid with diazomethane in ethereal solution gave a product identical with the methyl ester of the trimethyl ether of lecanoric acid (Fischer and Fischer, A., 1913, i, 477), thus confirming the structure of evernic acid as derived from that of lecanoric acid by substitution of a methyl group at the para-hydroxyl.

D. F. T.

**New Preparation of Phenylacetaldehyde and of its Derivatives.** PAUL JEHL (*Bull. Soc. ind. Mulhouse.*, 1913, 83, 805).—Phenylacetaldehyde is obtained in 75% yield by the following process. Bromine is added drop by drop to a solution of methyl cinnamate in methyl alcohol. On cooling, the liquid solidifies, and is then treated with an aqueous solution of sodium hydroxide, care being taken that the temperature does not rise above  $40^\circ$ . The yellow dibromide slowly dissolves, and is replaced by a white precipitate. After two hours, sufficient sulphuric acid is added to neutralise the sodium hydroxide, whereon an oil separates. Water and sodium carbonate are added, and the phenylacetaldehyde is isolated by steam distillation and extraction with ether.

*p*-Nitrocinnamic acid, in a similar manner, yields a solid aldehyde which has an odour of cinnamon.

H. W.

**Synthesis of a Methylcyclopentenone.** MARCEL GODCHOT (*Compt. rend.*, 1914, 158, 506—508).—A further proof of the constitution of the ketone,  $C_6H_8O$ , obtained from wood oils by Looft (compare A., 1893, i, 558 1894, i, 399) and Bouveault (compare A.,

1901, i, 400). *cyclopentane-1:2-dione* reacts as a keto-alcohol with magnesium methyl iodide, giving the *glycol*,  $\text{CH}_2 \begin{matrix} \text{CH}=\text{C}\cdot\text{OH} \\ \text{CH}_2\cdot\text{CMe}\cdot\text{OH} \end{matrix}$  b. p. 79—81°/15 mm.;  $D_D^{16}$  1.051;  $n_D^{16}$  1.4734. This glycol on heating at 100° for three hours with one part of oxalic acid and two parts of water is dehydrated and gives the ketone,  $\begin{matrix} \text{CH}_2-\text{CH} \\ \text{CH}\cdot\text{CMe} \end{matrix} > \text{CO}$ , b. p. 157°, identical in its properties and its derivatives with the ketone obtained from wood oils. W. G.

**Action of Zinc on Alcoholic Solutions of Halogenated Ketones.** SHIVON I. IOCITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 98—100).—The action of zinc dust on an alcoholic (80%) solution of phenyl dibromomethyl ketone yields acetophenone, whilst pulegone hydrobromide under similar conditions gives pulegone and menthone (compare Beckmann, A., 1891, 936).

The formation of chlorocrotonaldehyde and crotonaldehyde by the action of zinc dust on butylchloral (compare Zarnov, *Annalen*, 1872, **164**, 93) may be represented by one of the three schemes: I.  $\text{R}\cdot\text{CO}\cdot\text{CH}_2\text{X} + \text{H}_2 = \text{R}\cdot\text{CO}\cdot\text{CH}_3 + \text{HX}$ ; II.  $\text{R}\cdot\text{CO}\cdot\text{CH}_2\text{X} + \text{Zn} = \text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{ZnX}$ , and this  $+ \text{H}_2\text{O} = \text{R}\cdot\text{CO}\cdot\text{CH}_3 + \text{ZnX}\cdot\text{OH}$ ; III.  $\text{R}\cdot\text{CO}\cdot\text{CH}_2\text{X} + \text{H}_2\text{O} = \text{R}\cdot\text{C}(\text{OH})_2\cdot\text{CH}_2\text{X}$ ; the latter  $+ \text{Zn} = \text{R}\cdot\text{C}(\text{OH})\cdot\text{CH}_2 + \text{ZnX}\cdot\text{OH}$ , and  $\text{R}\cdot\text{C}(\text{OH})\cdot\text{CH}_2 = \text{R}\cdot\text{CO}\cdot\text{CH}_3$ .

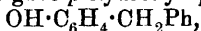
The considerable development of heat accompanying the reaction excludes scheme I. An attempt was made to decide between II and III, the action of zinc dust on alcoholic solutions of phenyl  $\gamma\gamma\gamma$ -trichloro- $\Delta^{\alpha}$ -propenyl ketone and methyl  $\gamma\gamma\gamma$ -trichloro- $\Delta^{\alpha}$ -propenyl ketone being investigated. The first gave a crystalline product, m. p. 50—51°, the composition of which corresponded with that of the original compound,  $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}_3$  less  $\text{HCl}$ ; the second gave an unstable liquid of the composition  $\text{COMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}_3$  less  $\text{HCl}$ . The investigation is being continued. T. H. P.

**Syntheses by means of Sodamide.** A. HALLER and ÉDOUARD BAUER (*Ann. Chim.*, 1914, [ix], **1**, 5—32).—The first part of the paper is a résumé of work already published on the decomposition of trialkylacetophenones by sodamide (compare A., 1909, i, 108, 654; 1911, i, 651, 726; 1913, i, 488), and the second a résumé of work on this reaction as applied to hexa-alkylacetones (compare A., 1910, i, 219, 300; 1912, i, 269; 1913, i, 591, 829). W. G.

**A General Method for the Reduction of the Carbonyl Group in Aldehydes and Ketones to the Methylene Group.** III. ERIK CLEMMENSEN (*Ber.*, 1914, **47**, 681—687. Compare A., 1913, i, 733; this vol., i, 271).—An extension of the investigation on the reduction of the carbonyl group by amalgamated zinc and hydrochloric acid.

Dibenzylacetone,  $\text{CO}(\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$ , b. p. 354—356°/747 mm., underwent reduction in a normal manner, yielding  $\alpha$ -diphenylpentane,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , a colourless, inodorous liquid, b. p. 326—327°/747 mm.

*p*-Hydroxybenzophenone gave *p*-hydroxydiphenylmethane,



m. p. 83—84°; 1-hydrindone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{CH}_2$ , yielded hydrindene,

b. p. 176—176·5°/742 mm.; benzoin gave *s*-diphenylethane, which was also obtained by reduction of benzil; anthraquinone yielded 9:10-dihydroanthracene which was not fluorescent in alcoholic solution; alizarin gave 1:2:3:4:9:10-hexahydroanthracene, tablets or broad needles, m. p. 60—62°, a little of which appeared also to be produced in the reduction of anthraquinone;  $\delta$ -keto-*n*-amyl alcohol yielded *n*-amyl alcohol, and cyclohexan-1:4-dione gave cyclohexane.

D. F. T.

**The Action of Acid Chlorides on Diphenylketen.** I. KONDAKOV (*Ber.*, 1914, 47, 688. Compare Staudinger, Göhring, and Schöller, this vol., i, 285).—In reference to the statement of Staudinger, Göhring, and Schöller to the effect that the addition of an acyl chloride molecule at an ethylenic linking had not previously been observed (*loc. cit.*), the author draws attention to the fact that such addition has already been effected by him (*A.*, 1896, i, 462; 1894, i, 113; 1893, i, 382).

D. F. T.

**Characteristic Behaviour of 1-Chloro-4-methylantraquinone towards Concentrated Nitric Acid. Formation of 3-Nitro-1:2-dihydroxy-4-methylantraquinone.** O. FISCHER and H. REBSAMEN (*Ber.*, 1914, 47, 461—466).—In connexion with the earlier work on 1-methylantracene (*A.*, 1912, i, 754; 1911, i, 279) it has been found that the nitration of 1-chloro-4-methylantraquinone by nitric acid (D 1·52) proceeds already at the ordinary temperature. When the reaction mixture is finally warmed at 60—70° to complete the change, a product crystallising in broad red needles or leaflets, m. p. 218°, is obtained. This substance is 3-nitro-1:2-dihydroxy-4-methylantraquinone. The yield is poor, but the addition of boric acid to the nitration mixture instead of improving the yield actually checked the formation of the desired substance, the product being a nitrohydroxymethylantraquinone, orange-yellow needles, m. p. 182°, possibly identical with the nitro-1-hydroxy-4-methylantraquinone already described (Fischer and Giegler, *A.*, 1912, i, 755). This substance on oxidation yielded phthalic acid, and so must contain all its substituents in one ring; further treatment with nitric acid in the absence of boric acid converted it into the dihydroxy-derivative, m. p. 218°, mentioned above; it is believed to be 3-nitro-1-hydroxy-4-methylantraquinone.

The dihydroxy-compound, m. p. 218°, can be oxidised to phthalic acid; it gives a bluish-black sodium salt, deep bluish-violet needles of a potassium salt, blue barium salt, and a diacetyl derivative, yellow needles, m. p. 188°. With ferric chloride in alcoholic solution a yellowish-green coloration is produced.

The parent substance is rather unstable, and is rapidly decomposed by warming in a solution of an alkali hydroxide or by boiling with sodium acetate and acetic anhydride. The centre of instability

appears to be the nitro-group, for reduction by zinc dust and acetic acid yielded a nitrogen-free substance, crystals, m. p. near 120°, possibly a *dihydroxymethyltetrahydroanthraquinone*, although reduction by stannous chloride in weakly alkaline solution gave 3-amino-1:2-*dihydroxymethylanthraquinone*, deep red needles, m. p. 285°.

D. F. T.

**The Polymorphism of Camphor.** FRED. WALLERANT (*Compt. rend.*, 1914, 158, 597—598).—Camphor crystallises from alcohol at the ordinary temperature in rhombohedral crystals, whereas on crystallisation by fusion it is quadrimorphic. On first solidification it crystallises in the cubic system, whilst at 97° these crystals are transformed into rhombohedra, which exhibit but slight birefracton and cleave along three planes. Small crystals gradually form at the edge of these crystals and gradually invade their whole mass. These new crystals are also rhombohedral, and resemble the primitive crystals in every respect. Finally, on cooling these crystals to -28° they are transformed into fresh rhombohedra, which are, however, highly birefractive.

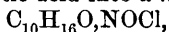
W. G.

**Terpenes and Ethereal Oils. CXVI.** O. WALLACH (*Annalen*, 1914, 403, 73—105. Compare this vol., i, 65).—[With ALAN R. ALBRIGHT and RUDOLF KLEIN.]—The supposed new modification, m. p. 66—67°, of *d*-carvotanacetoxime obtained by the regulated reduction of *d*-carvoxime by the Paal-Skita process (*loc. cit.*) is now shown to be a very stable solid solution of *d*-carvoxime, m. p. 72°, and *d*-carvotanacetoxime, m. p. 75°. The former erroneous view is all the more excusable because, in addition to the evidence of it already recorded, an equal molecular mixture of the *d*- and *l*-forms, m. p. 66—67° (obtained by the reduction of *d*- and *l*-carvoximes respectively), yields an apparently new *dl*-carvotanacetoxime, m. p. 87—88°. The incorrectness of the view is established by the facts that (i) the percentage of hydrogen is 0.2% too low; (ii) the m. p. 87—88° of the supposed *dl*-carvotanacetoxime is raised by repeated crystallisation; (iii) the supposed *d*-carvotanacetoxime, m. p. 66—67°, can be prepared by crystallising *d*-carvotanacetoxime (3 parts) and *d*-carvoxime (1 part) from methyl alcohol. The fact that *d*-carvotanacetone is the only ketone which can be isolated from the solid solution after hydrolysis by mineral acids (*loc. cit.*) is explained by the conversion of the carvone into carvacrol by the acid.

The author specially emphasises the fact that the molecules of carvone and of carvoxime are attacked in quite different manners by hydrogen from different sources, nascent hydrogen attacking the intracyclic double linking and molecular hydrogen in the presence of metals attacking in the first instance the extracyclic double linking. Carvone yields dihydrocarvone by reduction with nascent hydrogen, tetrahydrocarvone by the Paal process, and carvotanacetone by reduction with hydrogen and platinum black (Vavon, A., 1911, i, 730). Carvotanacetone is reduced nearly twice as readily as dihydrocarvone by regulated reduction by the Paal-Skita method. Carvoxime is reduced to carvotanacetoxime by regulated reduction by the Paal-Skita process, but with an excess of hydrogen in the Paal or the Paal-Skita

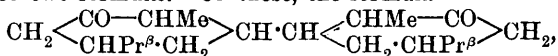
process yields tetrahydrocarvone, ammonia, carvacrylamine, and very little oxime (probably tetrahydrocarvoxime or carvotanacetoxime). It seems, therefore, that the saturation of the intracyclic double linking is rendered difficult by the presence of the neighbouring oximino-group. On the other hand, the juxtaposition of these two groups renders the oximino-group open to attack; dihydrocarvoxime is smoothly reduced to tetrahydrocarvoxime by hydrogen and colloidal palladium, whilst carvotanacetoxime yields very little tetrahydrocarvoxime and mainly tetrahydrocarvone, a result showing that hydrolysis of the oximino-group occurs more readily than reduction of the carvotanacetoxime.

[With RUDOLF KLEIN].—Although its semicarbazone is not quite individual and can be separated into a main constituent, m. p. 195—197° (202°, rapidly heated), and a minor constituent, m. p. about 163—165°, there is no doubt that the new dihydroeucarvone (called  $\beta$ -dihydroeucarvone), b. p. 213—214° (Wallach, *loc. cit.*), is different from Baeyer's dihydroeucarvone (called  $\alpha$ -dihydroeucarvone) obtained by the reduction of eucarvone by sodium and alcohol and oxidation of the resulting  $\alpha$ -dihydroeucarveol. In addition to the evidence already recorded it is shown that amyl nitrite and concentrated hydrochloric acid convert  $\alpha$ -dihydroeucarvone into a nitroso-derivative, m. p. 119—120° or 121—124° (Baeyer, A., 1894, i, 536), whilst the same reagents do not produce a nitroso-derivative from  $\beta$ -dihydroeucarvone, but convert it in glacial acetic acid into a *nitrosochloride*,

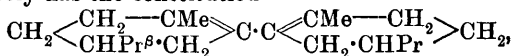


colourless crystals, which melts at 95° to a blue liquid.

[With ALFRED ERBEN].—Owing to its method of formation from  $\alpha$ -dicarvelone, tetrahydro- $\alpha$ -dicarvelone (Wallach, A., 1911, i, 469) can have one of two formulæ. Of these, the formula

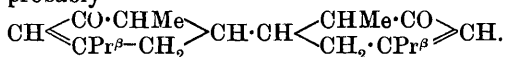


is the more probable, since the saturated diketone yields by oxidation with warm chromic and acetic acids an *acid* (silver salt,  $\text{C}_{20}\text{H}_{32}\text{O}_6\text{Ag}_2$ ), which reacts with alkaline sodium hypobromite with the formation of bromoform. Tetrahydro- $\alpha$ -dicarvelone is characterised by its *oxime*, m. p. 212—214°, and *glycol*,  $\text{C}_{20}\text{H}_{36}(\text{OH})_2$ , m. p. 209—210°, colourless needles. By heating the latter with zinc chloride at 220°, a *hydrocarbon*,  $\text{C}_{20}\text{H}_{34}$ , b. p. 190—195°/30 mm.,  $D^{20}_D$  0.945,  $n_D$  1.5172, is obtained which probably has the constitution



since the pronounced exaltation of its molecular refraction indicates the presence of a conjugated double linking.

$\beta$ -Dicarvelone (A., 1899, i, 530) does not react additively with hydrogen, and is therefore probably a substance of the carone type.  $\gamma$ -Dicarvelone (*oxime*, m. p. 178—179°) is reduced to tetrahydro- $\alpha$ -dicarvelone by the Paal-Skita method and therefore differs from  $\alpha$ -dicarvelone only in the position of the double linkings; its formula, therefore, is probably



The separation of the four products of the reduction of eucarvone



by zinc and aqueous sodium hydroxide (A., 1899, i, 530) is more readily accomplished by means of warm glacial acetic acid, fraction I, m. p. 174—176°, being obtained directly by cooling and the subsequent fractions by fractional precipitation of the filtrate by water.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Dieucarvelones, m. p. 177—178°, 140—142°, and 128° respectively, all have the formula  $C_{20}H_{30}O_2$  and are optically inactive.  $\alpha$ -Dieucarvelone forms an *oxime*, m. p. 260° (decomp.), and by reduction with sodium and alcohol yields a *glycol*,  $C_{20}H_{32}(OH)_2$ , m. p. 241—242°; by heating the latter with zinc chloride in a vacuum, an unstable *hydrocarbon*,  $C_{20}H_{30}$ , is obtained, which has a strong odour of oil of cedar-wood.

$\alpha$ - and  $\beta$ -Dieucarvelones are indifferent to hydrogen under Skita's conditions, whilst  $\gamma$ -dieucarvelone yields a *substance*,  $C_{20}H_{34}O_2$ , m. p. 105—106°, crystals.  $\gamma$ -Dieucarvelone also differs from the  $\alpha$ - and  $\beta$ -isomerides in its behaviour towards bromine in glacial acetic acid; the two latter undergo substitution, but the  $\gamma$ -compound yields a *tetrabromide*,  $C_{20}H_{30}O_2Br_4$ , m. p. 187—188°, needles. Possible formulæ of the three dieucarvelones are suggested. C. S.

Remarks on the Communication of G. Steimmig, "Synthetic Caoutchouc from Isoprene." C. HARRIES (*Ber.*, 1914, 47, 573—577. Compare this vol., i, 307).—The author develops arguments to show that the conclusions drawn by Steimmig lead too far. The main point which is criticised is that it is impossible to obtain a caoutchouc from isoprene which is identical with the natural product. Steimmig maintained that the artificial substance was a mixture of the polymerides of 1:5- and 1:6-dimethylcyclooctadienes, whereas the author found (A., 1911, i, 798) that a specimen obtained from pure isoprene was the former polymeride in a fairly pure state. He assumes that the material examined by Steimmig had been prepared from heterogeneous isoprene. Even with pure isoprene, quite inexplicable differences in the method of polymerisation lead to such different products that, even if it were proved that the caoutchouc obtained by the action of heat did sometimes happen to be a mixture in the above sense, yet it is too much to say that this must always be the case.

J. C. W.

Influence of the Nitrogenous and Resinous Constituents on the Vulcanising Capacity of Caoutchouc. HENRY P. STEVENS (*Kolloid. Zeitsch.*, 1914, 14, 91—96. Compare A., 1912, i, 789; 1913, i, 190).—In previous papers it has been shown that the removal of the nitrogenous constituents from caoutchouc reduces to a very large extent the capacity of the material to take up sulphur in the vulcanising process, and that the removal of the resinous constituents causes a marked deterioration in the quality of the caoutchouc.

Experiments are now described which indicate that the vulcanisability is more or less restored if nitrogenous substances, such as peptone and casein, are incorporated in the nitrogen-free caoutchouc previous to the treatment with sulphur. The incorporation of starch or lead oxide has a similar influence.

Other experiments have been made which show that if the resin,

extracted from caoutchouc by means of acetone, is re-incorporated previous to vulcanisation, the resulting material is very similar to that obtained when the original caoutchouc is vulcanised. If, however, resins of foreign origin are substituted for the caoutchouc resin, the vulcanised material is of a much inferior quality and behaves like an over-vulcanised caoutchouc. Contrary to statements made by Weber, it is found that the removal of the resinous constituents does not interfere appreciably with the vulcanisation of the caoutchouc.

H. M. D.

**Vulcanisation.** H. SKELLON (*Kolloid. Zeitsch.*, 1914, 14, 96—105).—A number of experiments are described which have a more or less direct bearing on the question of the nature of the vulcanisation process.

When layers of caoutchouc containing different amounts of Para-caoutchouc are placed in close contact during the vulcanisation process, it is found that the distribution of the sulphur between the two layers is determined by the content of Para-caoutchouc. In order to explain the form of the curves which are obtained when the vulcanisation is plotted as a function of time, the author considers it necessary to assume that a portion of the free sulphur is dissolved in the polyprène sulphide ( $C_{10}H_{16}S_2$ ). This solution is more concentrated than the solution of sulphur in the caoutchouc itself. At the vulcanisation temperature, the solubility in caoutchouc is about 10%. The dissolving of sulphur in polyprène sulphide will have a favourable influence on the rate of the vulcanisation process.

H. M. D.

**Synthetic Resins.** L. H. BAEKELAND (*J. Ind. Eng. Chem.*, 1914, 6, 167—170).—Polemical against Redman, Weith, and Brock's (*ibid.*, 1914, 6, 3) review of the literature on phenolic-methylene condensation products, and against the results of their research. T. S. P.

**Composition of Chlorophyll.** JULIUS STOKLASA, JOHANN ŠEBOR, and EMANUEL SENFT (*Chem. Zentr.*, 1914, i, 32; from *Bot. Zentr.*, 30, i, 167—235. Compare A., 1909, i, 248).—The results are summarised as follows: Phosphorus is not only utilised in the formation of cytoplasm and caryoplasm, but also in that of chlorophyll in the cells containing the latter in which it bears an important part. Chlorophyll consists of three different types of compounds: (1) phæophorbin and its metallic derivatives (compare Willstätter and Stoll, A., 1912, i, 287), soluble in alcohol and ether but not in light petroleum; (2) phæophytin and the phæophytides (compare Willstätter and Isler, A., 1912, i, 713), practically insoluble in ether, soluble in alcohol and ether, insoluble in light petroleum, and (3) the chlorolecithins or phæophorbinphosphatides. The latter, in accordance with the assumptions of Hoppe-Seyler, Gautier, and Stoklasa, are compounds of phæophorbin or of phæophorbin with phosphoglycerol, and, together with their metallic derivatives, are soluble in the three solvents previously mentioned. Phæophytin glyceride esters which do not contain phosphorus and chlorophyllins are also possibly present. The phosphoric acid is united to the glycerol esters of unsaturated acids or

hydroxy-acids. The unsaturated acids are formed during spring and summer. Oxidation to hydroxy-acids occurs simultaneously, and continues in preparations and in the acids obtained from them. Probably, the phæorobin behaves as a catalyst, causing reduction in sunlight, oxidation in the dark.

The metallic compounds contain chiefly magnesium together with calcium and potassium, and the first named is to be regarded as the active co-worker with the phosphorus in the formation and metabolism of plants. A method has been worked out which permits the approximate estimation of phæophorbin in the presence of phytol and a partial isolation of the acids.

The change of colour of leaves in autumn depends on the hydrolytic fission of chlorophyll and the formation of phæophytin and phosphatides; these substances, which themselves have a brownish colour, allow the yellow and red colour of xanthophyll and of the carotins to appear. The colourless lecithins and choline derivatives are not combined with the chlorophyll, but merely admixed, and are possibly intimately associated with the chlorolecithins.

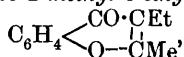
The authors are unable to confirm Willstätter's statement that preparations of chlorophyll, obtained from methyl alcohol and acetone extracts, contain only traces of phosphorus; their own preparations, examined at different times, show a considerable content of the latter.

H. W.

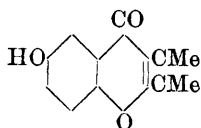
**Alkylated Chromones and their Fission Products.** H. SIMONIS and C. B. ALFRED LEHMANN (*Ber.*, 1914, **47**, 692—699).—A continuation of the investigation of Petschek and Simonis (*A.*, 1913, i, 890).

In the manner already described, methyl acetoacetate and *o*-cresol undergo condensation in the presence of phosphoric oxide, producing 2:3:8-trimethylchromone (annexed formula), colourless prisms, m. p. 122°; *oxime*, rhombic tablets or scales, m. p. 109°; the *oximes* of the isomeric 2:3:5- and 2:3:6-trimethylchromones (Petschek and Simonis, *loc. cit.*) form leaflets, m. p. 214°, and needles, m. p. 176°, respectively, whilst the three preceding isomeric trimethylchromones yield *dibromides*, as orange-coloured needles, m. p. 142°, 175°, and 115° respectively. Hydrolysis of 2:3:8-trimethylchromone by 3% potassium hydroxide solution gave rise to 3-methylsalicylic acid.

Phenol and ethyl ethylacetoacetate when heated together with phosphoric oxide give rise to 2-methyl-3-ethylchromone,



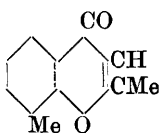
colourless leaflets, m. p. 90°, which on hydrolysis with dilute sodium hydroxide solution undergoes fission into salicylic acid and diethyl ketone.



A mixture of methyl acetoacetate and quinol containing a little alcohol was cooled in ice, whilst the phosphoric oxide was introduced. After subsequent heating on a water-bath, 6-hydroxy-2:3-dimethylchromone (annexed formula), colourless needles, m. p. 242°, was

obtained. Hydrolytic fission of this substance produced gentisic acid.

*o*-Cresol condensed with ethyl acetoacetate in the above general manner, yielding 2:8-*dimethylchromone* (annexed formula), colourless needles, m. p. 115°, which yielded *o*-homosalicylic acid on hydrolytic fission by dilute alkali hydroxides.



The method described earlier in detail (*loc. cit.*), therefore, supplies a fairly general synthesis for chromone derivatives, and the structure of the products is most readily examined by hydrolysis with dilute solutions of alkali hydroxides; under this treatment, taking 2:3-dimethylchromone as an example, fission into salicylic acid and methyl ethyl ketone is effected. 2:3:5-Trimethylchromone behaved abnormally towards hydrolysis, producing, after prolonged treatment, 2-hydroxy-6-methylpropio-phenone, a method of fission which could also be obtained with 2:3-dimethylchromone by the action of sodium ethoxide, producing *o*-hydroxy-propio-phenone.

When 2:3-dimethylchromone, m. p. 97°, is steam distilled in the presence of sodium phenoxide, about 50% of the chromone compound passes into the distillate, giving colourless needles (rhombic system,  $a:b:c = 0.9457:1:x$ ), m. p. 85°, which have the same composition as 2:3-dimethylchromone itself. The new product gives the same oxime as the parent substance, and can be reconverted into the latter by repeated crystallisation from water, with the addition of a little of the less fusible isomeride. The new substance is, therefore, designated iso-2:3-*dimethylchromone*, and it is suggested that the isomerism may be analogous to that of *allocinnamic acid*.  
D. F. T.

**Preparation of Thiophen from Acetylene.** WILHELM STEINKOPF and GEORG KIRCHOFF (*Annalen*, 1914, 403, 1—11).—By passing acetylene over pyrites heated to about 300° a brown, unpleasantly odorous liquid is obtained which does not contain benzene or carbon disulphide and consists, to the extent of about one-half, of thiophen, about 95% of which can be obtained therefrom by distillation. It is essential that the pyrites should be very finely powdered and should constantly expose a fresh surface to the acetylene. An apparatus designed for this purpose is figured and described, and by it about 320 grams of thiophen, b. p. 82—84°,  $D^{22}_{400} 1.040$ , can be prepared per diem. An unpleasantly odorous constituent is completely removed by the purification of the thiophen through its mercuriacetate derivative.

The pyrites may be replaced by marcasite or by synthetic pyrites prepared from ferrous sulphide and sulphur.  
C. S.

**Conversion of Homologous Butadienes into Homologous Thiophens.** WILHELM STEINKOPF (*Annalen*, 1914, 403, 11—16).—By passing the vapour of isoprene in a slow current of carbon dioxide over pyrites at a dull red heat, a poor yield of 3-methylthiophen, b. p. 109—115°, is obtained; this is identified by its colour reactions, and by the solubility and analysis of its mercurichloride.

In a similar manner  $\beta$ -dimethyl- $\Delta^{\gamma}$ -butadiene gives a poor yield of 3:4-dimethylthiophen, b. p. 142.5—146°.  
C. S.

**2-Thiopenine[2-Aminothiophen].** WILHELM STEINKOFF (*Annalen*, 1914, 403, 17—44).—[With GEORG LÜTZKENDORF.]—2-Nitrothiophen is obtained in about 70% yield by adding a mixture of acetic anhydride and nitric acid, D 1.52, to a well-stirred mixture of thiophen and acetic anhydride at 0—5°, air being drawn through the system during the operations. The mass is treated with water at 0°, and the resulting precipitate and oil are distilled with steam, whereby 2-nitrothiophen is obtained in the usual yellow, crystalline form, m. p. 44°. By distilling a small quantity with steam, or by shaking an alcoholic solution with animal charcoal and adding water, the authors have obtained it in almost entirely colourless crystals, m. p. 46.5°.

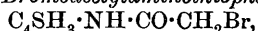
2-Nitrothiophen is best reduced by tin and concentrated hydrochloric acid at 40—45°, whereby the stannichloride of 2-aminothiophen is obtained in about 68% yield. An aqueous solution of the stannichloride in an atmosphere of hydrogen is treated with an excess of dilute sodium hydroxide at 0° in the presence of ether; the ethereal solution is removed, dried over sodium sulphate, and distilled, all the operations being performed in an atmosphere of hydrogen. 2-Aminothiophen is thus obtained as a faintly yellow liquid, b. p. 61—62°/1 mm., which has an odour resembling that of aniline. It can be kept for some days, but in the presence of a trace of oxygen it rapidly polymerises and subsequently oxidises. It forms a urethane, m. p. 52° (48°, Curtius and Thyssen); the *acetyl* derivative, m. p. 161—162°, colourless leaflets, can only be obtained in good yield by treating an aqueous solution of the stannichloride with acetic anhydride and ether and aqueous sodium hydroxide at 0°. 2-Acetylaminothiophen can also be obtained by the Beckmann transformation of the oxime of 2-acetylthiophen (by phosphorus pentachloride and ether), and thus for the first time are definitely proved the positions of the substituents in 2-aminothiophen and 2-nitrothiophen.

2-Acetylaminothiophen in xylene reacts with sodium at 140—160° to form the *sodio*-derivative, a grey substance, which is converted by methyl iodide in xylene at 120—130° into 2-acetylmethylaminothiophen,

$\begin{array}{c} \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{S} \end{array} \rightarrow \text{C} \cdot \text{NMeAc}$ , b. p. 123.5—124.5°/13 mm., m. p.

60°, colourless leaflets. By hydrolysing the last substance by boiling concentrated hydrochloric acid, cooling in an atmosphere of hydrogen, basifying with dilute sodium hydroxide, extracting the solution with ether and drying and distilling the extract, all operations being performed with the complete exclusion of oxygen, 2-methylaminothiophen, b. p. 88—92°/15 mm., is obtained as a colourless liquid which can be kept for a long time in the absence of oxygen. 2-Acetylmethylaminothiophen, b. p. 122—123°/15 mm., and 2-ethylaminothiophen, b. p. 85—89°/2—3 mm., are also described.

Other 2-acylaminothiophens have been prepared in the same manner as the acetyl derivative; they all crystallise well and are stable in the presence of oxygen. 2-Bromoacetylaminothiophen,



m. p. 160°, 2-propionylaminothiophen, m. p. 110—110.5°, and the corresponding *butyryl* derivative, m. p. 129.5°, *isovaleryl* derivative, m. p.

130—131°, *benzoyl* derivative, m. p. 172—173°, and *o-toluoyl* derivative, m. p. 184°, are described, the last two being prepared from benzoyl and *o*-toluoyl chlorides.

The nitration of 2-acetylaminothiophen in acetic anhydride by nitric acid, D 1.40, at 0° yields a mixture of nitro-derivatives from which, by fractional sublimation in a high vacuum, 3(?)*-nitro-2-acetylaminothiophen*, m. p. 165.5—166.5°, yellow needles, and 5(?)*-nitro-2-acetylaminothiophen*, m. p. 222—223°, brownish-yellow crystals, have been isolated. These two substances, in which the position of the nitro-groups is inferred from analogy to the nitroacetanilides, are soluble in aqueous ammonia and in dilute alkali hydroxides or carbonates, and yield the same 3:5-*dinitro-2-acetylaminothiophen*, m. p. 182°, yellow or orange-yellow needles, by further treatment with nitric acid, D 1.5.

C. S.

**Thiophen Mercurichlorides.** WILHELM STEINKOPF and MARTIN BAUERMEISTER (*Annalen*, 1914, 403, 50—72).—Volhard has shown (A., 1892, 828) that thiophen and its homologues react readily with mercuric chloride forming mono- and di-mercurichlorides. The authors have extended the investigation to other substituted thiophens and have ascertained the orientation of the mercurichloride groups. Thiophens having two unsubstituted  $\alpha$ -positions form mono- and di-mercurichlorides, thiophens having only one unsubstituted  $\alpha$ -position form, in general, monomercurichlorides, whilst thiophens having two substituted  $\alpha$ -positions either do not react with mercuric chloride or may form additive compounds of a thiophen derivative containing a mercurichloride group in position 3. However, the irregularities which not infrequently occur in the preceding reactions make mercuric chloride an unsafe reagent for the differentiation of isomeric thiophen derivatives.

Thiophen-2-mercurichloride is soluble in a large excess (120 mols.) of 4% sodium hydroxide. It reacts with sodium in boiling xylene to form *mercury 2:2'-dithienyl*,  $\text{Hg}(\text{C}_4\text{SH}_3)_2$ , m. p. 197°, colourless crystals, and with sodium iodide in acetone at the ordinary temperature to form *mercury 2:2'-dithienyl* and *thiophen 2-mercuri-iodide*, m. p. 116—117°, silvery leaflets; the latter, when moist, is decomposed by light into mercuric iodide and mercury dithienyl.

By heating with aqueous bromine, thiophen 2:5-dimercurichloride yields an oil which is volatile with steam and contains tetrabromothiophen and a little 2:5-dibromothiophen, identified as dibromodinitrothiophen, m. p. 139—140° (134°, Kreis).

The following mercurichlorides have been prepared by treating an alcoholic solution of the thiophen derivative with a cold saturated solution of mercuric chloride and 33% aqueous sodium acetate. 2-Methylthiophen mercurichloride has m. p. 204° (197°, Volhard). 3:4-Dimethylthiophen yields 3:4-*dimethylthiophen 2-mercurichloride*, m. p. 137—138°, colourless needles, and 3:4-*dimethylthiophen 2:5-dimercurichloride*, m. p. above 270°, which is insoluble in water and organic solvents. 2:5-Dimethylthiophen yields an additive compound,  $\text{C}_6\text{H}_9\text{OSHgCl}_2 \cdot \text{HgCl}_2$ , m. p. 186—187°, of mercuric chloride and 2-hydroxy-2:5-dimethyl-2:3-dihydrothiophen 3-mercurichloride, which

is decomposed by boiling alcohol, yielding 2:5-dimethylthiophen 3-mercurichloride, m. p. 156—157°, glistening needles. 2-Phenylthiophen yields 2-phenylthiophen 5-mercurichloride, m. p. 234°, colourless leaflets. 2-Chlorothiophen yields 2-chlorothiophen 5-mercurichloride, m. p. 218—219°, silvery leaflets, whilst 2-bromothiophen yields 2-bromothiophen 5-mercurichloride, m. p. 225°. 2:5-Dichloro- or bromo-thiophen does not react with mercuric chloride. 2-Iodothiophen yields 2-iodothiophen 5-mercurichloride, m. p. 225°, felted crystals, in which the position of the mercurichloride group is proved by the facts that the substance is converted into 2:5-di-iodothiophen by iodine and boiling water, and into 2-iodo-5-acetylthiophen (in very poor yield) by heating with acetyl chloride at 80—90°. 2-Nitrothiophen does not react with mercuric chloride.

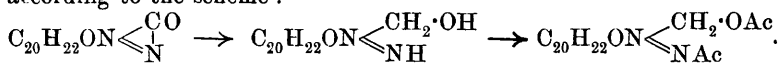
Since thiophen and mercuric chloride react readily to form thiophen 2-mercurichloride and the latter is converted into mercuric chloride and 2-acetylthiophen by acetyl chloride, it is clear that a small quantity of mercuric chloride should be sufficient to convert large amounts of thiophen and acetyl chloride into the corresponding ketone, and that the preceding reactions represent the individual steps of a catalytic process which is quite analogous to the Friedel-Crafts' reaction. A coloured by-product is obtained, but its amount is very greatly diminished by using thiophen 2-mercurichloride as catalyst instead of mercuric chloride. Thus thiophen and acetyl chloride, heated with one gram of the thiophen mercurichloride at 65° and finally at 90° for sixteen hours, give ultimately a 45% yield of 2-acetylthiophen. In other cases the yields are better than those obtained with aluminium chloride as catalyst; for example, thiophen and *o*-toluoyl chloride yield 73% of 2-*o*-toluoylthiophen, b. p. 180°/18 mm. In a similar manner have been prepared 2-benzoylthiophen, m. p. 55·5—56°, 2-*p*-toluoylthiophen, m. p. 75—76°, (*oxime*, m. p. 77—78°), and 2-*p*-nitrobenzoylthiophen, m. p. 172—173°, yellow crystals. C. S.

**Alkaloids of Ipecacuanha Root, Uragoga Ipecacuanha.** II. OSKAR KELLER (*Arch. Pharm.*, 1913, 251, 701—713. Compare A., 1911, i, 1014).—Improvements in the method of isolating the alkaloids are described. When the ethereal extracts are sufficiently concentrated and are kept for a long time in the cold, nearly the whole of the cephaeline crystallises; the subsequent addition of alcoholic hydrogen chloride to the filtrate (after dilution) causes the precipitation of emetine hydrochloride which contains very little cephaeline.

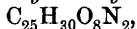
*Methylemetine hydriodide*,  $C_{81}H_{46}O_4N_2.HI$ , obtained by warming emetine with methyl iodide, is amorphous, does not yield a nitroso-derivative, but forms a benzoyl derivative, m. p. 50—55°, white powder (impure *platinichloride*,  $2C_{81}H_{45}O_2N_2.Bz.H_2PtCl_6$ , m. p. 100—110°, yellow, amorphous powder). *Methylemetine platinichloride* (impure), decomp. 252°, is a pale yellow, amorphous powder. By dry distillation, methylemetine dimethiodide (*loc. cit.*) yields ammonia, trimethylamine, tetramethylammonium iodide, tarry matter, and probably guaiacol; the last substance, identified in the form of its benzoyl derivative, is certainly obtained by the distillation, best with zinc dust, of the quaternary base. In the latter operation, an unknown base is produced which forms an *aurichloride*,  $C_6H_{16}N_2.2HAuCl_4(?)$ ,

m. p. 244—248°, yellow needles; the corresponding *platinichloride*, m. p. 239—240°, crystallises in orange-red octahedra, the *hydrochloride*, colourless needles, is very hygroscopic, and the *base* itself is an oil having an odour recalling that of piperidine. C. S.

**Strychnos Alkaloids. XXI. Some Experiments with Tetrahydrostrychnine.** HERMANN LEUCHS (*Ber.*, 1914, 47, 536—540).—In the degradation of strychnine and brucine, some of the products obtained contain the carboxyl group, others an imino-group, whilst others are acid-amides. Since strychnine itself contains an acid-amide grouping, it is of interest to study the degradation of a compound in which that characteristic is fundamentally changed. Such a compound is the diacetyl derivative of tetrahydrostrychnine, obtained according to the scheme:



This was oxidised by permanganate in acetone at 0°, but only 2% of a crystalline product, namely, *diacetylhexahydrostrychninonic acid*,



could be isolated. This forms small needles or very slender prisms with 1H<sub>2</sub>O, is hygroscopic when dried, and melts towards 140° with gas evolution.

Tetrahydrostrychnine, obtained by electrolytic reduction (Tafel, A., 1898, i, 703), was heated with acetic anhydride and sodium acetate, and the product was evaporated in a vacuum, dissolved in chloroform, and shaken with potassium hydrogen carbonate. The chloroform residue was recrystallised from 50 parts of petroleum (b. p. 90°), when the pure *diacetyl* derivative (*ibid.*) was obtained in tablets, m. p. 142—143°. It is alkaline to litmus and turmeric, and is hydrolysed by *N*-alkali to *N*-acetyl*tetrahydrostrychnine*, C<sub>23</sub>H<sub>28</sub>O<sub>3</sub>N<sub>2</sub>. This forms colourless, massive prisms with 1H<sub>2</sub>O, sinters or melts at about 160° with gas evolution, then resolidifies and melts again at 197—199°. J. C. W.

**Isolation of *iso*Phonopyrrolecarboxylic Acid from Hæmin and a New Method of Isolating the Acid Fission Products of Hæmin and Bilirubin.** HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1914, 47, 791—797).—The esters of phono- and *isophono*-pyrrole-carboxylic acids can be readily separated by means of their picrates. This can be effected mechanically, since the picrate of phonopyrrole-carboxylic ester is chocolate-brown (A., 1913, i, 71), whilst that of the *iso*-ester is yellow, but is more readily achieved by adding an insufficient quantity of picric acid to a mixture of the two esters, when, in general, the picrate of the ester present in greater amount separates; by gradual addition of picric acid, the separation can be controlled by observation of the colour of the precipitate. Finally, advantage may be taken of the fact that the picrate of phonopyrrole-carboxylic ester is very sparingly soluble in ethyl acetate in which the picrate of the *iso*-ester dissolves freely. With the help of this method, *isophonopyrrolecarboxylic acid* has been obtained in the pure state from hæmin, and its identity with the product obtained from bilirubin has been established. The mixture of acids contains about two-thirds phonopyrrolecarboxylic acid and one-third of the *iso*-acid.



Hæmin is decomposed with a mixture of glacial acetic acid and hydriodic acid in the usual manner, and the product, after treatment with phosphonium iodide, is distilled under diminished pressure and the bases removed from the alkaline solution in a current of steam. On acidification of the alkaline solution, a mixture of acids is obtained which are converted into their methyl ester by methyl alcohol and hydrogen chloride. The mixed esters are distilled, and the mixture, when preserved, deposits a certain amount of the pure phonopyrrole-carboxylic ester (m. p. of picrate  $120-121^{\circ}$ ). The separation of the esters in the liquid portion is effected by the gradual addition of picric acid, or, should this method fail, by the aid of ethyl acetate. In this manner, the picrates of methyl phonopyrrolecarboxylate and of methyl *isophonopyrrolecarboxylate*, m. p.  $112-113^{\circ}$ , are obtained in the pure state, the latter being identified by comparison with a specimen of the *iso*-ester picrate obtained from bilirubin. A third substance, m. p.  $95^{\circ}$ , probably the picrate of methyl trimethylpyrrole-propionate, is also obtained, the investigation of which is not yet complete.

The picrate of methyl *isophonopyrrolecarboxylate* is decomposed with sodium hydroxide and the ester hydrolysed with hydriodic acid (D 196), whereby *isophonopyrrolecarboxylic acid*, m. p.  $140^{\circ}$ , identical with the product obtained from bilirubin, is prepared. The picrate and oxime of the acid have m. p.'s  $155-156^{\circ}$  and  $219^{\circ}$  respectively, whereas Piloty and Dormann (A., 1912, i, 924) give  $146^{\circ}$  and  $210^{\circ}$ .

*iso*Phonopyrrolecarboxylic acid has previously been isolated from bilirubin in the form of its picrate. The preparation of the free acid is now described. Bilirubin is decomposed with glacial acetic acid and hydriodic acid in the usual manner. From the mixture of acids so obtained, bilirubic acid separates. The residual acids are converted into their methyl esters and then distilled in a vacuum. The first fraction (b. p.  $158-164^{\circ}$ ) consists of pure methyl *isophonopyrrolecarboxylate*, whilst the second and third fractions (b. p.'s  $164-174^{\circ}$  and  $174-230^{\circ}$  respectively) contain this substance mixed with methyl phonopyrrolecarboxylate. These are separated with the aid of picric acid. The picrate of the *iso*-ester, after decomposition in the manner described above, yields *isophonopyrrolecarboxylic acid*, m. p.  $142^{\circ}$ .

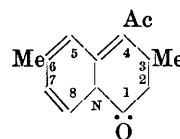
The method of isolating pyrrolecarboxylic acids by distillation of their esters has been found particularly advantageous in the production of trimethylpyrrolepropionic acid from hæmin after fission with potassium methoxide (compare A., 1913, i, 1080). After removal of phyllopyrrole from the product of the reaction, the mixture of acids is esterified and distilled, whereby two fractions are obtained. The first, b. p.  $162^{\circ}$ /vacuum, consists of methyl trimethylpyrrole-propionate (picrate, m. p.  $95-96^{\circ}$ ), whilst the second gives the Ehrlich aldehyde reaction, and, on treatment with picric acid, also yields the picrate, m. p.  $95-96^{\circ}$ .

Methyl trimethylpyrrolecarboxylate, b. p.  $157-158^{\circ}/10$  mm., is also prepared by the action of potassium methoxide on the mixture of phono- and *isophono*-pyrrolecarboxylic esters, a quantity of tetramethylpyrrole (picrate, m. p.  $126-127^{\circ}$ ) being also obtained. A specimen prepared in this manner yielded a picrate, m. p.  $97-98^{\circ}$ ,

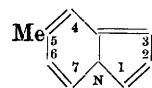
which showed no depression when mixed with the picrate obtained as above. On saponification, trimethylpyrrolepropionic acid, m. p.  $89^{\circ}$ , is obtained, the picrate of which has m. p.  $129-130^{\circ}$ , whereas Fischer and Bartholomäus (A., 1913, i, 210) found  $126-127^{\circ}$ . H. W.

**Conversion of Compounds of the Pyridine Series into Pyridine-pyrrole Compounds.** M. SCHOLTZ (*Arch. Pharm.*, 1913, 251, 666—681).—If the explanations of the constitutions of picolide and of pyrindole and of the reactions whereby these substances are produced are correct (A., 1912, i, 385, 648; Scholtz and Fraude, A., 1913, i, 514), it is at once obvious that similar substances can be prepared only from such pyridine derivatives as contain a methyl group in position 2. This has so far been the case. Characteristic products have not obtained by heating  $\beta$ -picoline,  $\gamma$ -picoline, or pyridine itself with acetic anhydride at  $200^{\circ}$ ; 2:4-dimethylpyridine and 6-phenyl-2-methylpyridine, however, yield methylpicolide and phenylpicolide respectively. These substances are quite analogous to picolide in their behaviour.

Methylpicolide (1-keto-4-acetyl-3:6-dimethylquinolizine) (annexed formula) forms an *oxime*, m. p.  $256^{\circ}$ , and *phenylhydrazone*, m. p.  $166^{\circ}$ , yellow needles, reacts with 2 mols. of an aromatic aldehyde in alcoholic, alkaline solution to form substances such as *dibenzylidenemethylpicolide*,



m. p.  $216^{\circ}$ , yellow needles, *difurfurylidenemethylpicolide*, m. p.  $218^{\circ}$ , yellow needles, and *dianisylidenemethylpicolide*, m. p.  $204^{\circ}$ , yellow needles, and is converted by boiling 25% hydrochloric acid into 5-methylpyrindole (annexed formula), m. p.  $81^{\circ}$ , b. p.  $206-207^{\circ}$ , colourless leaflets. 5-Methylpyrindole responds to the pine shaving and the isatin tests for a pyrrole, develops an indigo-blue coloration with dilute sulphuric acid and potassium iodate, and reacts readily with aldehydes in alcoholic solution to form substances such as *benzylidenedimethylpyrindole*,  $\text{CHPh}(\text{C}_9\text{H}_8\text{N})_2$ , m. p.  $221-222^{\circ}$ , colourless, crystalline powder rapidly becoming blue in moist air, and *furfurylidenedimethylpyrindole*,  $\text{C}_4\text{OH}_3\cdot\text{CH}(\text{C}_9\text{H}_8\text{N})_2$ , m. p.  $160-161^{\circ}$ . By heating with methyl iodide and methyl alcohol at  $120^{\circ}$ , 5-methylpyrindole is converted into *trimethylpyrindole methiodide*,

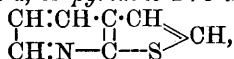


$\text{C}_8\text{H}_4\text{Me}_3\text{N}, \text{MeI}$ , m. p.  $168^{\circ}$ , colourless leaflets, an aqueous solution of which becomes strongly alkaline by shaking with silver oxide. 5-Methylpyrindole yields 1-acetyl-5-methylpyrindole, b. p.  $196-197^{\circ}/20 \text{ mm.}$  (*phenylhydrazone*, m. p.  $158^{\circ}$ , yellow needles), by boiling with acetic anhydride and sodium acetate, and condenses with benzenediazonium chloride in the presence of sodium acetate to form *benzeneazomethylpyrindole*,  $\text{C}_8\text{H}_5\text{MeN}\cdot\text{N}_2\text{Ph}$ , m. p.  $113-114^{\circ}$ , red needles.

*Phenylpicolide* (1-keto-4-acetyl-8-phenyl-3-methylquinolizine),  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ , m. p.  $232-233^{\circ}$ , greyish-yellow needles, prepared in 10% yield by heating 6-phenyl-2-methylpyridine with acetic anhydride at  $220^{\circ}$ , forms a *phenylhydrazone*, m. p.  $182^{\circ}$ , yellow needles, and a *dibenzylidene*

derivative, m. p.  $243^{\circ}$ , yellow prisms, and is converted by boiling 25% hydrochloric acid into 7-phenylpyrindole,  $C_{14}H_{11}N$ , m. p.  $123-124^{\circ}$ , colourless plates. The last substance exhibits colour reactions with a pine shaving, isatin, and iodic acid, has only a faint odour and feebly basic properties, is very sensitive to oxidising agents, and condenses with benzaldehyde and with benzenediazonium chloride to form benzylidenediphenylpyrindole,  $C_{35}H_{26}N_2$ , m. p.  $230-232^{\circ}$  (to a blue liquid), and benzeneazophenylpyrindole,  $C_{20}H_{15}N_3$ , decomp. above  $110^{\circ}$ , brown needles, respectively. C. S.

**Pyridino-2:3-thiophen.** WILHELM STEINKOFF and GEORG LÜTZKENDORF (*Annalen*, 1914, 403, 45-49).—The interaction of 2-aminothiophen stannichloride, 2-nitrothiophen (or arsenic acid), glycerol, and concentrated sulphuric acid at  $150^{\circ}$  and finally  $180^{\circ}$  leads to the production, in 5-7% yield, of pyridino-2:3-thiophen,



a yellow liquid, which has an odour similar to that of quinoline and resembles this base in forming a cobaltchloride,  $2C_7H_5NS, CoCl_2$ , corn-flower-blue powder, picrate,  $C_7H_5NS, C_6H_3O_7N_3, C_2H_5\cdot OH$ , m. p.  $185^{\circ}$ , greenish-yellow crystals (from ethyl alcohol), and dichromate,  $2C_7H_5NS, H_2Cr_2O_7$ , brownish-red powder; the N-methiodide, m. p.  $198.5^{\circ}$ , crystallises in yellow leaflets. C. S.

**The Constitution of Thionylphenylhydrazine.** C. G. HUTCHISON and S. SMILES (*Ber.*, 1914, 47, 514-516).—The chemical behaviour of thionylphenylhydrazine,  $NPh\cdot N\cdot SO$ , is such that the alternative formulæ  $NPh\cdot N\cdot SOH$  and  $NPh\cdot \begin{smallmatrix} NH \\ | \\ SO \end{smallmatrix}$ , have at different times (Michaelis and Ruhl, A., 1892, i, 1324; Stollé and Krauch, A., 1913, i, 97) been proposed.

A comparison of the absorption spectra of this substance and of its methyl derivative, which from its mode of formation and chemical properties must be indubitably of the structure  $NPhMe\cdot N\cdot SO$ , indicates a similarity of structure in the two substances, so that the unsubstituted compound in the free state and in neutral organic substances is represented by the formula  $NPh\cdot N\cdot SO$ .

As the absorption curve of the substance alters somewhat after a time, it is possible that some structural rearrangement slowly occurs or the change may be due to some decomposition. D. F. T.

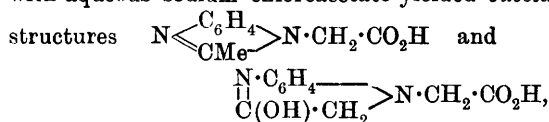
**The Preparation of Substituted Indigotins.** ARNOLD REISSERT (*Ber.*, 1914, 47, 672-681).—An account of experiments attempting the preparation of indigo dyes in which each of the nitrogen atoms forms part of a cyclic complex.

1:2:3-Benzotriazole-1-acetic acid  $N\leq\leq\begin{smallmatrix} C_6H_4 \end{smallmatrix}\rangle N\cdot CH_2\cdot CO_2H$ , is most conveniently prepared by the direct addition of sodium carbonate and chloroacetic acid solutions to a diazotised solution of o-phenylenedi-

amine sulphate, and heating the mixture for five hours on a water-bath. It forms colourless needles, m. p. 187—188°, and when heated in concentrated sulphuric acid at 165—170° undergoes conversion into an isomeric substance, *isobenzotriazole-1-acetic acid*, colourless needles, m. p. 212—213°.

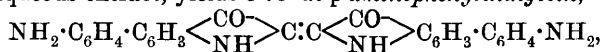
When the former of the above acids is distilled, carbon dioxide is lost with formation of 1-methylbenzotriazole,  $C_6H_4 \begin{smallmatrix} \text{NMe} \\ \text{N} \end{smallmatrix} > N$ , transparent leaflets or hexagonal tablets, m. p. 64—65°, b. p. 270—271° (*picrate*, yellow crystals, m. p. 149°), the structure of which was confirmed by a synthesis of the same substance from *o*-aminomethyl-aniline by diazotisation, and from benzotriazole by treatment with methyl sulphate and sodium hydroxide. On fusion with sodamide, the triazole ring of benzotriazole-1-acetic acid suffered disruption, the product being ordinary indigotin.

By treatment with acetic acid and chloroacetic acid respectively, *o*-phenylenediamine was converted into 2-methylbenziminazole and 3-hydroxy-1:2-dihydroquinoxaline, which on subsequent treatment with aqueous sodium chloroacetate yielded *substances* of the probable



m. p. 263—264° and 225° respectively. Fusion with sodamide failed to produce indigo colouring matters from these substances.

*Benzidinoacetic acid*,  $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H$ , a colourless, crystalline powder, m. p. 219—220° (decomp.), is obtainable by the action of chloroacetic acid on benzidine in hot aqueous solution; *sodium salt*, sparingly soluble in sodium hydroxide solution; the *hydrochloride*, gives a violet precipitate with ferric chloride. Fusion of the sodium salt with sodamide at 190°, with subsequent oxidation of the aqueous extract, yields 5:5'-*di-p-aminophenyindigotin*,



which closely resembles indigotin itself.

as-*Benzidinodiacetic acid*,  $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot N(CH_2 \cdot CO_2H)_2$ , which accompanies the previous acid in the above method of preparation, is obtained by the interaction of sodium chloroacetate and benzidine in boiling aqueous solution containing some sodium carbonate. It is a sparingly soluble substance, m. p. 210° (decomp.), which gives a blue precipitate with ferric chloride in acid solution. From the fact that it yields no dye when treated with sodamide, the acid must possess the unsymmetrical structure given.

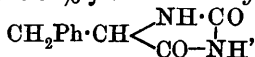
*Benzidinotetra-acetic acid*,  $C_{12}H_8[N(CH_2 \cdot CO_2H)_2]_2$ , is obtained by a process similar to the last, but with more prolonged treatment and an excess of sodium chloroacetate; it forms colourless needles, m. p. 221° (decomp.), and gives no dye when fused with sodium amide. When distilled in a vacuum, it yielded carbon dioxide and tetramethylbenzidine,  $NMe_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NMe_2$ , brownish-yellow crystals, m. p.

191—192°; the *hydrochloride* gives with ferric chloride solution a deposit of green needle crystals. D. F. T.

**Resolution of Inactive Carbamido-acids and Hydantoins into Active Components and Their Conversion into Amino-acids.** I.  $\alpha$ -Carbamido- $\beta$ -phenylpropionic Acid, Benzylhydantoin, and Phenylalanine. H. D. DAKIN and H. W. DUDLEY (*J. Biol. Chem.*, 1914, 17, 29—36).—*dl*- $\alpha$ -Carbamido- $\beta$ -phenylpropionic acid is resolved with great readiness by boiling it and an excess of strychnine with methyl alcohol, and adding acetone to the hot, filtered solution; about 80—95% of the theoretical quantity of *strychnine 1- $\alpha$ -carbamido- $\beta$ -phenylpropionate*,  $C_{31}H_{34}O_6N_4$ , m. p. 225·5—226°,  $[\alpha]_D - 33\cdot0^\circ$  in methyl alcohol ( $c=2\cdot0$ ), is deposited in glistening plates, whilst from the mother liquor, after removal of the strychnine by aqueous ammonia and subsequent acidification, more than 80% of *d*- $\alpha$ -carbamido- $\beta$ -phenylpropionic acid,  $C_{10}H_{12}O_4N_2$ , m. p. 195—196°,  $[\alpha]_D + 36\cdot3^\circ$  in aqueous ammonia ( $c=1\cdot0$ ), is obtained. *l*- $\alpha$ -Carbamido- $\beta$ -phenylpropionic acid, prepared from the strychnine salt, has m. p. 195—196° and  $[\alpha]_D - 36\cdot9^\circ$  in aqueous ammonia ( $c=1\cdot0$ ), and crystallises in prisms. The corresponding *d*-acid can also be obtained by warming *l*-phenylalanine with aqueous potassium cyanate and subsequently acidifying with hydrochloric acid; this method (including the resolution of *dl*-phenylalanine), however, is not so simple as that involving the resolution of *dl*- $\alpha$ -carbamido- $\beta$ -phenylpropionic acid.

The active  $\alpha$ -amino- $\beta$ -phenylpropionic acids cannot be obtained from the active  $\alpha$ -carbamido- $\beta$ -phenylpropionic acids, since the latter are almost completely racemised during hydrolysis by warm hydriodic acid, D 1·9, or boiling aqueous barium hydroxide; with the latter reagent it is just possible to detect the formation of *l*-phenylalanine from the *d*-carbamido-acid and vice versa.

By boiling with dilute hydrochloric acid, *l*- $\alpha$ -carbamido- $\beta$ -phenylpropionic acid gives about 90% yield of *d*-benzylhydantoin,



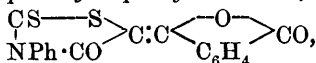
m. p. 181—183°, prisms,  $[\alpha]_D + 96\cdot4^\circ$  in 50% alcohol ( $c=0\cdot503$ ). *l*-Benzylhydantoin has m. p. 181—183° and  $[\alpha]_D - 79\cdot7^\circ$  in 50% alcohol.

By treatment with alkalis, the active benzylhydantoins, like other active hydantoins (Dakin, A., 1910, i, 590), are completely racemised, doubtless owing to the loss of asymmetry caused by enol-ketodesmotropy. C. S.

**isoThiohydantoins and Allied Substances.** FRANZ KUČERA (*Monatsh.*, 1914, 35, 137—157).—Phthalic anhydride is found to behave similarly to aldehydes towards substituted rhodanines (compare Andreasch, A., 1910, i, 694).

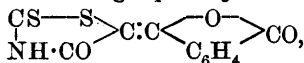
Phenylrhodanine and phthalic anhydride in molecular proportions fail to react in solution in a mixture of acetic acid and anhydride except with the additional presence of sodium acetate. The brownish-black

reaction product after extraction with water and alcohol successively, yields a residue of 5-phthalyl-3-phenylrhodanine,



deep yellow leaflets, m. p. 234°.

Rhodanine reacts more readily than the preceding substance with phthalic anhydride, the resulting 5-phthalylrhodanine,



separating from acetic acid in brownish-yellow scales, m. p. 245°(decomp.), which possess a bronze lustre; attempts to prepare a diphenylhydrazone yielded only phthalylphenylhydrazine. The crude phthalylrhodanine, as obtained by the above process, contained a considerable quantity of a substance which gives a red solution in alkalis. This solution on acidifying deposits an amorphous, yellow solid, and when treated with solutions of salts of magnesium, calcium, barium or zinc gives blood-red precipitates, whilst with a lead salt the precipitate is blue.

p-Nitrosodimethylaniline also condenses with phenylrhodanine in warm solution in acetic acid, yielding 3-phenylrhodanine-5-dimethyl-

aminoanil,  $\begin{array}{c} \text{CS} \text{---} \text{S} \\ | \qquad \qquad \qquad \diagup \quad \diagdown \\ \text{NPh} \cdot \text{CO} \quad \text{C} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2, \end{array}$  a deep brown, indistinctly crystalline powder, m. p. near 206°.

2:4-Diketotetrahydrothiazole and piperonal undergo condensation satisfactorily in acetic acid containing sodium acetate, the product being 2:4-diketo-5-methylene-3':4'-dioxymethylene-tetrahydrothiazole,

$\begin{array}{c} \text{CO} \text{---} \text{S} \\ | \qquad \qquad \qquad \diagup \quad \diagdown \\ \text{NH} \cdot \text{CO} \quad \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4 \quad \text{O} \\ \qquad \qquad \qquad \diagdown \quad \diagup \\ \qquad \qquad \qquad \text{CH}_2 \end{array}$  fine orange-coloured needles, m. p. 249°; potassium salt, colourless needles unfused at 295°.

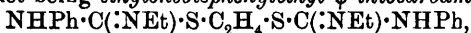
When shaken with water containing a little sodium hydroxide, 2-imino-4-ketotetrahydrothiazole (isothiohydantoin) condenses with benzaldehyde with formation of 2-imino-4-keto-5-benzylidenetetrahydro-

thiazole,  $\begin{array}{c} \text{NH} : \text{C} \text{---} \text{S} \\ | \qquad \qquad \qquad \diagup \quad \diagdown \\ \text{NH} \cdot \text{CO} \quad \text{C} : \text{CHPh} \end{array}$  pale yellow leaflets which commence to sinter at 280° and have an indistinct m. p.; sodium salt, colourless, broad needles.

Oxidation of 2-ethylimino-4-ketotetrahydrothiazole by hydrochloric acid and barium chlorate gave allophanylmethanesulphonic acid,  $\text{NH} \cdot \text{Et} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$ , which is already known to be also the oxidation product of 2-imino-4-ketotetrahydrothiazole itself.

Ethylene dibromide and phenylthiocarbamide in molecular proportion interact vigorously when heated at 125°, giving ethylenebis-phenyl-ψ-thiocarbamide,  $\text{NHPh} \cdot \text{C}(:\text{NH}) \cdot \text{S} \cdot \text{C}_2\text{H}_4 \cdot \text{S} \cdot \text{C}(:\text{NH}) \cdot \text{NHPh}$ , as a dihydrobromide, needles, m. p. 220° (decomp.); dipicrate, yellow, hair-like crystals, m. p. 201°. The structure of the product is demonstrated by the formation of ethylenedisulphonic acid on oxidation with barium chlorate and hydrochloric acid.

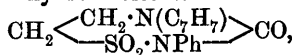
s-Phenylethylthiocarbamide and ethylene dibromide react readily at 95°, the product being ethylenebisphenylethyl-ψ-thiocarbamide,



as the *dihydrobromide*, stout prisms or needles, m. p. 204—205° (decomp.).

*s*-Phenylbenzylthiocarbamide and ethylene dibromide at 150—160° react with formation of amorphous 2-benzylimino-3-phenyltetrahydrothiazole,  $\begin{matrix} \text{CH}_2 \cdot \text{NPh} \\ | \\ \text{CH}_2 - \text{S} \end{matrix} > \text{C} : \text{N} \cdot \text{CH}_2 \text{Ph}$ ; oxidation of this product by hydrochloric acid and potassium chlorate produces *s*-phenylbenzylcarbamidoethanesulphonic acid as the *anhydride*,  $\text{CH}_2 < \begin{matrix} \text{NPh} \cdot \text{CO} \\ \text{CH}_2 \cdot \text{SO}_2 \end{matrix} > \text{N} \cdot \text{CH}_2 \text{Ph}$ , needles, m. p. 139—140°, the structure being indicated by the molecular weight in acetic acid, as also by the formation of benzylamine on hydrolysis.

At 170°, equimolecular quantities of ethylene dibromide and *s*-phenyl-*p*-tolylthiocarbamide interact with formation of 2-phenylimino-3-*p*-tolyltetrahydrothiazole,  $\text{CH}_2 < \begin{matrix} \text{S} - \text{C} : \text{NPh} \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_7\text{H}_7 \end{matrix} >$ , colourless leaflets, m. p. 92° (compare Will and Bielschowski, A., 1882, 1090). That the structure of the product is as stated and not that of the possible 2-tolylimino-3-phenyl compound is indicated by oxidation with potassium chlorate and hydrochloric acid to the *anhydride*,



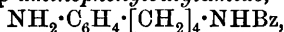
of *s*-phenyl-*p*-tolylcarbamidoethanesulphonic acid.

D. F. T.

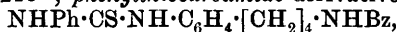
**Phenol Bases.** II. J. VON BRAUN (*Ber.*, 1914, 47, 492—505).—The earlier result as to the effect of the homologues of hordenine on the blood pressure of animals (von Braun and Deutsch, A., 1912, i, 845) is corrected; the lengthening of the carbon chain between the benzene ring and the amino-group causes a considerable weakening of the power of the molecule to increase the blood pressure, but the effect is not sufficient to induce an actual reversal of the change.

Compounds are now described in which the hordenine molecule has undergone still further modification.

[With H. DEUTSCH.]—The production of compounds of the formula  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_n \cdot \text{NH}_2$ , by nitration of benzophenylamylamide or benzophenylhexylamide, to be followed by the necessary subsequent treatment (compare Barger and Walpole, T., 1909, 95, 147) was not satisfactory as the product of this first stage was, in each case, a mixture of isomeric mononitro-compounds which could not be separated. Benzophenylbutylamide, on the other hand, gave a mixture which partly solidified, and the oily portion could be removed by washing with alcohol; the residue formed needles, m. p. 128—129°, and consisted of *benzo-p-nitrophenylbutylamide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_4 \cdot \text{NHBz}$ ; this yielded *p*-nitrobenzoic acid on oxidation. Reduction of this new compound in alcoholic solution by stannous chloride and hydrochloric acid produced *benzo-δ-p-aminophenylbutylamide*,



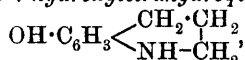
needles, m. p. 106°; *hydrochloride*, m. p. 232° (decomp.); *platinichloride*, m. p. 205°; *sulphate*; *picrate*, crystalline powder, m. p. 200°; *benzoyl derivative*, m. p. 215°; *phenylthiocarbamide derivative*,



m. p. 160°. If the above base is diazotised and the resulting solution

boiled, *benzo-δ-p-hydroxyphenylbutylamide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_4 \cdot \text{NHBz}$ , is obtained, in colourless leaflets, m. p. 120—121°; *benzoyl* derivative, m. p. 147—148°. The hydrolysis of this hydroxy-compound to *δ-p-hydroxyphenylbutylamine*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_4 \cdot \text{NH}_2$ , offered considerable difficulty on account of the narrow range between temperatures which produced no effect and caused resinification. Heating for six hours at 135°, however, gave a fairly good yield of the desired base, which had m. p. 106—108°; *hydrochloride*, m. p. 194—195°; *platinichloride*, m. p. 212° (decomp.); benzoyl chloride gives rise to the dibenzoyl derivative, m. p. 147—148°, mentioned above. The corresponding hydroxyphenylpropylamine has already been prepared (Goldschmidt, A., 1913, i, 643).

[With O. KRUBER.]—In order to reduce 7-nitro-1-benzoyltetrahydroquinoline (von Braun, Grabowski, and Rawicz, A., 1913, i, 1380) without causing hydrolysis of the benzoyl radicle, it is necessary to use stannous chloride and hydrochloric acid without external application of heat; the product is then 7-amino-1-benzoyltetrahydroquinoline,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{NBz} \cdot \text{CH}_2 \end{smallmatrix}$ , leaflets, m. p. 133°; *hydrochloride*, m. p. 158—159°; *phenylthiocarbamide*,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_5\text{H}_5\text{NBz}$ , leaflets, m. p. 148°; *salicylidene* derivative, yellow solid, m. p. 119°; the *carbamide* produced by reaction with potassium cyanate exhibits but little tendency to crystallisation. The above amino-compound can be easily converted in the general manner into 7-hydroxy-1-benzoyltetrahydroquinoline, colourless crystals, m. p. 194°; *benzoyl* derivative, m. p. 146°. By heating with concentrated hydrochloric acid at water-bath temperature for twelve hours, the preceding hydroxy-compound undergoes hydrolysis to 7-hydroxytetrahydroquinoline,



m. p. 94—95°, b. p. 200—202°/16 mm.; *hydrochloride*, m. p. 159°; *platinichloride*, m. p. 218°; *picrate*, m. p. 174°.

Reduction of 6-nitro-1-benzoyl-2-methyldihydroindole by stannous chloride at water-bath temperature yields 6-amino-2-methyldihydroindole,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} > \text{CHMe}$ , which can be obtained more conveniently by reducing 6-nitro-2-methyldihydroindole itself; the product was a reddish-brown liquid, b. p. 182—184°/17 mm.; *dihydrochloride*, m. p. 235—238°; *dipicrate*, m. p. 127°; the *dibenzoyl* derivative is best prepared by careful reduction of 6-nitro-1-benzoyl-2-methyldihydroindole without loss of the benzoyl group to 6-amino-1-benzoyl-2-methyldihydroindole,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{NBz} \end{smallmatrix} > \text{CHMe}$ , leaflets, m. p.

150°, followed by treatment with benzoyl chloride. 6-Amino-1-benzoyl-2-methyldihydroindole gives a *hydrochloride*, m. p. 237°, and condensation products with benzaldehyde, phenylthiocarbamide, and potassium cyanate, but the latter have little tendency to crystallise; the amino-group can be replaced by hydroxyl with formation of 6-hydroxy-1-benzoyl-2-methyldihydroindole,  $\text{OH} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{NBz} \end{smallmatrix} > \text{CHMe}$ .

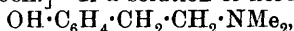


a colourless, crystalline solid, m. p. 235°, which gives a badly crystalline *benzoyl* derivative, and is hydrolysed with difficulty to 6-hydroxy-2-methyldihydroindole,  $\text{OH} \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} \right\rangle \text{CHMe}$ , m. p. 86—87°, b. p. 186—188°/16 mm.; *hydrochloride*, m. p. 165°; *picrate*, m. p. 178°.

6-Aminodihydroscatole,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{CHMe} \\ \text{NH} \end{smallmatrix} \right\rangle \text{CH}_2$ , prepared by reduction of the corresponding nitro-compound, is a deep red oil, which is distillable without decomposition in a vacuum; it gives a *hydrochloride*, m. p. 265°, and a *picrate*, m. p. 146°. Its *benzoyl* derivative, 6-amino-1-benzoyldihydroscatole is a crystalline solid, m. p. 167°; *hydrochloride*, m. p. 218°; yellow *salicylidene* derivative, m. p. 151°; the *carbamide* produced by interaction with potassium cyanate has m. p. 134°. Only a very poor yield of 6-hydroxy-1-benzoyldihydroscatole, m. p. 249°, is obtainable from the corresponding amino-compound by diazotisation, and a satisfactory hydrolysis of the product is so difficult that 6-hydroxydihydroscatole was not obtained pure, but was recognisable as a solid substance, generally resembling the above 6-hydroxy-2-methyldihydroindole.

Pharmacological examination of 7-hydroxytetrahydroquinoline and 6-hydroxy-2-methyldihydroindole indicates that in these substances the considerable structural change has only somewhat weakened the characteristic effect of hordenine on the blood pressure.

[With A. SCHMATLOCH.]—If a solution of hordenine,



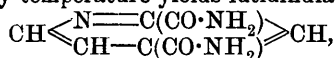
in dilute alkali is shaken for a half hour with a cooled ethereal solution of *p*-nitrobenzoyl chloride, the *p*-nitrobenzoyl derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$ , is obtained as leaflets, m. p. 89—90°; *hydrochloride*, m. p. 228°; *picrate*, m. p. 219°; *methiodide*, unfused at 250°. Reduction of the nitro-compound by stannous chloride and hydrochloric acid at a temperature not exceeding 50° gives *p*-aminobenzoylhordenine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$ , colourless leaflets, m. p. 156—157°; *dihydrochloride*, unfused at 240°; *picrate*, m. p. 204—205°. The free base possesses the anæsthetic effect which is common to acyl derivatives of aliphatic alkamines, but it also has considerable poisonous action. This result is especially interesting on account of the structural relationship to novocaine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$ . D. F. T.

Diamines of the Pyridine Group. III. Derivatives of Lutidinic Acid and 2:4-Diaminopyridine. HANS MEYER and HANS TROPSCH (*Monatsh.*, 1914, 35, 189—206. Compare Meyer and Staffen, A., 1913, i, 530).—By a modification of the method of Weidel and Herzig (A., 1886, 477) for the oxidation of commercial mixture of pyridine homologues, b. p. 156—160°, the authors have been able to increase the purity of the lutidinic acid produced without rendering the process more complex. The mixture of *isocinchomeric* acid and lutidinic acid obtained by the oxidation can be very conveniently separated by making use of the very sparing solubility of the methyl ester of the former acid in cold methyl alcohol, when the *methyl lutidinate*, odourless needles, m. p. 58°, of bitter taste resembling

quinine can be obtained from the solution. The hydrolysis of the ester is best effected by acids, when the resulting acid, which forms needles of a *hydrochloride* which are stable only in contact with concentrated hydrochloric acid, is obtained as pearly leaflets (containing  $1\text{H}_2\text{O}$  expelled at  $100^\circ$ ), m. p.  $248-250^\circ$ .

The acid can be converted by thionyl chloride into *lutidinyl chloride*, m. p.  $54-56^\circ$ ; the chloride, m. p.  $203^\circ$ , obtained by Voigt's method with phosphorus pentachloride (A., 1885, 813), is apparently a chlorolutidinyl chloride, for treatment with methyl alcohol gave a methyl ester, needles, m. p.  $117^\circ$ , which contained chlorine.

Methyl lutidinate with concentrated ammonia solution after twelve hours at the ordinary temperature yields lutidindiamide,



silky needles, m. p.  $254-255^\circ$ , whilst with an alcoholic solution of hydrazine hydrate the product is the corresponding *dihydrazide*, needles, m. p.  $256^\circ$  (decomp.), which in aqueous solution condenses with benzaldehyde, *o*-chlorobenzaldehyde and vanillin, forming respectively a *dibenzylidene* derivative, colourless crystals, m. p.  $233^\circ$ , a *di-o-chlorobenzylidene* derivative, colourless needles, m. p.  $274^\circ$ , and an amorphous *di-3-methoxy-4-hydroxybenzylidene* derivative, which sinters at  $150^\circ$  and has m. p.  $260^\circ$ . The last product becomes deep red when moistened with concentrated hydrochloric acid, subsequent careful addition of ammonia first destroying and then restoring the colour. By the action of potassium nitrite on a solution of the dihydrazide in ice-cold  $2\text{N}$ -hydrochloric acid the corresponding *diazoidime*,  $\text{C}_7\text{H}_5\text{O}_2\text{N}_7$ , is obtainable as a colourless solid, decomp. at  $98^\circ$  on rapid heating.

If the diazoidime just mentioned is kept in boiling alcoholic solution with exclusion of atmospheric moisture for three to four hours, by which time the liberation of nitrogen will have ceased, *2:4-dicarbethoxyaminopyridine*, colourless needles, m. p.  $170^\circ$ , is obtained, which by treatment with boiling hydriodic acid or alcoholic potassium hydroxide can be converted into *2:4-diaminopyridine*,  $\text{CH} \begin{array}{c} \text{N}-\text{C}(\text{NH}_2) \\ \text{CH}:\text{C}(\text{NH}_2) \end{array} \text{CH}$ , the latter hydrolytic agent first giving a substance, probably of the structure  $\text{CH} \begin{array}{c} \text{N}-\text{C}(\text{NH}\cdot\text{CO}_2\text{K}) \\ \text{CH}:\text{C}(\text{NH}\cdot\text{CO}_2\text{K}) \end{array} \text{CH}$ , which gives the diamino-pyridine when subsequently treated with acid. *2:4-Diaminopyridine* forms colourless leaflets or needles, m. p.  $107^\circ$ , which deliquesce in moist air; it can be titrated as a monacid base if methyl-orange is used as indicator. Unlike *2:5-diaminopyridine* it is very stable towards light and air; *hydrobromide*, long needles; *hydriodide*, needles; *platini-chloride*, golden-yellow needles, m. p.  $224^\circ$  (decomp.); *aurichloride*, reddish-brown needles, m. p.  $183^\circ$  (decomp.); *dibenzoyl* derivative, colourless needles, m. p.  $191-192^\circ$ . D. F. T.

**Diamines of the Pyridine Group. IV. Dinicotinic Acid and its Degradation to 3:5-Diaminopyridine; 2:6-Diaminopyridine.** HANS MEYER and HANS TROPSCH (*Monatsh.*, 1914, 35, 207-217).—Dinicotinic acid, which has been but little studied, is best obtained by the condensation of ethyl acetoacetate, form-

aldehyde, and ammonia to ethyl dihydrolutidinedicarboxylate (Schiﬀ and Prosio, A., 1896, i, 250) followed by oxidation with a mixture of nitric and sulphuric acids to ethyl lutidinedicarboxylate, which after hydrolysis to the free acid can be oxidised in neutral solution by potassium permanganate with formation of pyridine-2:3:5:6-tetracarboxylic acid. This can be separated as the sparingly soluble lead salt, when the free acid can be isolated, and then by heating with acetic acid for three hours can be converted into dinicotinic acid (pyridine-3:5-dicarboxylic acid), m. p. 320°.

The *methyl* ester, needles, m. p. 84—85°, of this acid when treated in alcoholic solution with hydrazine hydrate undergoes conversion into the amorphous *dihydrazide*, which condenses with acetone, producing the *di-isopropylidenehydrazide*,  $C_{13}H_{17}O_2N_5$ , needles, m. p. 230—232°. The dihydrazide when treated with nitrous acid passes into the *diazomide*, colourless leaflets, m. p. 83°, decomp. at a higher temperature. Boiling with alcohol converts the last substance into 3:5-dicarbethoxyaminopyridine, m. p. 179—181° (decomp.), which on hydrolysis by alkali passes into 3:5-diaminopyridine. The resultant base forms colourless leaflets, m. p. 110—111°, which are deliquescent in moist air, and gives strongly alkaline solutions; *hydrochloride*, very soluble needles; *dihydrobromide*, lustrous prisms, m. p. 275° (decomp.), almost insoluble in concentrated hydrobromic acid; *platinichloride*, orange, microcrystalline precipitate, decomp. near 220°; *dibenzoyl* derivative, silky needles, m. p. 211—212°.

The 2:6-diaminopyridine, prepared by Meyer and Mally (A., 1912, i, 515), has now been prepared in larger quantity; its m. p. is 119—120°; *platinichloride*, orange-red needles, decomp. near 190°; *dibenzoyl* derivative, needles, m. p. 176°.

Attention is drawn to the analogous stability of the diaminopyridines and the phenylenediamines; the compounds containing the amino-groups in a meta-position to each other are very stable, whilst the 2:5-aminopyridine is unstable and easily undergoes atmospheric oxidation. The diaminopyridines are all more strongly basic than the phenylenediamines.

D. F. T.

Purines. XIV. 2:8-Dioxy-1:7:9-trimethyl-1:2:8:9-tetrahydropurine, an Isomeride of Caffeine, and 2:8-Dioxy-1:7-dimethyl-1:2:8:9-tetrahydropurine, an Isomeride of Theobromine. CARL O. JOHNS (*J. Biol. Chem.*, 1914, 17, 1—7. Compare A., 1913, i, 1397).—Methyl sulphate is a better reagent than methyl iodide for the alkylation of purines, larger yields being obtained in shorter times. By shaking with methyl sulphate and *N*-sodium hydroxide, 2:8-dioxy-1:9-dimethyl-1:2:8:9-tetrahydropurine is converted into 2:8-dioxy-1:7:9-trimethyl-1:2:8:9-tetrahydropurine,

$$\begin{array}{c} \text{NMe} \cdot \text{CH} : \text{C} \cdot \text{NMe} \\ | \qquad \qquad | \\ \text{CO} - \text{N} = \text{C} \cdot \text{NMe} \end{array} > \text{CO},$$
 m. p. 240°, globular clusters of flattened crystals, which is isomeric with caffeine, but differs from it in its much greater solubility in water and in not developing a purple coloration when the residue obtained by its evaporation with chlorine water is moistened with aqueous ammonia.

By a similar process of methylation, 2:8-dioxy-1-methyl-1:2:8:9-tetrahydropurine (A., 1912, i, 588) yields a *substance*, decomp. below

320°, felted needles, which is not 2:8-dioxy-1:9-dimethyl-1:2:8:9-tetrahydropurine (nacreous plates which do not decompose at 350°), and must therefore be 2:8-dioxy-1:7-dimethyl-1:2:8:9-tetrahydropurine, since it yields the preceding 2:8-dioxy-1:7:9-trimethyl-1:2:8:9-tetrahydropurine by further methylation.

In one experiment on the methylation of 2:8-dioxy-1-methyl-1:2:8:9-tetrahydropurine, a mixture of the nacreous plates of 2:8-dioxy-1:9-dimethyl-1:2:8:9-tetrahydropurine and the needles of 2:8-dioxy-1:7-dimethyl-1:2:8:9-tetrahydropurine was obtained which was separated by fractional crystallisation from water, the former being the less soluble. C. S.

**Uric Acid Glycol.** HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1914, 47, 459—461).—The preparation of uric acid glycol from alloxan and carbamide has already been described (Biltz and Heyn, A., 1912, i, 489). It is now found that uric acid can be converted into the glycol in one operation by the action of bromine on an aqueous suspension at 0°. The course of this reaction is believed to be the primary oxidation of uric acid to alloxan and carbamide, which then interact to produce uric acid glycol. This view is supported by the occurrence of crystals of alloxan tetrahydrate in the reaction product, and suggests that bromine must exert a catalytic effect on the condensation of alloxan with carbamide which proceeds but slowly under the usual conditions at 0°. Experiment verifies this deduction, and the interaction of alloxan and carbamide in aqueous solution containing a little bromine proves to be the most convenient process for the preparation of uric acid glycol, 80—85% of the theoretical quantity of a pure product being directly obtained. D. F. T.

**Benzeneazomethane.** HANS STOBBE and ROBERT NOWAK (*Ber.*, 1914, 47, 578—580).—The absorption curve obtained in the case of benzeneazoethane (A., 1913, i, 1200) did not coincide at all with the curve given by Baly and Tuck for benzeneazomethane (T., 1906, 89, 985). The authors have now prepared the latter substance by Tafel's method (A., 1885, i, 1061) and find, as they expected, that the absorption bands are identical with those of benzeneazoethane. They have also attempted to repeat Baly and Tuck's experiments and, in a detailed account, show that they could obtain only a 0.05% yield of optically pure material. J. C. W.

**Fibrinogen and the Oxalated Plasma.** M. PIETTRE and A. VILA (*Compt. rend.*, 1914, 158, 637—640).—Dilute acids are capable of converting the fibrinogen of plasma or fibrinogen in solution into a substance possessing all the characteristic properties of fibrin. This phenomenon cannot be attributed to a coagulating ferment, since the transformation takes place equally well in a decalcified liquid under conditions where such a ferment could not act. Whilst an amount of acid just sufficient to change the reaction of the medium produces coagulation, an excess of acid causes the fibrous clot to redissolve, but this solution after a few hours sets to a jelly. Mineral and organic acids are equally effective in producing the coagulation. W. G.

**Caseinogen and Casein.** ARTHUR GEAKE (*Biochem. J.*, 1914, 8, 30—37).—The differences in elementary analysis and Hausmann

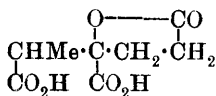
numbers for casein and caseinogen are so slight as to be inappreciable. The same is true for different fractions of casein. W. D. H.

**The Action of Coagulating Enzymes on Caseinogen.** ARTHUR HARDEN and ARCHIBALD BRUCE MACALUM (*Biochem. J.*, 1914, 8, 90—99).—The conversion of caseinogen into casein by enzyme action is accompanied by the cleavage of nitrogen, phosphorus and calcium. Rennin action produces no soluble nitrogen or phosphorus; trypsin splits off both soluble nitrogen and phosphorus, and the curdling enzyme of *Withania coagulans* also produces soluble nitrogen and phosphorus, but in smaller quantities. The cleavage products are specific for each enzyme, and variations in the resulting casein are thus explained. The precipitation of calcium caseinate by soluble calcium salts is not due to any chemical combination with these. The caseinogen once exposed to enzyme action and re-dispersed cannot be rendered more precipitable by further enzyme action. If the enzyme is sufficiently concentrated, precipitates are obtained without the addition of calcium salts, and this also occurs over 45° with more dilute enzyme solutions. W. D. H.

**Synthesis of Hæmatic Acid.** WILLIAM KÜSTER and JOHANNES WELLER (*Ber.*, 1914, 47, 532—536).—When hæmatic acid is boiled for some time with 40% potassium hydroxide, it combines with the elements of water. About four-fifths of the substance are changed into a mixture of stereoisomerides, from which a lactone of  $\gamma$ -hydroxypentane- $\beta\gamma\epsilon$ -tricarboxylic acid may be isolated. This can be reconverted into hæmatic acid by further boiling with alkali or by heating under reduced pressure. These facts encouraged the authors to prepare a structural isomeride of the above hydroxy-acid by the addition of hydrogen cyanide to  $\alpha$ -acetylglutaric acid, followed by hydrolysis. A mixture with the lactone was obtained, which yielded hæmatic acid when heated at 183° under 9 mm. pressure. The synthesis is therefore represented as follows:  $\text{COMe}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{OH}\cdot\text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow$

$$\begin{array}{c} \text{MeC}=\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{OC} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$$

The calculated quantity of hydrochloric acid was added at intervals to a cold mixture of ethyl  $\alpha$ -acetylglutarate, potassium cyanide, and ether, which was shaken for two days. The residue from the ethereal filtrate was hydrolysed by heating with 25% hydrochloric acid for fourteen hours, when the product was extracted with ether, and the residue left on evaporation was dissolved in water and shaken with chloroform to remove the by-product,  $\gamma$ -acetylbutyric acid. The colourless syrup from the chloroform extract contained the  $\beta$ -hydroxypentane- $\beta\gamma\epsilon$ -tricarboxylic acids and the lactone. From the very soluble barium salt, the silver salt,  $\text{C}_8\text{H}_9\text{O}_7\text{Ag}_3$ , was prepared, and from this the methyl ester,  $\text{C}_8\text{H}_9\text{O}_7\text{Me}_3$ , b. p. about 170°/10 mm.



The lactonic acid (annexed formula), obtained from hæmatic acid,

has m. p. 169—170°, and yields methylethylmaleic anhydride when heated to 245°.

J. C. W.

**Peptone.** I. ALESSANDRO BERNARDI (*Biochem. Zeitsch.*, 1914, 60, 56—61).—On the addition of 5% Witte's peptone to a mixture of equivalent amount of barium hydroxide and copper sulphate, a blue soluble copper salt is formed on heating, which can be precipitated from solution by alcohol, and purified by resolution and re-precipitation. The acid regenerated from this salt differs from the peptone in that it is not precipitated by acetic acid and potassium ferrocyanide and the author expresses the opinion that it will be possible by the preparation of the above copper salt to obtain a definite chemical entity from the peptone.

S. B. S.

**The Use of  $\beta$ -Naphthalenesulphonyl Chloride Method for the Recognition of Partial Hydrolysis of Flesh-protein.** PETER BERGELL (*Zeitsch. physiol. Chem.*, 1914, 89, 465—474).—The usefulness of this reagent introduced by the author has been abundantly verified. It forms insoluble compounds with the majority of amino-acids and polypeptides; free dibasic monoamino-acids alone yield no insoluble precipitates. It may be used in conjunction with other methods (Kjeldahl's for total nitrogen, etc.) to ascertain the degree of cleavage in a given digest, and examples of the analytical procedure recommended are given in relation to autolysed flesh and various commercial meat extracts.

W. D. H.

**The Theory of the Electrolytic Dissociation of Ferments.** L. MICHAELIS (*Biochem. Zeitsch.*, 1914, 60, 91—96).—If the activity of a ferment is a function of the hydrion concentration, a curve of the form of a dissociation curve can be deduced, which has been experimentally verified. The parameter of this curve  $q$  was formerly regarded as the electrolytic dissociation constant of the ferment  $k$ . This statement, it is now shown, requires modification for  $q = k/l + \alpha S$ , where  $S$  is the concentration of the decomposable substrate,  $\alpha$  is its affinity constant to the active ferment molecules, which in some cases are the electrically neutral undissociated molecules, in others the anions and cations.

S. B. S.

**Pepsin** D. LÉNARD (*Biochem. Zeitsch.*, 1914, 60, 43—55).—If trypsin is made acid by hydrochloric acid, it loses its digestive properties, which can only be restored to a very slight extent, if at all, by subsequent addition of alkalis. With pepsin, on the other hand, it is possible to restore the digestive properties which have been lost on treatment with alkalis, by the subsequent addition of acids. This does not happen, however, with all samples of pepsin. The best results were obtained with dog's pepsin; with human and pig's pepsin, the regeneration only succeeds very occasionally. The rennetic and peptic actions were always parallel in these experiments. The conditions of optimal acidity for ferment action varied with the different descriptions of pepsin, being highest for human pepsin and lowest for pig's pepsin, dog's pepsin acting best in acidity between these two.

S. B. S.

**Behaviour of Trypsin in the Presence of a Specific Precipitate.** AGNES ELLEN PORTER (*Biochem. J.*, 1914, 8, 50—58. Compare this vol., i, 214).—Trypsin is only partly inhibited in the presence of 10% ox serum, but on saturating the serum with carbon dioxide the precipitate formed binds the enzyme and completely removes it from solution. The absorbed enzyme is partly recoverable from the precipitate by protein especially in solution. In the presence of a specific precipitate (immune rabbit serum and egg white), trypsin is more inhibited than by immune serum alone or by normal serum and egg white. This occurs both when free trypsin is tested by a solid protein and with protein in solution. E. F. A.

**The Resistance of Trypsin Solutions to Heat.** EDWARD STAFFORD EDIE (*Biochem. J.*, 1914, 8, 84—89).—Whereas neutral or alkaline solutions of trypsin are rendered inactive by boiling, acid solutions do not behave thus, and in some cases suffer no loss of activity at all. This confirms a recent statement of Mellanby and Woolley. The groupings in trypsin on which digestion depends appear to be more stable than those which curdle milk. W. D. H.

**The Conditions of the Action of Maltase from Beer-yeast.**  
 III. **The Nature of the Various Kinds of Inhibitors of the Ferment Action.** L. MICHAELIS and P. RONA (*Biochem. Zeitsch.*, 1914, 60, 62—78).—The following assumptions are made: (I) the ferment  $F$  combines with the substrate  $S$  to form a compound  $FS$ , (II) which decomposes according to the laws of a unimolecular reaction. (III) The ferment can also combine with other substances, which do not undergo hydrolysis, but which withdraw part of the ferment from combination with the substrate. If  $k$  is the dissociation constant of the substrate ferment combination, then  $[F][S]/[FS] = k$ , and if  $v$  is the rate of the decomposition of the substrate, then  $v = -d[S]/dt = c[FS]$ . It is now assumed that the inhibitors of ferment action can act in one of two ways: (a) they can either combine with the ferment, or (b) they can diminish the reaction constant  $c$ . If  $v$  is the rate of change of substrate without inhibitor, and  $v_1$  is that in its presence,  $v - v_1/v = h$ , where  $h$  is the inhibition constant. It is now shown by the authors that the following relationship holds:  $k_1/k = [R]/([S] + k)(h/1 - h)$ , where  $k_1$  is the dissociation constant of the compound of the ferment with the inhibitory substance,  $k$  that of the compound of the ferment with the decomposable substrate,  $[R]$  is the concentration of the inhibiting substance,  $[S]$  that of the substrate.  $h$  can be experimentally determined from the reaction rates in the presence and absence of inhibitors from the equation given above. If now, the inhibition depends on the action of the inhibitor on the rate of decomposition of the substrate-ferment compound (the constant  $c$  as defined above), then the factor  $h$  will remain a constant, with varying concentrations of the substrate. If, however, the inhibitor acts by combining with the substrate,  $h$  will no longer remain a constant, but the function of  $h$  in the equation given above, namely,  $k_1/k$ .

The eleven theoretical considerations were applied to the investigation of various inhibitors on the action of the maltase of beer-yeast

on  $\alpha$ -methylglucoside. Sodium chloride, sodium nitrate, and glycerol act by diminishing the reaction constant (as defined above), whereas lithium chloride and dextrose act by combining with the ferment. Lævulose and  $\beta$ -methylglucoside have no inhibitory action and no affinity to the ferment. The affinity of dextrose to the ferment is five times greater than that of  $\alpha$ -methylglucoside. S. B. S.

**The Nature of the Inhibitors of Invertase Action.** L. MICHAELIS and H. PECHSTEIN (*Biochem. Zeitsch.*, 1914, 60, 79—90).—The theoretical deductions from the preceding paper are applied to the study of invertase action. Lævulose inhibits the action, owing to its affinity to the ferment. Glycerol and  $\alpha$ -methylglucoside, on the other hand, do not combine with the ferment, but they diminish the rate of decomposition of the sucrose-invertase compound. Maltose, lactose, and  $\beta$ -methylglucoside have no appreciable inhibitory action. The results lead to the generalisation that hydrolysable sugars (disaccharides or glucosides) which are not degraded under the influence of invertase have no affinity to the ferment. The determining factor for hydrolysis is the power of the ferment to combine with its substrate. The question as to whether invertase can react with a non-hydrolysable sugar can only be determined by an indirect method. S. B. S.

**Influence of Acids on the Activity of Dialysed Maltase.** W. KOPACZEWSKI (*Compt. rend.*, 1914, 158, 640—642).—A comparison of the activating influence of various acids on dialysed and non-dialysed maltase. In general the optimum activity for dialysed maltase occurs with a lower acid concentration than in the case of non-dialysed maltase. The influence of the various acids cannot be accounted for entirely by the concentration of the hydrogen ions. It is necessary to take into account the nature of the anions. To determine the exact conditions of activity of maltase, it is necessary to work with dialysed solutions. W. G.

**The Character of the Action of the So-called Tyrosinase.** A. BACH (*Biochem. Zeitsch.*, 1914, 60, 221—230).—Experiments are quoted which tend to show that the so-called tyrosinase contains a mixture of ferments, including phenolases or peroxydases. In addition, it contains an amino-acidase, which acts on the tyrosine, producing, in the first instance, readily oxidisable substances. These in the presence of the oxydases (or phenolases) give rise to the pigmented substances. S. B. S.

**The Enzymes of Washed Zymin and Dried Yeast (Lebedev).** II. Reductase. ARTHUR HARDEN and ROLAND VICTOR NORRIS (*Biochem. J.*, 1914, 8, 100—106).—Fermentable sugar favours the reduction of selenite by living yeast, but has little influence on the reducing-power of zymin unless present in high concentration, when inhibition occurs. Sodium selenite (0.5%) almost totally inhibits the fermentation of dextrose by zymin and dried yeast. When zymin or dried yeast is washed with cold water, it loses its power of reducing



methylene-blue and sodium selenite. The washed preparations, however, reduce methylene-blue in the presence of many aldehydes and of bouillon, but these do not restore to it the power of producing alcoholic fermentation. Addition of the boiled washings to these washed preparations restores the power of reducing methylene-blue and of producing alcoholic fermentation.

W. D. H.

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## Physiological Chemistry.

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**Dialysis of Normal Circulating Blood.** C. L. VON HESS and H. MCGUIGAN (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, **33**, xii—xiii).—The method consists in attaching artificial collodion vessels between the carotid artery and jugular vein, and was adopted independently of Abel's work (this vol., i, 217); the apparatus is simpler than Abel's, and hirudin as an anti-coagulant was not employed. The results obtained show that most of, if not all, the sugar of the blood is present in a free state, and that phloridzin does not increase the rate of dialysis even when the urine is rich in sugar. In one experiment (not aseptic) diastase was found in the dialysate. Hexamethylenetetramine is not decomposed in the circulating blood. W. D. H.

**The Partition of Dextrose in Human Blood, and its Dependence on Temperature.** ERNST MASING (*Pflüger's Archiv*, 1914, **156**, 401—417).—In human blood, the amount of dextrose in the corpuscles and the fluid of the blood, respectively, depends, not only on the concentration, but on temperature; at 0° the saturation of the corpuscles with sugar is very slow; at 25° it is fifty times more rapid. Previous treatment of the corpuscles with formaldehyde increases the rate at 0°. In this the effect of temperature coincides with what is known of other vital phenomena (heart frequency, development of the egg, etc.). W. D. H.

**The Rate at which Sugar Disappears from the Blood in Eviscerated Animals (Dogs).** J. J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1914, **33**, 378—381).—Even when the diabetic state due to depancreatisation has lasted for over a week, there is no evidence of depressed glycolytic power in eviscerated animals. In the present research, sources of error were avoided by using decerebrate animals, so that the influence of anæsthetics might be avoided, and, further, the percentage of hæmoglobin in the blood was estimated, so as to gauge the degree to which the blood was diluted by tissue juice. The use of adrenaline was avoided as much as possible, but when the animal's state was very depressed, an adequate blood-pressure could only be maintained by giving

adrenaline; glycolysis here went up, probably because of the increased activity of the heart. Irregularities in the results are confessedly present, and more trust should be placed on the behaviour of the respiratory exchange, as in Murlin's work.

W. D. H.

**The Rapid Disappearance from the Blood of Large Quantities of Dextrose Injected Intravenously in Dogs.** I. S. KLEINER and S. J. MELTZER (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, 33, xvii—xviii).—Ninety-seven % of the injected sugar disappears in about an hour and a-half; of this, 53% appears in the urine; if the liver is excluded, 84% disappears. Even in dead animals 52% vanishes in a short time. The muscles contain a large increase of carbohydrate, but whether this will account for all the lost sugar, or what changes it undergoes in the muscles, are not yet settled.

W. D. H.

**Proteins of the Blood.** HANS FREUND (*Zeitsch. öffentl. Chem.*, 1914, 20, 61—65).—Hæmoglobin (from horse) in relatively large doses (0.1 gram intravenous and 0.4 gram subcutaneous) has but little toxic effect on guinea-pigs. The globin prepared from this is, however, much more toxic. For guinea-pigs, the toxic dose is between 0.03 and 0.06 gram, and even the smaller dose produces convulsions and dyspnoea. A re-injection into sensitised animals of a sub-toxic dose produces anaphylactic effects. A dog, after injection of 0.5 gram of horse-globin, showed rise of temperature and difficulty in breathing. Dog-globin produced the same effect in guinea-pigs as horse-globin. A dose of 1.2 gram of dog-globin injected intravenously into a dog was toxic, and death resulted from respiratory paralysis. The relative non-toxicity of hæmoglobin as compared with globin is of interest. The toxicity of globin is ascribed to its histidine content, and attention is directed to the pathological significance of the fact that hæmochromogen diminishes the toxicity of the globin.

S. B. S.

**Concentration of Haemoglobin in the Blood of Rabbits.** A. E. BOYCOTT (*J. Path. Bact.*, 1914, 18, 417—418).—The extreme range of the percentage of hæmoglobin in 404 normal rabbits is from 54 to 101 on the human scale; the majority, however, approximate to the average of 76. There is no proof of any sex difference.

W. D. H.

**The Fermentative Activity of the Blood and Tissues after Extirpation of the Pancreas. I. Antitrypsin.** W. STAWRAKY (*Zeitsch. physiol. Chem.*, 1914, 89, 381—407).—The antitrypsin of the blood in dilutions varying from 1 in 10 to 1 in 500 is completely inactivated by heating at 68° for one hour. Higher temperatures have the same effect more rapidly, but are not recommended, as the high temperature has other effects also (coagulation of protein, etc.), and so completely alter the physical properties of the fluid. Antitrypsin is a colloid; it is not dialysable. In dogs minus a

pancreas, there is a rise in fats and lipoids, but a lessening of anti-trypsin; it does not appear to be a lipid-protein union. The loss of antitrypsin in blood of other organs begins immediately after the operation, is very marked ten days later, and reaches its maximum at the time of death. The stimulus for the formation of antitrypsin (antitryptase) is the presence of trypsin; in other words, trypsin is the antigen, antitrypsin the anti-substance produced. Peritonitis does not increase the antitrypsin of the blood. In fatty degeneration of the liver there is for the first few days an increase of antitryptic action. The sub-maxillary gland shows, in comparison with other organs, a very strong inhibiting influence on the digestive action of trypsin. W. D. H.

**Peculiar Position of Human Blood-corpuscles with Regard to Permeability for Monosaccharoses.** SHUZO KOZAWA (*Chem. Zentr.*, 1914, i, 159; from *Zentr. Physiol.*, 1913, 27, 793—795).—Blood corpuscles of man, cat, rabbit, guinea-pig, wether, ox, pig, goat, and horse have been centrifuged in isotonic solutions of various non-lipotropic substances (mannitol, dulcitol, galactose, dextrose, mannose, sorbose, lævulose, methylglucose, methylgalactoside, adonitol, arabinose, xylose, rhamnase, glucoheptose, lactose, maltose, sucrose, glycine, alanine, sodium pyruvate, sodium tartrate, and sodium acetate). The blood corpuscles of man alone behave as permeable, and then only towards the simple sugars. Permeability is indicated by increase in volume, and is verified by chemical analysis. H. W.

**The Behaviour of Red Blood-corpuscles considered in Reference to the Species. I. Hæmolysis under the Joint Influence of Normal Salts and Cytolytic Substances.** RUDOLF HÖBER and OTTO NAST (*Biochem. Zeitsch.*, 1914, 60, 131—145).—The authors have investigated hæmolysis in the presence of various salts of blood-corpuscles from different species of animals by saponin, sapotoxin, agaricin, sodium taurocholate, and solanine hydrochloride. They draw the conclusion that the salts affect the state of the colloids of the corpuscles, and that the difference of action in the various species of the combined action of salts and cytolytic substances is to be ascribed to the differences in the electrolytes contained within the cells. These electrolytes have a definite function in maintaining a certain consistency of the protoplasm. S. B. S.

**The Behaviour of Red Blood-corpuscles considered in Reference to the Species. II. Cataphoresis and Hæmolysis.** SHUZO KOZAWA (*Biochem. Zeitsch.*, 1914, 60, 146—157).—Cataphoresis of the corpuscles of various animals in phosphate mixtures was investigated, and it was found that the electrically neutral point varied with the species. The same kind of species difference was observed in discharging the corpuscles with lanthanum salts. The hydrion concentration necessary to produce hæmolysis in phosphate mixtures also varies with the species. There is a certain critical concentration of lanthanum in which the corpuscles hæmolyse most

readily; in concentrations above and below this point, the corpuscles are less sensitive. There is also a critical concentration in which proteins agglutinate most readily. The results indicate that hæmolysis is due to an agglutination of the cell colloids at the isoelectric point. S. B. S.

**The Behaviour of Red Blood-corpuscles considered in Reference to the Species. III. The Permeability of the Corpuscles of Various Species.** SHUZO KOZAWA (*Biochem. Zeitsch.*, 1914, **60**, 231—256).—By means of the hæmatocrite, as well as by chemical analysis, the following facts were established. The blood-corpuscles of man, ape, and dog are permeable for hexoses and pentoses, but impermeable for heptose, methylglucosides, methylpentose, hexitol, pentitol, disaccharides, amino-acids, and salts of organic acids. The blood-corpuscles of ox, pig, guinea-pig, rabbit, horse, goat, cat, and sheep are, on the other hand, impermeable for all the substances investigated. The permeability for hexoses and pentoses increases in the following order: lævulose > dextrose > sorbose, galactose, mannose > xylose, arabinose. It was not found possible to alter the permeabilities either by lactic acid, by substances which inhibit ferment activity, by the products of internal secretion, or by salts. S. B. S.

**Speed of Coagulation of Blood.** W. B. CANNON and W. L. MENDENHALL (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, **33**, xxxviii—xxxix).—Stimulation of the splanchnic nerves hastens the coagulation time of the blood; so, also, do small doses of adrenaline. Splanchnic stimulation produces its effect only when the adrenal glands are intact, and the hastening effect on blood-clotting is attributed to increased activity of the adrenal glands. W. D. H.

**The Condition of the Blood in Hæmophilia, Thrombosis and Purpura.** W. H. HOWELL (*Arch. int. Med.*, 1914, **13**, 76—95).—Eight c.c. of human blood are withdrawn from an arm vein by a sterilised syringe, oxalated, and centrifuged. The plasma is heated to 60°, which coagulates the fibrinogen, and destroys prothrombin and thrombin. The antithrombin is unaffected, and its effects noted by adding the previously heated plasma in known amounts to mixtures of thrombin and fibrinogen. The relative amount of prothrombin was ascertained by determining the coagulation time of oxalated plasma after the addition of the optimum amount of calcium chloride. The blood of hæmophilic patients clots slowly; this is due to diminution in prothrombin, and so a relative excess of antithrombin is present. In cases of "spontaneous" thrombosis in veins, antithrombin is deficient, and prothrombin normal, in amount. In various forms of so-called purpura, no departure from the normal was found. W. D. H.

**Metabolism of Depancreatized Dogs.** JOHN R. MURLIN and B. KRAMER (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, **33**, xxxii—xxxiii).—Sodium hydroxide and disodium hydrogen phos-

phate increase the output of urinary sugar, and calcium hydroxide reduces it. Sodium increases, and calcium decreases, the permeability of the kidney. Pancreatic extract has little or no effect on respiratory metabolism in depancreatized dogs. W. D. H.

**Problems of Growth.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, 33, xxvii).—With inappropriate feeding, rats and mice cease to grow; when suitable food is given at dates far beyond the age when growth is ordinarily completed, the power to grow returns. When zein is the only protein given, rats decline rapidly in weight; an addition of 3% of tryptophan maintains body-weight; a further addition of 3% of lysine causes a nearly normal rate of growth; when one quarter of the zein is replaced by lactalbumin, growth is normal; but casein or edestin cannot act thus. Addition of tryptophan to the zein-casein diet, or of lysine to the zein-estedin diet, caused nearly normal growth. Lysine added to gliadin also led to normal growth. W. D. H.

[**Entero-amylase**]. E. S. LONDON (*Zeitsch. physiol. Chem.*, 1914, 89, 511).—The work of te Groen supports the view that "adaptation" occurs in the alimentary canal of the enzymes secreted in relation to the kind of food given, and is thus in contradiction with all recent work on this subject. He does not seem to have taken into account the amount of juice secreted in response to the stimulation. W. D. H.

**Rôle of Nascent Oxygen in Protecting the Body from Self-digestion.** W. E. BURGE (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, 33, xxvi).—Ptyalin, lipase, pepsin, trypsin and other enzymes are rapidly destroyed by small amounts of nascent oxygen. It is stated that as oxidation in the stomach wall occurs at a low temperature, there must be nascent oxygen formed there, and this, by destroying pepsin, protects the stomach from self-digestion. Similarly, diastatic enzymes in plants decrease during the day when nascent oxygen is being evolved, and increase in the dark when starch formation ceases. W. D. H.

**The Influence of Continuous Ingestion of Fluorine on the Chlorine and Calcium Metabolism.** F. SCHWYZER (*Biochem. Zeitsch.*, 1914, 60, 32—42).—The results were obtained by experiments on rabbits. Continuous ingestion of small doses (1—2 mg. per kilo. of body-weight) causes injury to health, with increased coagulability of the blood, tendency to thromboses in the veins, and pains in the bones, due to stimulation of the bone-marrow. The bones lose chlorine and calcium, due to the increased capacity of resorption by the stimulated bone-cells; the increased chlorine excretion is also due to the difference of affinity between chlorine and fluorine. The chlorine is excreted by the kidneys, the calcium by the kidneys and in the faeces. The organism finally becomes so poor in chlorine, that the excretion in the urine is only a fraction

of 1 per mille. In this stage, a considerable part of the chlorine of the blood is combined with calcium, and the coagulability of the blood is thereby increased. The content of fat in the bones is also diminished, due, according to microscopical examination, to the replacement of the fat cells of the bone-marrow by lymphoid elements. Fluorine preparations must therefore be regarded as toxic, even in relatively small doses.

S. B. S.

**The Replacement of Chlorine by Bromine in the Animal Body.** III. M. BÖNNIGER (*Chem. Zentr.*, 1914, i, 482; from *Zeitsch. exp. Path. Ther.*, 14, 452—461).—If all cells of the body, like those of the kidney, possess no power of discriminating between chlorine and bromine, a condition of equilibrium should gradually be established throughout the whole body after a single administration of bromine, that is to say, a definite relationship of the chlorine to bromine, which would only be disturbed by fresh doses of chlorine or bromine. As a consequence of the equilibrium, there should be a regular excretion of chlorine and bromine in the urine. Estimations of the Cl: Br ratio in hourly portions of urine, after a single dose of bromide, show that the condition of equilibrium is soon attained, and after the second hour, even, the halogen ratio is a constant. The same ratio was found in all possible secretions and body-fluids (gastric juice, ascitic fluids, etc.). The sodium chloride content of the body can be calculated from this ratio and the bromide dose.

S. B. S.

**Osmotic Phenomena of Yolk of Egg.** WILLIAM ALEXANDER OSBORNE and HILDA ESTELLE KINCAID (*Biochem. J.*, 1914, 8, 28—29).—The yolk of an egg may be used in class demonstrations as a red corpuscle; thus it swells and then bursts with water, shrinks in glycerol, and is unaltered in normal saline solution. The analogy, however, does not hold for many other reagents; for instance, in ether and similar materials, and in strong salt solution, the effects are different, and depend on whether or not the fluid permeates the outer membrane or not.

W. D. H.

**The Cholesterol of the Brain.** II. **The Presence of Oxycholesterol and its Esters.** MARY CHRISTINE ROSENHEIM (*Biochem. J.*, 1914, 8, 74—81. Compare A., 1906, ii, 241).—The examination of the whole human brain by Windaus's method has confirmed the statement previously made that cholesterol esters are wholly absent. There are, however, esters of oxycholesterol which give the reactions of that substance as described by Lifschütz. These are present to the extent of at least 0.01%. In addition, the adult brain contains free oxycholesterol, but this is absent in the brains of young children.

W. D. H.

**The Cholesterol of the Brain.** III. **Cholesterol Contents of Human and Animal Brain.** MARY CHRISTINE ROSENHEIM (*Biochem. J.*, 1914, 8, 82—83).—The estimations recorded were made by a combination of O. Rosenheim's method of preparation with Windaus's

digitonin quantitative method. The figures given include any oxysterol which may be present. In dry brain, the figures are highest in dog (11·6%), ox (12%), and cod (12%); the lowest in fowl (7·4%), and human children and foetus (4 to 5%). In adult man, the amount was 9%. Approximately the same figures were yielded by the brains of sheep, rabbit, and cat. W. D. H.

**Formation of Cerebro-spinal Fluid.** F. C. BECHT (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, **33**, xxxii).—Pilocarpine is stated not to stimulate the secretion of cerebro-spinal fluid; any increase in outflow from a cannula in the subcerebellar cisterna is believed to be secondary to vascular changes. W. D. H.

**The Action of Certain Cations on the Polarisation-picture of Nerve.** BRIGITTE SCHREITER (*Pflüger's Archiv*, 1914, **156**, 314—330).—A stained nerve under the action of the constant current undergoes a change, in which the anodal region becomes colourless, and the cathodal region strongly coloured. This is called the "polarisation-picture" by Bethe, whose methods are followed in the present research. Fluid electrodes consisting of Ringer's solution as a basis were used. The presence of calcium is necessary for the production of the picture, and the present work aims at finding whether other bases can take its place. Barium and strontium in certain stated concentrations can do so; magnesium and aluminium cannot, probably because they injure the semi-permeable membrane of the axis cylinder. In high concentrations, lanthanum, and in smaller degree nickel, can replace calcium. Manganese and cobalt in the concentrations used are inactive, though there are indications that in small quantities, insufficient to produce toxic effects, they can act like calcium, but they do not inhibit the swelling effect produced by sodium.

W. D. H.

**The Effect of Dextrose on the Gaseous Metabolism of the Isolated Mammalian Heart.** C. LOVATT EVANS (*J. Physiol.*, 1914, **47**, 407—418).—The addition of dextrose to the circulating blood of a heart-lung preparation raises the respiratory quotient; the isolated organ has therefore the same power as the entire organism to complete the oxidation processes which it commences. The quotient is even more increased by previous carbohydrate feeding. The normal heart of the dog is calculated to obtain about one-third of its energy supply by oxidation of carbohydrate.

W. D. H.

**The Effect of Adrenaline on the Gaseous Metabolism of the Isolated Mammalian Heart.** C. LOVATT EVANS and SAGORO OGAWA (*J. Physiol.*, 1914, **47**, 446—459).—Adrenaline greatly increases the gaseous metabolism of the heart, and this is roughly proportional to its increased rate. The increase of carbon dioxide production follows later. There is no change in the respiratory quotient, or in the power to utilise carbohydrate.

W. D. H.



**The Influence of Lipoids on the Action of Oxydases. II.** H. M. VERNON (*Biochem. Zeitsch.*, 1914, 60, 202—220).—The concordance between the concentration of narcotics necessary to stop the action of the “succinicoxydones” and that necessary to produce precipitations of nucleoproteins, as found by Battelli and Stern (A., 1913, i, 929), does not hold for the indophenol-oxydase. Attention is also directed to the fact that the precipitability of tissue suspensions in water is a variable factor. The volume of the precipitate decreases in passing from narcotics which exert their action in high concentrations to those acting in low concentrations. Furthermore, the precipitability of liver suspensions is different to that of kidney suspensions. Again, if the liver is kept for twenty-four hours before the experiment different results are obtained to those got with fresh tissue. The conclusion is drawn that the concordance between the action on oxydases and that on nucleoproteins is an accidental one, and that the particular action of narcotics is due to their influence on the lipoids. Further experiments are given to show the parallelism between the action on oxydases and the narcotic action. The stage of growth has some influence on the oxydase as regards its behaviour to narcotics; thus, 6*M*-alcohol destroys 90% of the kidney-oxydase of new-born rats, but only 46% of that of adult animals. This influence of age was not observed in the case of heart-muscle. It is suggested that changes in the cell-lipoids take place during growth. S. B. S.

**Physico-chemical Analysis of the Contraction Curve of Muscle.** J. BERNSTEIN (*Pflüger's Archiv*, 1914, 156, 299—313).—The energy of muscular contraction is derived from two chemical processes, the first an oxidative decomposition leading to the formation of carbon dioxide and sarcolactic acid; the second not necessarily oxidative, although oxidation may occur, which leads to the building together, in the presence of alkali and with the consumption of oxygen, of the products of decomposition. Both are unimolecular, and take place in accordance with the law of mass-action. The subject is treated mathematically throughout.

W. D. H.

**Chemical Features of the Diaphragm.** FREDERIC S. LEE (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, 33, xxiv—xxv).—The diaphragm exhibits a greater resistance to interference with its rhythmical action than do other voluntary muscles. It contains more glycogen, and reduces oxyhæmoglobin more rapidly than the other skeletal muscles examined. It also contains rather less lipid phosphorus and lipid sulphur.

W. D. H.

**The Content of the Tissues of Cold-blooded Animals with Respect to Fatty Acids and Cholesterol.** (Mlle.) JEANNE WEILL (*Compt. rend.*, 1914, 158, 642—645. Compare Mayer and Schaeffer, A., 1913, i, 424, 1017).—From an examination of the tissues of certain reptiles, batrachians, fish, molluscs, and crustaceæ to determine the proportion of fatty acids and cholesterol, the author finds

that this ratio is not constant for a given tissue, as in the case of warm-blooded animals. The tissues, such as of the kidneys, are nearest in their behaviour to that of the warm-blooded animals, whilst the glandular tissues are very variable in cold-blooded animals, the fat accumulating in some, but not in other, tissues.

W. G.

**Protein Sugar and Virtual Sugar.** HENRI BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1914, 158, 516—518. Compare this vol., i, 218).—Polemical against Lépine. The authors state that their protein sugar must not be confused with the "virtual" sugar of Lépine and his co-workers, the existence of which various workers have been unable to confirm (compare Macleod, A., 1913, i, 1258).

W. G.

**The Fat of the Water-Hen (*Fulica atra*); the Reason of the Smell and Taste of its Flesh.** SIGISMUND BLAHA (*Zeitsch. physiol. Chem.*, 1914, 89, 456—464).—The various constants (acid number, saponification number, iodine number, etc.) were determined with the fat of this bird, also the amount of free and combined cholesterol. The characteristic smell and taste of its flesh are due, not to fat admixture, but to the presence of methylamine.

W. D. H.

**The Pigment of a Bermuda Nudibranch.** W. J. CROZIER (*J. Physiol.*, 1914, 47, 491—492).—The spectroscopic characters of a blue pigment obtained from *Chromodoris zebra* (soluble in weak formaldehyde, alcohol, or acetone, insoluble in ether and chloroform) are described. The blue substance is bleached by potassium hydroxide, and is turned pink by hydrochloric acid. Attempts to obtain it in crystalline form failed.

W. D. H.

**Milk: its Sugar, Conductivity, and Depression of Freezing Point.** LILIAS CHARLOTTE JACKSON and ARTHUR CECIL HAMEL ROTHERA (*Biochem. J.*, 1914, 8, 1—27).—The lactose content and the electrical conductivity of milk are reciprocal. After milking or suckling, the composition of further milk secreted is different, because the blood from which it is formed is then of slightly different composition. Evening milk (cow) has usually a higher conductivity than morning milk. Every 1% of protein in milk lowers the conductivity by 2.76%. Boiling has no effect on the soluble calcium salts in a state of ionisation. Hot, dry weather increases, wet, cold weather lessens, the conductivity of cows' milk.

W. D. H.

**Estimation and Significance of the Ammonia Content of Milk.** J. TILLMANS, A. SPLITTGERBER, and H. RIFFART (*Zeitsch. Nahr. Genussm.*, 1914, 27, 59—76).—Milk fresh from the cow contains from 3 to 4 mg. of ammonia per litre; this quantity increases when the milk is kept and decomposition proceeds, the increase being more rapid in the case of dirty milk than in clean milk. Whilst the

quantity of ammonia affords no evidence as to the presence of added impure water in milk, it indicates the bacterial condition of the latter, and the authors are of opinion that any milk having an ammonia content of more than 10 mg. per litre cannot be considered to be fresh milk. The ammonia may be determined either by distilling the milk serum (obtained by treating the milk with mercuric chloride and hydrochloric acid, or with basic lead acetate and sodium phosphate) under reduced pressure in the presence of magnesium oxide, or by treating the serum with magnesium chloride, sodium phosphate, and a slight excess of sodium hydroxide, separating the precipitate formed, and distilling it with magnesium oxide.

W. P. S.

**The Sulphur Compounds of the Urine.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1914, 89, 485—510).—In rabbits fed on white cabbage, the urine contains a considerable amount of thiosulphate, and also, as Rubner found, traces of mercaptan. The relation of thiosulphate-sulphur to sulphate-sulphur varies from 1 to 2.9—1.8. On other foods, thiosulphate and mercaptan are absent. By heating urine free from thiosulphate with silver nitrate solution, some silver sulphide is formed; the same is true for urine which contains thiosulphate; the sulphur compound to which this is due is probably cystine, or a cystine derivative. This substance is included in the term "neutral sulphur," but part of the latter is not decomposed by boiling silver nitrate solution. The term "non-sulphate sulphur" would include thiosulphate sulphur when present, and the so-called neutral sulphur.

W. D. H.

**An "Acid-soluble" Protein from Urine.** RENÉ GUYOT (*J. Pharm. Chim.*, 1914, [viii], 9, 245—248).—The author describes a urine which contains a protein which is precipitated on acidification after heating, but not if the acid is added first. It is then only precipitated on addition of a salt. A protein of this class he differentiates from other proteins, and designates it as "acido-soluble."

S. B. S.

**Beri-beri. VIII. The Relationship of Beri-beri to Glands of Internal Secretion.** CASIMIR FUNK and MACKENZIE DOUGLAS (*J. Physiol.*, 1914, 47, 475—478).—Most of the glands of the body of the bird are lessened in size, and show signs of cellular degeneration, when the animal is fed on polished rice. The thymus, which is very large and persistent in normal pigeons, disappears completely.

W. D. H.

**Beri-beri. X. Experimental Evidence against the Toxic Theory of Beri-beri.** CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1914, 89, 373—377; *Proc. physiol. Soc.*, 1913; *J. Physiol.*, 47, xxv—xxvi).—Abderhalden and Lampé explain the cause of beri-beri to be a toxin in polished rice, since cooking the rice delays the onset of the disease in birds. This is the case, but the explanation here advanced is that cooked rice is less readily assimilated, and con-

sequently less of the body vitamines is mobilised during the assimilation. If the birds are fed on Osborne and Mendel's diet of protein, fat, carbohydrate, and salt, beri-beri develops, and the richer the diet the sooner the symptoms appear. W. D. H.

**Effect of Large Bleedings from Immunised Horses.** R. A. O'BRIEN (*J. Path. Bact.*, 1914, 18, 423—427).—The relationship between the processes of reproduction of diphtheria antitoxin and "globulins" is not disturbed by the withdrawal of large quantities of blood. There is no interdependence between the processes of reproduction of hæmolyisin and albumins and globulins.

W. D. H.

**Hæmolytic Icterus.** J. W. McNEE (*J. Path. Bact.*, 1914, 18, 325—342).—Experiments on dogs and geese show that true hæmolytic jaundice may occur. After the liver is excluded, or the circulation confined to head and thorax, injection of hæmoglobin leads to the production of bile-pigment. It is suggested that the transformation may be effected by the spleen, bone-marrow, muscles, and the endothelial coat of the blood-vessels.

W. D. H.

**The Water Content of the Tissues in Experimental Nephritis.** R. A. CHISOLM (*J. Path. Bact.*, 1914, 18, 404—413).—Necrosis of the renal tubules in the rat, produced by uranium nitrate, potassium dichromate, or potassium chromate, when excess of Ringer's solution is given intraperitoneally, leads to an excess of water in the kidneys, muscles, subcutaneous tissues, and possibly the alimentary canal. The subcutaneous oedema is no measure of the amount of water in the muscles and subcutaneous tissues.

W. D. H.

**The Bactericidal, Physiological, and Deodorising Action of Ozone.** EDWIN O. JORDAN and A. J. CARLSON (*J. Amer. Med. Assoc.*, 1913, 61, 1007—1012).—In both men and animals ozone has an injurious action primarily on the respiratory passages. Its claims as a bactericidal agent have little or no foundation, even in concentrations which are irrespirable by man. Although it is a deodorant in small concentration, it is probable that the masking of odours leads to a concealment of what is a danger signal in ordinary conditions. This, added to its injurious effects, should lead to its abandonment as a disinfectant.

W. D. H.

**The Active Groups in the Adrenaline Series. The Influence of the Position of the Hydroxyl Group on the Action of the *o*:*m*-(2, 3) and *m*:*p*-(3, 4)Dihydroxybenzylamines.** M. TIFFENEAU (*Chem. Zentr.*, 1914, i, 689; from *Ch. Richet Jubilee*, 1912, 399—412).—The pharmacological action of the hydrochlorides of the 2:3-compound (m. p. 186°) and the 3:4-compound (m. p. 172°) were compared. The toxic dose for both, on subcutaneous injection into mice, was 0.09 gram. The 2:3-compound has a more powerful action on the heart, both as regards

rate and beat, than the 3:4-compound (rabbit and frog); it is, however, more toxic. The 3:4-compound causes a more marked contraction of the blood-vessels and greater rise of pressure than the 2:3-substance. The 3:4-position of the hydroxy-group has a favourable influence, therefore, as regards contraction of the vessels and the rise of blood pressure. S. B. S.

**Paradoxical Action of Antipyrin.** HENRY G. BARBOUR and CLYDE L. DEMING (*J. Pharmacol. expt. Ther.*, 1913, 5, 149—184).—After rabbits are decerebrated, or their corpus striatum (which contains the heat-regulating centre) is removed; antipyrin, which usually lowers body temperature, raises it if the dose is 0.4 gram per kilo. of body-weight. There is also an absence of vasodilatation. W. D. H.

**Physiological Action of Aporeine.** VITTORIO PAVESI (*Chem. Zentr.*, 1914, i, 165); from *Riv. sanit. Piacentina*, 1913, 2, reprint, 41 pp.).—The author has investigated the physiological action of aporeine,  $C_{18}H_{16}O_2N$ , greenish-yellow prisms, m. p. 88—89° (compare A., 1907, i, 870), on frogs, guinea-pigs, mice, rabbits, and cats, the alkaloid being used in the form of its hydrochloride and hydrogen tartrate. The lethal subcutaneous dose for frogs is about 20—25 mg. of alkaloid per 100 grams; it varies considerably, however, with the physiological condition of the animals, and according to whether the sparingly soluble hydrochloride or the more readily soluble hydrogen tartrate is administered. Doses of 0.005% of the weight of the frog are practically without action. For guinea-pigs and mice, the minimum lethal dose is 0.01% of the weight of the animal; the rabbit is less, the cat more, sensitive. The interval between injection and death varies greatly, but usually lies between two and ten hours. The pharmacological action is analogous to that of thebaine. H. W.

**The Action of Benzoic Acid and its Sodium Salt on the Organism.** E. ROST, FR. FRANZ, and A. WEITZEL (*Chem. Zentr.*, 1914, i, 562—563; from *Arch. Kais. Gesundh. Anst.*, 1913, 45, 425—490).—Benzoic acid or its sodium salt, when the dose exceeds a certain limit, produces vomiting in animals such as dogs, which are capable of this act. After repeated daily administrations, it produces typical symptoms like epilepsy in man, and unlike those produced by any other drug. Repeated doses cause death, with paralysis of the central nervous system. The toxic dose, when repeatedly administered, is relatively high for benzoic acid (7 grams for dogs of 4—8 kilos. in weight). The smallest toxic dose of the benzoate is 1 gram per kilo. of body-weight. Doses even slightly below the toxic quantity could be repeatedly given without effect. In certain cases, doses of 8—11 grams were necessary to produce toxic effects on dogs of the above weight, and there were considerable individual variations as regards toxicity. Similar variations were found in the case of rabbits. The symptoms produced by the acid and its sodium salt were the same. Glycine was found to be an effective

antidote to benzoate poisoning, and its application to human epileptics is suggested. It causes about 90% of the administered benzoate to be eliminated in the urine within three days. In the first hour only about 13—34% is excreted as hippurate; later, the relative amount of the latter substance increases. After big doses of benzoic acid it appears in the urine in some other form of combination, possibly a glucuronate. When glycine was administered simultaneously with the benzoate, there was neither an increased output of benzoic acid nor hippuric acid, in spite of its antidotic action. It is possible that the glycine inhibits the accumulation of the benzoic acid in the organism in the concentration necessary for toxic action, as it is then more rapidly converted into the hippurate than when the organism must provide its own glycine.

S. B. S.

**The Direct Application of Drugs to the Temperature Centres.** HENRY G. BARBOUR and ELIHU S. WING (*J. Pharmacol. expt. Ther.*, 1913, 5, 105—147).—Puncture by a sterilised needle of the caudate nucleus causes hyperpyrexia. Chloral hydrate, antipyrin, and quinine hydrochloride injected into the circulation lower the body temperature. These drugs have the same effect in much smaller doses when directly applied to the caudate nucleus. The effects of alcohol vary with the dose used. Adrenaline introduced into the brain also lowers the temperature. Caffeine has no effect on temperature when injected intravenously; intracerebrally, it raises it. Tetrahydro- $\beta$ -naphthylamine raises the temperature and produces toxic effects more readily when introduced into the brain than into the general circulation. The experiments were made on rabbits.

W. D. H.

**The Action of Cotoin and Similar Substances.** E. IMPENS (*Chem. Zentr.*, 1914, i, 688; from *Münch. med. Woch.*, 1913, 60, No. 38).—The specific action of cotoin is the diminution of the tone and the peristaltic movement of the intestinal muscular tissue. Resaldol is ethyl benzoylresorcinolcarboxylate, and is obtained by the scission of the resorcinol molecule from fluorescein. It has m. p. 134°, a pepper-like taste, and it irritates the mucous membranes. The preparation used by the author was not identical with the amorphous commercial preparation with the same name. It is similar to cotoin, and has a similar action on the intestine, and is to be preferred to this substance on account of its tastelessness and the absence of certain subsidiary actions. It is recommended as a remedy against diarrhoea.

S. B. S.

**The Behaviour of Certain Iodised Fatty Acids in the Animal Body.** G. GASTALDI (*Chem. Zentr.*, 1914, i, 690, from *Arch. Farmacol. Sperim.*, 1913, 16, 470—480).— $\alpha$ -Iodostearic and  $\alpha$ -iodopalmitic acids, their calcium salts and amides, are not well tolerated by dogs after administration by mouth. The acids and salts are well absorbed by well-nourished animals, and up to 91% of the iodine is excreted in the urine in inorganic form. The

amides are not absorbed, and all the iodine is recovered in the faeces. Fasting dogs, on the other hand, show great intolerance to the preparations, and no iodine is excreted in the urine. After taking small quantities of food, however, the iodine commences to appear in the urine. The absorption of the iodine appears to depend, therefore, on the secretion of the digestive juices.

S. B. S.

**The Behaviour of *m*-iodoanisole in the Animal Body.** R. LUZZATTO and G. SATTÀ (*Chem. Zentr.*, 1914, i, 690—691; from *Arch. Farmacol. Sperim.*, 1913, 16, 393—402).—The drug, when introduced *per os* into dogs, is excreted in the form of the sulphate, and in certain cases partly as the glucuronate. It could not be ascertained whether the ester formation takes place at the methoxyl group after hydrolysis, or with a hydroxyl group, produced in the ring by oxidation in the organism.

S. B. S.

**Mutual Relations of Oxalates, Magnesium Salts, and Calcium Salts.** F. L. GATES and S. J. MELTZER (*Proc. Amer. physiol. Soc.*, 1913; *Amer. J. Physiol.*, 33, xxi—xxii).—If sodium oxalate is injected at the same time as magnesium sulphate, the anæsthesia produced by the latter salt is deeper, and lasts longer, than when it is given alone. This is due to the oxalate decreasing the calcium available in the blood for the antagonism of the magnesium. The anæsthesia rapidly passes off when calcium salts are injected. Magnesium sulphate and calcium chloride prolong the life of animals (rabbits) poisoned with sodium oxalate.

W. D. H.

**The Influence of Certain Derivatives of Phenylcinchoninic Acid on the Excretion of Uric Acid.** E. IMPENS (*Chem. Zentr.*, 1914, i, 563—564; from *Pamphlet*, 23 pp.).—The action of the following quinoline derivatives on individuals on a purine-poor diet was investigated, with the object of throwing light on the action of atophan: (1) 2-phenylquinoline; (2) 6:8-dihydroxyquinoline; (3) 2-phenylquinoline-4-carboxylic acid; (4) sodium 2-phenylquinoline-4-carboxylate with sodium theobromine; (5) sodium 6-amino-2-phenylquinoline-4-carboxylate; (6) 6-benzoylamino-2-phenylquinoline-4-carboxylic acid; (7) 8-methoxy-2-phenylquinoline-4-carboxylic acid; (8) 8-carbethoxy-2-phenylquinoline-4-carboxylic acid; (9) 2-*o*-hydroxyphenyl-7-methylquinoline-4-carboxylic acid; (10) 8-methoxy-2-phenylquinoline-4-carboxylic acid; (11) 3-phenyl-2-*p*-anisylquinoline-4-carboxylic acid; (12) 2-*p*-tolylquinoline-4-carboxylic acid; (13) 2-phenyl-3-ethylquinoline-4-carboxylic acid; (14) 2-*p*-anisylquinoline-4-carboxylic acid; (15) anhydride of 2-phenylquinoline-4-carboxylic acid; (16) 2:3-diphenylquinoline-4-carboxylic acid; (17) 2-phenylquinoline-4-carboxylamide; (18) 2-phenylquinoline-4-carbonyl carbamide; (19) 2-phenylquinoline-4-carboxylethanolamide; (20) 2:3-diphenylquinoline-4-carboxylamide; (21) ethyl 2-phenylquinoline-4-carboxylic acid; (22) acetylcarbiny 2-phenylquinoline-4-carboxylate; (23) phenyl 2-phenylquinoline-4-carboxylate; (24) cyclohexyl 2-phenylquinoline-4-carboxylate;

(25) salicylic acid ester of 2-phenylquinoline-4-carboxylate; (26) ethylene salicylate 2-phenylquinoline-4-carboxylate. These preparations were administered in daily doses of 0.5 gram. As a result of the experiments, the following conclusions were drawn. To bring about the uric acid secretion, it is essential that a phenyl group should occupy position 2 of the quinolinecarboxylic acid. If an alkyl group is substituted for a phenyl group, the drug is inactive. In addition to the phenyl group, a second substituent in the quinoline ring is necessary. The best is a carboxylic group in the 4-position. No. (1), for example, is inactive. Doubling the phenyl group (16) and the carboxyl group does not inhibit the action, although the dicarboxylic derivatives are somewhat less active. The introduction of a hydroxyl group into the phenylic residue in the ortho-position does not destroy the activity, although the introduction of methyl or methoxyl groups in the para-position (12 and 14) or of two hydroxyl groups does. The introduction of a hydroxyl group in the 3-position of phenylcinchonic acid does not interfere with the action, but the substance becomes inactive after introduction of a hydroxyl or methoxyl group into position 6. An amino-group in position 6 weakens the action (5), and a benzoyl-amino-group destroys it altogether (6). The introduction of lower alkyl radicles into phenylcinchonic acid influences the action in varying ways, according to the position. The action is intact in position 6, weakened in position 3 (13), and absent in 7 (7 and 9). Esterification of the acid with alcohol (21) or acetylcarbinol (22) exerts no action, but esterification with higher alcohols, such as *cyclohexanol* (24), half-esterified glycols (26), and phenols (23 and 25), diminishes the action. The conversion of the carboxyl group in the case of phenylcinchonic acid into the amide does not influence its action (19), although it does in the case of 2:3-diphenylquinoline-4-carboxylic acid (20). The effect is also annulled in the former amide by the introduction of the carbethoxy-group. The action of the esters is slower than that of the acids, owing, apparently, to the smaller solubility. The author believes that the action is due to the mobilisation in, and more rapid elimination of, the urates by the kidneys. Compared with this action, the stimulative action on the enzymes which oxidise the purine substances is of small account.

S. B. S.

**Effect of Nuclein and Nucleic Acid on the Normal Anti-Substance.** S. PHILLIPS BEDSON (*J. Path. Bact.*, 1914, 18, 416).—Injection of nuclein causes a resistance to infection, and raises the opsonic index. Other substances which, like nuclein, cause leucocytosis, do not have the same effect. Pure preparations of nucleic acid are also ineffective; probably, therefore, the effect is due to an impurity; calcium salts do not appear to be the agent concerned.

W. D. H.

**Spermine as an Oxidation Ferment.** A. REPREW (*Pflüger's Archiv*, 1914, 156, 331—360).—Poehl's formula ( $C_5H_{14}N_2$ ) is accepted, and his statements regarding the beneficial effects of the adminis-



tration of spermine are regarded as proven. In rabbits, when injected under the skin or into the blood, Poehl's spermine increases the intake of oxygen and output of carbon dioxide; the amount given is immaterial. Spermine is therefore regarded as an "oxidation ferment" activating oxidative processes, and especially those of a synthetic nature. W. D. H.

**The Solubility of White Lead in Human Gastric Juice and its Bearing on the Hygiene of Lead Industries.** A. J. CARLSON and A. WOELFEL (*Amer. J. Publ. Health*, 1913, 755—769).—The solubility of various white lead paint powders in human gastric juice is given; from 45% to 83% of lead carbonate preparations pass into solution in various conditions; lead sulphate is less soluble and less toxic than the carbonate; both salts produce acute lead poisoning in quantities of 0.1 gram per kilo. of body-weight daily in animals. It is recommended that the use of the carbonate should be abandoned in all industries as far as possible, and that workers should take milk between meals in order to lessen the chances of any swallowed lead being dissolved in the gastric juice of the empty stomach. Milk and gastric juice in equal proportions have no solvent action on the lead salts, because the milk fixes the acid of the juice. W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Chemistry of Bacteria. III.** SAKAE TAMURA (*Zeitsch. physiol. Chem.*, 1914, 89, 289—303. Compare A., 1913, i, 1280, 1421).—Earlier investigations with *Bacillus tuberculosis* and *Mycobacterium lacticola* showed the presence, in the cells, of a diamino-monophosphatide and an alcohol ( $C_{29}H_{56}O$ ), for which the name *mycol* was suggested, and a preponderance of phenylalanine in the products of hydrolysis. Similar work with *Bacillus diphtheriae* indicates specific differences between this and the former organisms, as the latter contains a monoaminomonophosphatide; there is an absence of mycol, and the chief product of hydrolysis is tyrosine, and not phenylalanine. Gram-positiveness of the three species appears to be due to the presence of lipid substances.

H. B. H.

**Chemistry of Bacteria. IV.** SAKAE TAMURA (*Zeitsch. physiol. Chem.*, 1914, 89, 304—311).—The bacterial mass was extracted with ether and alcohol, and then macerated with sulphuric acid (2: 1). The resulting liquid was then diluted, and showed reduction of Fehling's solution, the orcinol hydrochloride reaction, and gave the phenylbenzylhydrazone of *l*-arabinose. Xylose could not be detected. The cell wall of the three species investigated was found to consist of hemicellulose (araban). A non-fermentable hexose was also detected.

H. B. H.

**Reduction of Nitrates to Nitrites and Ammonia by Bacteria.** M. KLAESER (*Ber. deut. bot. Ges.*, 1914, **32**, 58—61).—Out of twenty-eight different species of spore-forming bacteria, twenty reduced nitrates in solutions containing 1% of dextrose, but no peptone. The rest, except *B. robustus*, reduce nitrates in presence of peptone. In some cases only nitrites accumulate (*B. cylindricus*), in others only ammonia (*B. tumescens*), whilst in the case of *B. asterosporus* both ammonia and nitrites were found.

Nitrites were found to be attacked by only sixteen of the twenty-seven bacteria which reduce nitrates, and the action was usually only feeble.

In presence of peptone, *B. tumescens* and *B. subtilis* are able to resist the toxic action of 4% nitrite solutions.

In alkaline solutions, nitrites are produced, whilst acidity is favourable to the production of ammonia. Either nitrite or ammonia production may be induced by the presence of appropriate carbon compounds which give rise to alkalinity (salts of organic acids) or acidity (dextrose).

The conclusion is drawn that bacteria reduce nitrates in order to obtain nitrogen; no evidence was obtained that the oxygen is utilised.

N. H. J. M.

**The Ferments of the Milk among the Touaregs.** G. DE GIRONCOURT (*Compt. rend.*, 1914, **158**, 737—740).—A bacteriological examination of the milk in the Soudan, to determine the cause of its rapid, spontaneous coagulation. The following organisms have been detected in the cheese made from this milk: (1) a bacillus resembling the *B. lacticus* (Pasteur) in every respect except that it is not pathogenic; (2) a streptobacillus similar in properties to the *B. bulgaricus* (Grigorov); (3) a white yeast of the *Saccharomyces* type; (4) a species of *Penicillium*. A detailed account of the properties of these micro-organisms is given.

W. G.

**A Ferment Contained in Waters; An Agent of Dehydration of Glycerol.** E. VOISENET (*Compt. rend.*, 1914, **158**, 734—736. Compare *ibid.*, 1914, **158**, 195).—The products of the dehydration of glycerol, either in a purely mineral culture medium or one containing peptone, by a ferment present in various samples of water, are  $\alpha$ -propanolaldehyde and acetaldehyde. When the rate of dehydration is at its maximum, the second aldehyde is the main product; when at its minimum, the first is the main product.

W. G.

**Proteolytic Organism.** JOHN MALCOLM DRUMMOND (*Biochem. J.*, 1914, **8**, 38—43).—An organism isolated from sewage sludge is described which causes the rapid liquefaction of gelatin, owing to the presence of an extracellular proteolytic enzyme. The presence of a peptone in the medium is essential to the production of the enzyme. In gelatin cultures, the enzyme can act in both acid and alkaline solutions. No enzyme is secreted when the organism is

grown on egg albumin. Acids inhibit the rate of liquefaction. Different acids act in the order of their degree of dissociation.

E. F. A.

**The Nitrogen Nutrition of German Yeast.** H. J. WATERMAN (*Chem. Zentr.*, 1914, i, 484—485; from *Folia microbiol., Holländ. Beitr. gesamt. Mikrobiol.*, 1913, 2, reprint, pp. 7).—The development of a pure culture of yeast in sterilised solutions containing tap-water, 2% of dextrose, 0.2% of potassium dihydrogen phosphate, 0.1% of magnesium sulphate, and 0.1% of a large variety of nitrogen compounds, has been studied. In tap-water alone, the compounds caused no development. The aliphatic amines, aromatic amines, especially with the substitution in a side-chain, ammonium chloride, and ammonium nitrate furthered development particularly well. Potassium nitrate, sodium nitrite, nitromethane, and the compound,  $C(CH_2 \cdot OH)_3 \cdot NO_2$ , were unsuitable. Acid amides, except those which readily produce ammonia, such as carbamide, formamide, oxamide, and palmitamide, also failed as sources of nitrogen, but those amides which are at the same time amines, such as asparagine, aspartic acid, hippuric acid, and  $\alpha$ -aminocinnamamide furthered development.

J. C. W.

**The Plasmolysis of Yeast Cells.** HANS EULER and BJÖRN PALM (*Biochem. Zeitsch.*, 1914, 60, 97—111).—The relationship between the amount of plasmolysis of a bottom-yeast, and the concentration of a glycerol solution for a definite time of action of this solution, was investigated, and the "adaptation" of the yeast to these solutions was quantitatively measured. It appears as if this adaptation to an unusual osmotic pressure is due to a change in the permeability of a plasma membrane. The rate of plasmolysis of yeast in 25% glycerol solution was also measured, and the results fall on what is approximately a logarithmic curve. These results may be ascribed to a difference of behaviour of the younger and older cells towards an external osmotic pressure.

S. B. S.

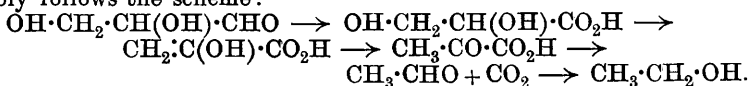
**Adaptation of Micro-organisms to Poisons.** HANS EULER and HARALD CRAMÉR (*Biochem. Zeitsch.*, 1914, 60, 25—31).—The authors have studied the adaptation of yeast to sodium fluoride, estimating the fermentative inverting power and weight of crop of yeasts grown in fluoride, and comparing the results with those obtained from similar media under similar conditions, but without the poison. With the fluoride, the amount of dried material produced in the growth is increased, but the yeast has a smaller fermentative power and a larger inverting power than the control. The addition of the extract of a yeast grown on a fluoride medium to a culture fluid has nearly the same effect on the growth as the addition of fluoride itself.

S. B. S.

**The Mechanism of Alcoholic Fermentation. III. Cell-free Fermentation of Polyhydroxycarboxylic Acids.** A. von LEBEDEV (*Ber.*, 1914, 47, 660—672. Compare A., 1913, i, 144).—The view recently expressed by the author (*loc. cit.*), attributing

the fission of glyceraldehyde during fermentation to the intermediate formation of methylglyoxal, is somewhat discredited by the doubtful fermentability of methylglyoxal itself. The author was therefore led to the possibility of glyceric acid as an intermediate product, and experiment has demonstrated that ordinary racemic glyceric acid is fermentable by yeast extract, or, better, by dried yeast. The products of the action, which appears to be of genuine enzymatic character, are carbon dioxide, acetaldehyde, and ethyl alcohol, the latter probably being produced, as indicated in the scheme already suggested (*loc. cit.*), by the subsequent reduction of some of the aldehyde. Comparative experiments indicate that glyceric acid undergoes fermentation much more readily than glyceraldehyde, and the amount of carbon dioxide produced shows that both stereoisomeric constituents of the racemic acid must be attacked, although possibly to an unequal extent.

The course of the degradation of glyceraldehyde therefore probably follows the scheme:



The fermentation, therefore, induces a dehydration of glyceric acid analogous to the effect produced by heating, and even if it should be proved later that glyceric acid is not an intermediate stage in sugar fermentation, such enzymatic dehydration of a polyhydroxy-acid probably plays a part.

Fermentation of *d*-gluconic acid by extract of yeast gave rise to carbon dioxide, and possibly some hydrogen, but no volatile aldehyde or alcohol was produced. D. F. T.

**Action of an Electric Current on the Work of the Enzymes of Alcoholic Fermentation.** V. I. PALLADIN and G. I. MILLIAK (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 247—265).—Experiments made on the action of hefanol and of yeast, dried according to Lebedev's method, on sucrose and pyruvic acid, show that different behaviour is exhibited by zymase and carboxylase towards direct and alternating currents. Carboxylase is not affected in its action by an alternating current, whilst with a direct current an increased amount of carbon dioxide is liberated in the anode chamber and a diminished amount in the cathode chamber, both the electrodes being of platinum. On the other hand, the action of zymase is appreciably intensified under the influence of an alternating current, and is weakened to approximately equal extents in the anode and cathode compartments when a direct current is employed. Consequently, if the function of carboxylase consists in intramolecular oxidation, that of zymase must be regarded as alternate oxidising and reducing actions at the expense of water.

The initial stage in the fermentation of potassium pyruvate is evidently represented by the combination of a whole molecule of water to form  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{K}, \text{H}_2\text{O}$ , the latter then undergoing intramolecular rearrangement, so that carboxylase acts in the same manner as diastase, emulsin, and similar enzymes. Like these, it

does not form ions from the water, and is not influenced by methylene blue.

T. H. P.

**The Significance of Water in the Processes of Alcoholic Fermentation and Respiration of Plants.** V. I. PALLADIN (*Biochem. Zeitsch.*, 1914, 60, 171—201).—When water is replaced by various solvents, such as glycerol, ethylene glycol, formamide, pyridine, or ethyl alcohol, the activity of the zymase, carboxylase, and reductase of yeast is reduced, or even destroyed. Without water, both alcoholic fermentation and the anærobic stages of respiration are rendered impossible. On the ground of these and numerous other experiments by the author and his pupils, as well as those by other investigators, he seeks to explain the part played by water in respiratory processes. It is assumed that the oxidation of dextrose takes place half at the expense of its own oxygen and half at that derived from water. Hydrogen is thereby set free, and reduces the “respiratory chromogens” to the leuco-form. These leuco-substances, in the presence of oxygen and under the influence of the peroxydases, are again oxidised. According to these conceptions, carbon dioxide produced in respiration is of anærobic origin, whereas the water is derived aerobically, the respiratory pigments acting as oxygen “acceptors.” The anthocyanins, however, do not play an immediate part in this reaction, being possibly derived from the other pigments by some other change. The above conceptions are illustrated by numerous examples of the influence of artificial hydrogen acceptors, such as methylene-blue, on the respiration of plants, and by other experiments.

S. B. S.

**Decomposition of Fatty Acids by the Higher Fungi. II. Degradation of the Fatty Acids.** A. SPIECKERMANN (*Zeitsch. Nahr. Genussm.*, 1914, 27, 83—113. Compare A., 1912, ii, 590).—Results are recorded of experiments on the assimilation by fungi of a large number of saturated and unsaturated fatty acids, the degradation of fatty acids, and the nutritive value of the fatty acids as influenced by their molecular weight and constitution. The lower members of the series of fatty acids were assimilated more rapidly than the higher; this is also the case with mixtures of fatty acids, the acid having the lowest molecular weight being most readily assimilated. The final products of the decomposition of the fatty acids by the fungi were carbon dioxide and water. There is generally a marked decrease in the iodine number of fatty acids during the time these are being acted on by fungi; with mixtures, the iodine number may increase.

W. P. S.

**The Fatty Matters Formed by *Amylomyces Rouxii*.** R. GOUPIÉ (*Compt. rend.*, 1914, 158, 522—525. Compare A., 1913, i, 567).—The percentage of fat in the dry matter of *Amylomyces Rouxii* steadily increases with the age of the culture up to a maximum corresponding with the maximum development of the plant, similar results being obtained in aerated as in non-aerated cultures.

At the same time there is a partial saponification of the glycerides, but the quantity of acid liberated never exceeds 21% (expressed as oleic acid) of the fat. If the mucorin is completely separated from the nutritive liquid, the fats are attacked, 60% being decomposed in the first two months. The index of saponification gradually diminishes, showing that the plant first consumes the glycerides of low molecular weight.

W. G.

**The Selection of Nutrition by *Aspergillus niger*. Sucrose, Maltose, Raffinose, Mixtures of *d*- and *l*-Tartaric Acid as Organic Foodstuffs.** H. I. WATERMAN (*Chem. Zentr.*, 1914, i, 485; from *Folia Microbiologica*, 1913, 2, part 2).—In the study of metabolism processes, it is necessary to take into account the quantity of the organism formed, together with the rate of reaction and the amount of reaction products formed. The value of sucrose as a source of carbon for *Aspergillus niger* is equal to that of lævulose and dextrose; maltose and potato meal have about the same plastic equivalent. Glycogen gives only a small crop, a fact to be ascribed to the mutation which takes place. By cultivation of the mould in raffinose solution, melibiose is set free, giving a yield of 68%. *l*-Tartaric acid is obtained in a yield of 60% from racemic acid. An appreciable part of the *d*-acid (40%) is therefore assimilated. The plastic equivalent of the *d*-acid is approximately that of the *l*-acid. A change in the concentration of the racemic acid has no influence on the magnitude of its plastic equivalent. The maximal lævorotation attained with a given form of *Aspergillus niger* is, within certain limits dependent only on the concentration of the racemic acid; the larger this is, the bigger the crop of the mould and the larger the rotation. An alteration of the ratio of the *d*- to the *l*-acid in favour of the *d*-acid causes a better assimilation of the *l*-acid, and the resulting lævorotation will consequently fall. On the other hand, an increase of the *l*-acid will alter the *l*-rotation, and relatively small amounts of the *l*-acid will be attacked by the mould. After very long periods (two months), however, a considerable development sometimes occurs, and mutation will have been found to take place. The result led to the expectation that the mutants II and III, previously obtained by cultivation on galactose, would behave differently towards *d*- and *l*-tartaric acids as compared with the parent form (I). This expectation has been confirmed. II and III assimilate the *l*-form more rapidly than I does. Mesotartaric acid is not attacked by *Aspergillus niger* except after long intervals, when mutation also takes place. The researches indicate the importance of taking into account the form of the organisms used in biochemical researches.

S. B. S.

**Formation of Carbohydrates in Plants.** HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1914, 27, 8—21).—The author is of opinion that, during assimilation, the reduction of carbonic acid is accompanied by the formation of a chain containing two carbon atoms; glycolaldehyde is the chief intermediate product, and from this sugars and other vegetable substances are formed by condensation.

The assumption that glycolaldehyde is the intermediate product in the formation of sugars is in better agreement with known facts than is the formaldehyde hypothesis.

W. P. S.

**The Chemistry of Vegetable Cell-membrane.** FR. HÜHN (*Zeitsch. Nahr. Genussm.*, 1914, 27, 21—33).—A synopsis of the history of the chemistry of cellulose, etc., is given, together with the literature dealing with the subject.

W. P. S.

**Acetylcholine, a New Active Principle of Ergot.** ARTHUR JAMES EWINS (*Biochem. J.*, 1914, 8, 44—49).—An active principle of ergot, recognisable by its inhibitory action on the heart and its stimulant action on intestinal muscle, has been identified by its mercuric chloride compound, its aurichloride, and its platinum-chloride (elementary analysis and melting-point determinations) as acetylcholine, the intense physiological activity of which was first shown by R. Hunt and Taveau.

W. D. H.

**The Biological Formation and Function of Alkaloids.** J. GADAMER (*Ber. Deut. pharm. Ges.*, 1914, 24, 35—55).—The author reviews critically the various theories that have been advanced to explain the formation of alkaloids, and the views that have been put forward as to their function, in plants. It is shown that Pictet's theory that the alkaloids are formed from the decomposition products of proteins, and that they are to be regarded as waste products of plant metabolism, affords a clear and logical explanation of many of the facts. It is, however, not in harmony with observations made by the author, in association with Klee, that *Papaver orientale* (a plant which botanically is placed between *P. somniferum* [the opium poppy] and the perennial *Fumariaceæ*, containing the *Corydalis* group) contains thebaine only when at the height of vegetative activity, and *isothebaine* only when in a resting state; the former is an opium alkaloid, the latter is closely related to the bulbocapnine sub-group of the *Corydalis* alkaloids. Throughout the life of the plant, the percentage of alkaloid remains approximately constant. These observations show that in this plant, at least, the alkaloid has some definite biological function. Observations made by Lotsy on cinchonas, Müller on the opium poppy, Clautriau on *Thea sinensis*, and by Weevers and Dekker on cocoa and kola, all tend in the same direction.

T. A. H.

**"The Vegetable Chameleon." Anthocyanin.** M. CVET (*Ber. Deut. bot. Ges.*, 1914, 32, 61—68).—When the violet alcoholic extract of red cabbage is precipitated with ether, and then shaken with anhydrous sodium sulphate, the anthocyanin is readily adsorbed by the salt. The dye is then almost insoluble in alcohol. Addition of alcohol and a little acetic acid to the salt changes the colour to red without dissolving the dye. Alcoholic hydrochloric acid, or strong acetic acid, dissolves a portion. The violet-coloured salt is bleached by being kept in alcohol; addition of acid restores



the colour. The colourless alcoholate becomes violet when evaporated down, and again colourless when redissolved in alcohol. When 3 c.c. of the colourless, alcoholic solution is treated with different amounts of water (1 to 9 c.c.), a coloration is produced which increases with the amount of water; the regeneration of the chromophore groups is quickened by heating. The effect can be reversed by adding increasing amounts of alcohol to the aqueous solution.

The conclusion is drawn that decoloration of anthocyanin by alcohol cannot be a process of reduction, either by loss of oxygen or addition of hydrogen.

Alcoholic extracts of apples acquire a violet colour when treated with strong hydrochloric acid and formaldehyde. In presence of alkali and formaldehyde, the alcoholic extract yields a yellow precipitate, which gradually becomes bluish-green when heated; addition of a drop of hydrochloric acid causes the flakes to dissolve, whilst the colour changes to red (compare Peche, *ibid.*, 1913, **31**, 462).

N. H. J. M.

**The Pigments of the Chromoleucites.** V. LUBIMENKO (*Compt. rend.*, 1914, **158**, 510—513).—The pigments which replace chlorophyll in autumn leaves or in ripening fruit can be classed into two groups, namely, that of lycopin and that of rhodoxanthin (compare Monteverde and Lubimenko, this vol., i, 240). The representatives of the first group are the most numerous and most frequent. They approach more or less closely to the type lycopine, and are provisionally named "lycopinoids." They can be divided into four series, according to their physical and chemical properties, three out of the four series commencing with a crystalline substance, and containing a number of amorphous pigments. The three absorption bands for each series are given, measured for carbon disulphide solutions of the pigments. Temperature is the most important external factor in the formation and accumulation of these lycopinoids. Light is not indispensable, and it appreciably accelerates the phenomenon. The accumulation stops if the plant tissues are killed by chloroform. Free oxygen from the air is necessary for the formation of these lycopinoids. W. G.

**Cestrum Parqui.** J. MERCIER and J. CHEVALIER (*Chem. Zentr.*, 1913, ii, **26**, 2142; from *Bull. Sci. Pharmacol.*, 1913, **20**, 584—603).—An account of the botany and chemistry of this plant, a native of South America, is given. It contains 0.8% of an alkaloid, *parquine*,  $C_{21}H_{39}O_8N$  (?), m. p. 180—181°, which forms small, yellowish cubes, possesses an extraordinarily bitter taste, is unstable in light and air, is soluble in alcohol or chloroform, sparingly so in ether, and insoluble in light petroleum. It is a nerve and muscle poison, resembling both strychnine and atropine in action.

The plant also contains a *glucoside*, to which its unpleasant odour is due. The glucoside is hydrolysed by an enzyme in the plant, yielding valeric acid and a new glucoside, which on hydrolysis yields a sugar and a phytosterol-like substance.

T. A. H.

**Narcosis in Leaves of the Wild Indigo (*Baptista tinctoria*) and the Production of a New Phenol, Baptisol.** ERNEST D. CLARK (*Proc. Amer. Soc. Biol. Chem.*, 1913 ; *J. Biol. Chem.*, **17**, xxxiii—xxxiv).—Ordinary volatile anæsthetics, and still more so substances of the ester type and acetone, anæsthetise the leaves of this plant and blacken them; the blackening is probably an enzymic effect. A crystalline substance appears in the blackened leaves, which is a new phenol, *baptisol*,  $C_{15}H_{12}O_5$ , melting at  $213^{\circ}$ . It contains three hydroxyl and one methoxyl groups. It is nearly insoluble in water. The crystals give a bright, evanescent cherry colour with ferric chloride, and a typical red reaction with Millon's reagent.

W. D. H.

**Environmental Influences on the Physical and Chemical Characteristics of Wheat.** J. A. LE CLERC and P. A. YODER (*J. Agric. Research*, 1914, **1**, 275—291).—The wheat was grown on small plots in California, Kansas, and Maryland, both in the undisturbed soil and in interchanged soil—Kansas and Maryland soils transferred to California, Californian and Kansas soils transferred to Maryland, and Californian and Maryland soils transferred to Kansas.

The results of the experiments, over a period of four years, showed that the physical and chemical properties of the wheat do not depend mainly on the soil, but rather on climatic conditions. As regards influence of climate, it is suggested that differences in humidity may affect transpiration, and hence the composition of the crop. Variations in the amount and distribution of the sunlight may cause variations in the photosynthesis; and variations in temperature and in the succession of hot and cold periods may cause varying vegetative activities. Besides these direct actions, all these conditions may cause alterations (physical, chemical, and biological) in the soil, which, in turn, will influence the crop.

The full results are given in tables.

N. H. J. M.

**Action of Sulphur on Plant Production. Adaptation of the Results of Field Experiments to Gauss' Law of Chances of Error.** TH. PFEIFFER and E. BLANCK (*Landw. Versuchs.-stat.*, 1914, **83**, 358—383).—The results of field experiments with oats failed to show any increase either in yield or the utilisation of nitrogen. If anything, the application of sulphur had a very slightly depressing effect.

Evidence is given that the results of field experiments adapt themselves satisfactorily to Gauss' law.

N. H. J. M.

**Effect of Lime in the Form of Calcium Oxide and Calcium Carbonate on the Physical Properties of Different Soils.** O. ENGELS (*Landw. Versuchs.-stat.*, 1914, **83**, 408—466).—Eight different kinds of soils were employed. Application of lime results in the precipitation of colloids; the water capacity of the soil is increased, and also the permeability, especially of heavy soils. Other effects

of lime are diminution of the hygroscopicity of the soils, a diminished power of raising water by capillarity, and diminished shrinkage on drying. The effects of calcium oxide and carbonate are similar, that of the oxide being greater. For heavy soils, lime is the more suitable, whilst calcium carbonate and marls may be applied to lighter soils.

N. H. J. M.

**Effect of Heat on the Solubility of the Mineral Constituents of the Soil.** WILLIAM McGEORGE (*J. Ind. Eng. Chem.*, 1914, **6**, 223—227).—Results obtained during an investigation on the effect of heat on Hawaiian soils show that the solubility of the various constituents in water and in dilute nitric acid is increased when the soils have been heated previously. Generally, the maximum solubility was observed when the soil had been heated for eight hours at 250°, although, in the case of the lime and magnesia, the solubility in nitric acid reached a maximum in the samples heated for eight hours at 100°. Ignition of the soils for eight hours over a Bunsen burner caused certain constituents to become less soluble and others more soluble.

W. P. S.

**Action of Hydroxyl Ions on Clays and Clay Soils when Marled.** J. G. MASCHHAUPT (*Landw. Versuchs-stat.*, 1914, **83**, 467—470. Compare Rohland, *Landw. Jahrb.*, 1913, Heft 3).—A reply to Rohland (*loc. cit.*). The results of experiments in which suspensions of a sandy loam were treated with different amounts of sodium hydroxide showed that whilst concentrations from 0.015 to 0.0375*N*. have a flocculating action, the reverse effect is produced with 0.005 to 0.0137*N*-sodium hydroxide, sedimentation being slower than in water alone. Similar results were obtained with suspensions of soot.

N. H. J. M.

**Ferrous Iron in Soils.** C. G. T. MORISON and H. C. DOYNE (*J. Agric. Sci.*, 1914, **6**, 97—101).—Estimations of ferrous iron in soils by the usual method (extraction with dilute sulphuric acid and titration with permanganate) gave, with four different soils, results varying from 0.26% to 1.72%, corresponding in the case of the highest results with about 30,000 lb. per acre. It was found, however, that results obtained by this method depend largely on the presence of ferric oxide and of organic matter which reduces the ferric to ferrous iron. Addition of peat to the soil considerably increased the amount of ferrous iron found.

Employment of acetic acid instead of sulphuric failed to give satisfactory results.

Experiments in which the four soils (10 grams) were shaken for sixteen hours with 500 c.c. of a solution of ferrous ammonium sulphate showed that no conversion with ferric iron occurred, and that more or less of the iron was absorbed, an equivalent amount of calcium going into solution.

The conclusion is drawn that the existence of ferrous iron in normal soils to any extent is unlikely, and that the presence of

ferric iron in the normal soil solution is equally unlikely. The question arises, in what form does iron reach the plant?

N. H. J. M.

**Formation and Decomposition of Manganic Compounds under the Influence of Micro-organisms.** N. L. SÖHNGEN (*Chem. Weekblad*, 1914, 11, 240—244).—The formation in the soil of higher oxides of manganese from manganous salts is promoted by a high concentration of hydroxyl ions, and the reduction of these oxides by the presence of peroxides, peroxydases, and oxydases. The presence of dextrose in the soil leads to the formation of hydroxy-acids capable of decomposing the higher oxides of manganese.

A. J. W.

**Humus of Acid and Alkaline Peats.** J. A. HANLEY (*J. Agric. Sci.*, 1914, 6, 63—76).—The results of estimations of humus in acid and alkaline peats showed that in the case of acid peat as much humus is in some cases dissolved by direct treatment with ammonia (4%) as when previously extracted with acid. Some alkaline peats yielded more than half the total soluble humus when directly extracted with ammonia. The percentage of nitrogen in the soluble humus is about the same whether the peat is previously extracted with acid or not. Potassium hydroxide of a strength equivalent to that of the ammonia dissolves less nitrogen than ammonia does.

When alkaline peats are hydrolysed with 20% hydrochloric acid, small amounts of ammonia are produced. No ammonia was obtained from acid peat.

A number of experiments are described in which solutions of sucrose were boiled with different soils, and the amount of invert sugar estimated. A correction was applied for the amount of cuprous oxide produced when the soil is boiled with water alone and the extract heated with Fehling solution.

N. H. J. M.

**Nature and Amount of the Fluctuations in Nitrate Contents of Arable Soils.** EDWARD JOHN RUSSELL (*J. Agric. Sci.*, 1914, 6, 18—57. Compare J. B. Lawes, J. H. Gilbert, and R. Warington, A., 1884, 357).—The results of numerous estimations of nitrates in arable soils at different periods showed that nitrogen in this form rarely exceeds 6 per million in sandy soil, 23 per million in loam, and 14 per million in clay. These amounts correspond with 28, 115, and 60 lb. per acre respectively in the first 18 inches of soil. The accumulation of nitrates is generally found to take place most rapidly in the late spring or early summer after which the soils usually gain little if any nitrates, and frequently show a loss. In the hot, dry autumn of 1911, however, the accumulation went on, in some cases, until September.

Comparing different kinds of soils, it was found that the fluctuations in the amount of nitrates were more marked on loams than on clays or sands. In clays the winter losses are less; on the other hand, they accumulate smaller amounts in June and July.

The soils of fallow land were found to contain more nitrates than

cropped soils, allowing for the amounts of nitrates taken up by the crop.

The rapid rise in the amounts of nitrates in the spring takes place not immediately, but some time after the warm weather begins.

N. H. J. M.

**The Organic Nitrogen of Hawaiian Soils. II. The Effects of Heat on Soil Nitrogen.** W. P. KELLEY (*J. Amer. Chem. Soc.*, 1914, **36**, 434—438. Compare this vol., i, 368).—Rise in temperature above 100° causes considerable loss in nitrate nitrogen, so that at 200° nitrates are no longer present; on the other hand, the ammonia content is increased very largely at 150—200°, but at 250° the amount again decreases, probably on account of expulsion from the soil. Of the organic nitrogen, the non-basic constituents are notably diminished by heating, the change in amide and basic nitrogen being much less marked.

D. F. T.

**The Organic Nitrogen of Hawaiian Soils. III. The Nitrogen of Humus.** W. P. KELLEY and ALICE R. THOMPSON (*J. Amer. Chem. Soc.*, 1914, **36**, 438—444).—The humus was extracted from the soil by 3% sodium hydroxide after first treating with 1% hydrochloric acid. The humus nitrogen varied with different samples, but on the average amounted to approximately 62% of the total nitrogen of the soil. When the solution of humus was neutralised with acid, the precipitate obtained contained about 46% of the total humus nitrogen, further acidification then produced a deposit containing approximately 12%, whilst the acid liquid retained about 42% of the humus nitrogen in solution.

Analysis showed that the nitrogen of the humus comprised relatively more amide and basic nitrogen and less non-basic nitrogen than did the soil nitrogen as a whole.

D. F. T.

**Nitrogen and Chlorine in Rain and Snow.** G. H. WIESNER (*Chem. News*, 1914, **109**, 85—87).—Estimations of nitrogen in the forms of ammonia, nitrates, nitrites, and organic matter, and of chlorine in thirty-one samples of rain and snow, collected from February 23rd to June 5th, 1912, at Mount Vernon, Iowa. During this period the snow and rain amounted to 17.75 and 15.30 inches respectively. The following results were obtained:

	Nitrogen.			Organic.	Chlorine.
	As $\text{NH}_3$ .	As $\text{N}_2\text{O}_3$ .	As $\text{N}_2\text{O}_5$ .		
Per million, in rain .....	0.931	0.0018	0.15	1.13	4.8
„ in snow ...	3.35	0.0021	0.19	3.84	4.7
Per acre (lb.) in 14 weeks	2.703	0.005	0.524	3.353	6.59

Nitrites were found in nearly all the samples. As regards chlorides, Mount Vernon is 1200 miles from the Atlantic.

N. H. J. M.

## Organic Chemistry.

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**Pure Propane; Weight of a Normal Litre.** JEAN TIMMERMANS (*Compt. rend.*, 1914, 158, 789—791).—The pure propane was prepared either by the action of sodamide on propyl iodide (compare Lebeau, A., 1905, i, 501), the issuing gas being passed through sulphuric acid, bromine, a concentrated solution of potassium hydroxide, pure sulphuric acid containing some vanadium pentoxide, and over phosphoric oxide and finally fractionally distilled; or by the action of sodium on butyronitrile. The mean value obtained for the weight of a normal litre of propane prepared by these methods is 2.0196 grams. W. G.

**Some Physical Properties of Ethane, Ethylene and Acetylene.** O. MAASS and D. MCINTOSH (*J. Amer. Chem. Soc.*, 1914, 36, 737—742).—The vapour pressures and densities of ethane have been determined between the temperatures  $-107.9^{\circ}$  and  $-81.7^{\circ}$ ; the boiling point at normal pressure is  $-88.5^{\circ}$ , the heat of vaporisation  $14.6 \times 10^{10}$  ergs per mol., and the density at the boiling point, 0.5490.

For ethylene, the densities were determined between  $-114.2^{\circ}$  and  $-99.4^{\circ}$ , the density at the boiling point,  $-102.5^{\circ}$ , being 0.5650. In the case of acetylene, the densities and molecular surface energies were measured between  $-77.4^{\circ}$  and  $62.4^{\circ}$ . The variation of the molecular surface energy with temperature is 2.40 per degree, and the density at the boiling point is 0.618.

The molecular volumes of the above three substances at their boiling points are respectively 54.7, 49.6, and 42.1, and if 5.5 is taken as the atomic volume of hydrogen, the atomic volumes of carbon for different linkings are: single 10.9, double 13.8, triple 15.5.

Additive compounds of acetylene and hydrogen bromide could not be obtained, even at temperatures as low as  $-115^{\circ}$ .

With acetylene, which has a high vapour pressure at the boiling point, the phenomenon of freezing and boiling occurring simultaneously is shown in a striking way. Liquid acetylene in a sealed tube can be supercooled about  $5^{\circ}$ ; as crystallisation takes place the remaining liquid boils vigorously. T. S. P.

**New Processes for the Preparation of Unsaturated Hydrocarbons with Conjugated Double Bonds.** I. L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1914, 36, 663—670).—It is possible to prepare hydrocarbons of the butadiene group by dehydration of the corresponding oxides above  $350^{\circ}$  in the presence of catalysts: a reduced pressure is essential to the attainment of a satisfactory result.

When  $\alpha\beta$ -oxido- $\beta$ -methylbutane,  $\begin{array}{c} \text{O} \\ | \\ \text{CH}_2 \end{array} \text{---} \text{CMeEt}$  (Kyriakides, this vol., i, 506), was made to pass in the vapourous state over aluminium silicate powder at  $400^{\circ}$  the issuing vapours were found, on condensation, to consist of isoprene and  $\beta$ -methyl- $\Delta^2$ -butene, the formation of the latter being due to a secondary reduction of some of the isoprene.

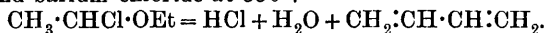
The catalyst soon became covered with carbon, with the result that instead of the desired dehydration a mere isomerisation to  $\alpha$ -methylbutaldehyde was produced.

On working with the pressure reduced to 60 mm. and with a temperature of 440—460°, about four-fifths of the hydrocarbon product were found to consist of isoprene, but a certain amount of  $\alpha$ -methylbutaldehyde was also obtained. With the catalyst at 450° and a pressure of less than 1 mm., the isoprene obtained was almost pure, but again some  $\alpha$ -methylbutaldehyde was concurrently formed.

Although  $\alpha$ -methylbutaldehyde can be made to yield isoprene in this way (compare Ipatiev and Leontovitch, A., 1903, i, 598), the process does not take place so readily, neither is the isoprene as pure as when the above oxide is used. The dehydration of  $\alpha\beta$ -oxido- $\beta$ -methylbutane is therefore regarded as a direct process.

D. F. T.

**New Methods for Obtaining Erythrene from Derivatives of Ethyl Ether.** I. I. OSTROMISLENSKI and S. S. KELBASINSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 123—133).—Increased yields (20%) of erythrene may be obtained by heating  $\alpha$ -chloroethyl ethyl ether with alumina and barium chloride at 350°:



The catalyst rapidly becomes covered with a layer of brown resin and gradually loses its effect; the yield is also lowered by "poisoning" of the alumina by the hydrogen chloride formed in the reaction and by decomposition of part of the chloro-ether into aldehyde and alcohol.

The more stable  $\alpha$ -hydroxyethyl (or  $\alpha$ -ethoxyethyl) ethyl ether also gives good yields of erythrene when heated with alumina at 300—380°, no increase in the yield being effected by carrying out the reaction under reduced pressure.

T. H. P.

**Hexanitroethane.** W. WILL (*Ber.*, 1914, **47**, 961—965).—*Hexanitroethane* is obtained in a 90% yield by nitrating, in sulphuric acid, pure *s*-tetranitrodipotassioethane,  $\text{C}_2(\text{NO}_2)_4\text{K}_2$  (Scholl and Brenneisen, A., 1898, i, 345). The author prepared the latter compound, by a modification of Scholl and Brenneisen's method, from bromopicrin [prepared by Bolas and Groves' method (this Journ., 1870, 153) slightly modified].

Hexanitroethane forms colourless crystals, m. p. 142° (decomp.), and is less volatile than camphor and much less so than tetranitromethane. It is insoluble in water, sparingly soluble in cold alcohol, but readily so in ether, light petroleum, benzene, or chloroform, and it has an odour recalling that of camphor and similar to, but not as strong as, that of tetranitromethane.

It forms an unstable red compound with naphthalene, and its solutions in benzene and toluene are yellow, whilst phenol, resorcinol, etc., are converted into red compounds. *o*-Nitroaniline gives an explosive product, and quinol is oxidised to quinhydrone. Acetone, diphenylamine, and diphenyldimethylcarbamide are also attacked by the substance. By treatment with stannous chloride and hydrochloric acid, it yields methylamine and hydroxylamine, and it forms explosive mixtures with hydrogenous organic substances.

J. C. C.

**$\beta$ -Fluoroethyl Alcohol and Acetate.** FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1914, 7—17).— $\beta$ -Fluoroethyl acetate,  $\text{CH}_3\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{F}$ , prepared by the action of mercurous or silver fluoride on the corresponding bromo-derivative, is a colourless liquid with the odour of ethyl acetate, b. p.  $119\cdot3^\circ/753$  mm. (corr.),  $45\cdot5^\circ/27$  mm.,  $D^{20}$  1.0982,  $n_D^{10}$  1.37792, and is rapidly hydrolysed by water, in which it is readily soluble; it forms a compound with calcium chloride.

$\beta$ -Fluoroethyl alcohol,  $\text{CH}_2\text{F}\cdot\text{CH}_2\cdot\text{OH}$ , obtained by hydrolysing the acetate by means of dilute acid, is a colourless liquid with the odour of ethyl alcohol, b. p.  $103\cdot35^\circ/757$  mm.,  $D^0$  1.12972,  $D^{18\cdot3}$  1.11124,  $n_D^{18\cdot4}$  1.36470; it crystallises in long, transparent needles at  $-26\cdot45^\circ$ , and its heat of combustion at constant volume is 290.16 cal. It mixes with water in all proportions, and readily dissolves calcium chloride and nitrate. Phosphorus tribromide converts it into *s*-bromofluoroethane,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{F}$ , b. p.  $71$ — $72\cdot5^\circ$ , but attempts to transform it into the corresponding aldehyde by treatment with sodium dichromate and sulphuric acid yielded only fluoroacetic acid.

T. H. P.

**Iodohydrins and Methyliodohydrins Derived from  $\zeta$ -Methyl- $\Delta^a$ -heptene.** B. DE RESSÉGUIER (*Bull. Soc. chim.*, 1914, [iv], 15, 182—186. Compare this vol., i, 528).—The author has shown that the addition of hypiodous acid and its esters to cyclohexylpropene occurs in each of the manners theoretically possible, and that, a priori, the same behaviour may be expected from an unsaturated aliphatic compound. Since, however, the cyclohexyl group may exert a marked directive influence, the addition of hypiodous acid and its esters to a purely aliphatic substance,  $\zeta$ -methyl- $\Delta^a$ -heptene, has been investigated. The behaviour of this substance has been found to be similar to that of cyclohexylpropene.

$\zeta$ -Methyl- $\Delta^a$ -heptene, b. p.  $113$ — $115^\circ$ , is prepared by the action of magnesium isoamyl bromide on allyl bromide (compare Barbier and Grignard, *Bull. Soc. chim.*, 1904, [iii], 31, 841). When dissolved in moist ether and treated with iodine and yellow mercuric iodide, it yields a mixture of iodohydrins,  $D^0$  1.374, from which, by treatment with silver nitrate solution, two series of mixtures are obtained. One of these, b. p.  $140$ — $150^\circ/13$ — $14$  mm.,  $D^0$  1.0582, consists essentially of the mononitric esters of methylheptanediol, containing, however, a little iodine. The other, b. p.  $70$ — $80^\circ/13$ — $14$  mm., yields two semicarbazones. The more soluble of these, m. p.  $135^\circ$ , yields an aldehyde on treatment with sulphuric acid; the less soluble, m. p.  $155^\circ$ , regenerates a ketone. In consequence of their identity with the products of isomerisation of methylheptene oxide, the substances are considered to be  $\beta$ -methylheptan- $\eta$ -al and  $\beta$ -methylheptan- $\zeta$ -one respectively.

Methylheptene oxide, b. p.  $156^\circ/\text{normal pressure}$ ,  $65$ — $67^\circ/25$  mm.,  $D^0$  0.8524, is obtained by the action of dry potassium hydroxide on an ethereal solution of the mixture of iodohydrins. Partial isomerisation occurs during distillation under ordinary pressure, since the distillate combines to some extent with sodium hydrogen sulphite and colours Schiff's reagent. The warm product of isomerisation is isoamylacetone (semicarbazone, m. p.  $155^\circ$ ).



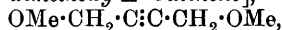
A mixture of the *methyl iodohydrins* of  $\zeta$ -methyl- $\Delta^{\alpha}$ -heptene, b. p. 116—119°/15 mm.,  $D_0^{20}$  1.357, is obtained by the gradual addition of iodine to a methyl-alcoholic solution of  $\zeta$ -methyl- $\Delta^{\alpha}$ -heptene containing yellow mercuric oxide. On treatment with alcoholic potassium hydroxide and subsequent distillation, a product, b. p. 160—165°,  $D_0^{20}$  0.8208, is obtained, which is probably a mixture of the compounds  $\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{C}(\text{OMe}) \cdot \text{CH}_2$  and  $\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CH} \cdot \text{CH} \cdot \text{OMe}$ , which, on hydrolysis with sulphuric acid, gives a fraction, b. p. 168—173°; this colours Schiff's reagent, and reduces ammoniacal silver nitrate solution. Nevertheless, only one semicarbazone, m. p. 155° (identical with the semicarbazone described above), can be isolated from it; this, when hydrolysed, yields a liquid, b. p. 170—171°, which does not colour Schiff's reagent, but combines with sodium hydrogen sulphite, and is thus a methyl ketone.

Decomposition of the mixture of methyl iodohydrins is effected by silver nitrate solution in the usual manner. On distillation of the product, a fraction, b. p. 112—113°/12 mm.,  $D_0^{20}$  1.0913, is obtained, consisting of the *nitric* esters of the *methyl ethers of methylheptanediol*. The second fraction yields, on re-distillation, a portion, b. p. 168—171°/ordinary pressure, from which the two semicarbazones, m. p.'s 135° and 155°, respectively are obtained, which, when hydrolysed, give an aldehyde and ketone. The similarity of these semicarbazones with those obtained from the iodohydrins of  $\zeta$ -methyl- $\Delta^{\alpha}$ -heptene is explained by the elimination of the methoxy-group by hydrolysis due to the nitric acid liberated during treatment with silver nitrate.

H. W.

**Passage from the Dimethyl Ethers of Acetylenic Glycols to these Glycols.** R. LESPIEAU (*Compt. rend.*, 1914, 158, 707—708. Compare Iocitsch, this vol., i, 375, 403, 405).—Starting with the dimethyl ethers of acetylenic glycols, two atoms of bromine are added, giving the corresponding dibromoethylene glycols. These are easily demethylated by heating for several hours at 100° in a flask through which passes a current of hydrogen bromide. The bromides crystallise out on cooling, and with silver acetate give the corresponding acetins, which on hydrolysis give the bromo-glycols. The latter on treatment with zinc dust in the presence of alcohol give the required glycol.

The glycol ether [*αδ*-dimethoxy- $\Delta^{\beta}$ -butinene],



gives the bromo-compound,  $\text{OMe} \cdot \text{CH}_2 \cdot \text{CBr} \cdot \text{CBr} \cdot \text{CH}_2 \cdot \text{OMe}$  (compare A., 1907, i, 580), which with hydrogen bromide yields *αβγδ*-tetra-bromo- $\Delta^{\beta}$ -butene,  $\text{CH}_2\text{Br} \cdot \text{CBr} \cdot \text{CBr} \cdot \text{CH}_2\text{Br}$ , m. p. 69.5°—70.5°. This with silver acetate gives the *acetin*,  $\text{OAc} \cdot \text{CH}_2 \cdot \text{CBr} \cdot \text{CBr} \cdot \text{CH}_2 \cdot \text{OAc}$ , m. p. 61°, which on saponification gives *βγ*-dibromo- $\Delta^{\beta}$ -butene-*αδ*-diol,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CBr} \cdot \text{CBr} \cdot \text{CH}_2 \cdot \text{OH}$ , m. p. 116.5—117.5°, yielding a *diphenyl-urethane*, m. p. 186—187°. The bromoglycol with zinc dust and alcohol gives the required acetylenic glycol [ $\Delta^{\beta}$ -butinene-*αδ*-diol].

*αε*-Dimethoxy- $\Delta^{\beta}$ -butinene,  $\text{OMe} \cdot \text{CH}_2 \cdot \text{C} \equiv \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , gives the bromo-compound,  $\text{OMe} \cdot \text{CH}_2 \cdot \text{CBr} \cdot \text{CBr} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , b. p. 132°/

15 mm., yielding  $\alpha\beta\gamma$ -tribromo- $\Delta^{\beta}$ -penten- $\epsilon$ -ol,  
 $\text{CH}_2\text{Br}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ ,  
 m. p. 64—65°, which gives the *acetin*,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ ,  
 b. p. 168°/16 mm. This on saponification gives a liquid, which could  
 not be purified.

A similar series of reactions with  $\alpha\theta$ -dimethoxy- $\Delta^{\beta\epsilon}$ -octadienene,  
 $\text{OMe}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OMe}$ , gives in turn the compound  
 $\text{OMe}\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{OMe}$  (compare *loc. cit.*),  
 the *bromide*,  $\text{CH}_2\text{Br}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\text{Br}$ , m. p.  
 86—87°; the *acetin*,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{OAc}$ ,  
 m. p. 59—60°;  $\beta\gamma\xi\eta$ -tetrabromo- $\Delta^{\beta\epsilon}$ -octadiene- $\alpha\theta$ -diol,

$\text{OH}\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{OH}$ ,  
 m. p. 116—117°, giving a *diphenylurethane*, m. p. 205—206°, and  
 finally  $\Delta^{\beta\epsilon}$ -octadienene- $\alpha\theta$ -diol,

$\text{OH}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OH}$ ,  
 m. p. 88.5—89.5°, giving a *diphenylurethane*, m. p. 180°. W. G.

**Preparation of Diglycerides.** R. R. RENSHAW (*J. Amer. Chem. Soc.*, 1914, 36, 537—545).—The preparation of diglycerides presents considerable difficulty owing to the simultaneous production of triglycerides, fatty acids, and, possibly, small quantities of isomeric diglycerides.

An attempt was made to prepare  $\beta\gamma$ -distearin by heating  $\beta\gamma$ -dibromopropyl alcohol with sodium stearate according to Guth's method (*A.*, 1903, i, 226), but it was found that the product contained tristearin, which is exceedingly difficult to separate, as it has almost the same solubility as the diglyceride; a substance was also formed containing bromine and stearic acid. Better results were obtained by using lead stearate instead of the sodium salt, and a yield of nearly 20% of distearin was thus obtained which was almost free from tristearin and could therefore be comparatively easily purified. This method has proved the best of those so far investigated.

$\beta\gamma$ -Dibromopropylammonium bromide, m. p. 170.2° (corr.), prepared by the action of bromine on allylamine hydrobromide, was heated with sufficient sodium or lead stearate to react with three bromine atoms. When the substances were heated together in the dry state, charring took place, and when heated in solution some decomposition occurred, but relatively large quantities of stearic acid were formed, together with a small amount of an amino-compound, m. p. 88—90° (uncorr.).

E. G.

**Basic Function of Methoxyl.** HUGO KAUFFMANN (*Ber.*, 1914, 47, 1031. Compare Kauffmann and Kieser, this vol., i, 53).—Polemical. The author does not consider that his theory is identical with that advanced by Flürschheim (compare this vol., i, 377), since the actual cause of the increased ionisation is the sundering of the valency exercised by the auxochrome groups and influencing the acid residue and not the greater valency demand of the central carbon atom (compare Kauffmann, this vol., i, 40). His method of expressing the formulæ is also defended.

H. W.

**Products Obtained by the Action of Bromine on Ether by Schützenberger, McIntosh and the Author.** A. E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 135—152).—Objection is raised to Tschelincev's calculations (this vol., i, 135) referring to the calorimetric data obtained by the author, the latter's accidental numerical error having no bearing on the final conclusions (A., 1913, i, 815). The value 9.13 Cal. given by Tschelincev refers to this author's dibromide, the existence of which can be demonstrated neither chemically nor calorimetrically. For the tribromide this result would become  $9.13 \times 1.5 = 13.69$  Cal., which is identical, within the limits of experimental error, with the values, 13.26 and 13.41 Cal., found by the author for the heat of formation of Schützenberger's tribromide.

The results of further experiments confirm the observation that the action of excess of ether on the tribromide is accompanied by no positive heat effect, although part of the ether dissolves in the tribromide in the proportion, 2 of ether tribromide : 1 of ether. The formation of two distinct layers when ether and bromine interact in presence of chloroform is also confirmed. T. H. P.

**Trimethylene Oxide.** A. V. IPATOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 62—70).—Henri's method (A., 1907, i, 377) of preparing  $\gamma$ -chloropropyl alcohol is simpler and gives better yields than Reboul's method (A., 1874, 1154), but does not give a very pure product. Trimethylene oxide, obtained by treating  $\gamma$ -chloropropyl alcohol with coarsely powdered potassium hydroxide, is a colourless liquid with a pungent odour, b. p.  $45-46^\circ/736$  mm.,  $D_4^{20}$  0.8975,  $D_4^{21}$  0.8734,  $n_D^{25}$  1.3901. When heated in a sealed tube on the water-bath with hydrobromic acid saturated at  $0^\circ$ , trimethylene oxide yields  $\alpha\gamma$ -dibromopropane. T. H. P.

**Distillation of Nitroglycerin [Glyceryl Trinitrate] at a Low Temperature.** D. CHIARAVIGLIO and O. M. CORBINO (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 37—40).—By means of an apparatus described and figured in this paper, the authors have succeeded in distilling 10 grams of this substance. The temperature of the evaporating liquid was  $25^\circ$ , that of the condensing surface  $0^\circ$ , and the pressure was kept below 0.0001 mm. by the operation of a Gaede pump when necessary. Except for the fact that it is perfectly colourless, the distillate does not present any obvious differences from the original liquid. R. V. S.

**Behaviour of the Boric Ethers with Alcoholates.** LIVIO CAMBI (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 244—252).—The salt,  $\text{NaB(OMe)}_4$ , is obtained by mixing methyl-alcoholic solutions of sodium methoxide and trimethyl or triethyl borate; it forms colourless prisms containing  $1\frac{1}{2}\text{MeOH}$ . The potassium salt,  $\text{KB(OMe)}_4$ , is similarly obtained, and crystallises in prisms with  $1\frac{1}{2}\text{MeOH}$ . The lithium salt,  $\text{LiB(OMe)}_4$ , is prepared from lithium chloride and the potassium salt in methyl-alcoholic solution; it crystallises in long, silky prisms with  $2\frac{1}{2}\text{MeOH}$ . The calcium salt,  $\text{Ca[B(OMe)}_4]_2$ , is obtained when metallic calcium is dissolved in a methyl-alcoholic solution of trimethyl or triethyl borate.

The salt,  $\text{NaB}(\text{OEt})_4$  (Copaux, A., 1899, i, 183), can be obtained from sodium ethoxide and triethyl borate; it crystallises in colourless, rhombic prisms with  $1\frac{1}{2}\text{EtOH}$ . The *potassium* salt,  $\text{KB}(\text{OEt})_4$ , forms flattened prisms with  $1\frac{1}{2}\text{EtOH}$ . When an absolute alcoholic solution of this salt is treated with an absolute alcoholic solution of thallous acetate, the *thallium* salt,  $\text{TlB}(\text{OEt})_4$ , is obtained.

The salt,  $\text{NaB}(\text{OPr}^a)_4$ , is obtained by adding a propyl-alcoholic solution of *n*-tripropyl borate to a propyl-alcoholic solution of sodium propoxide; it crystallises in minute scales with  $1\text{Pr}^a\text{OH}$ .

All the salts described have the character of true salts and are stable towards atmospheric oxygen. R. V. S.

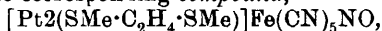
**Preparation of Carbonic Esters.** ARMIN HOCHSTETTER (D.R.-P. 268452. Compare A., 1913, i, 4).—Carbonates of carbohydrates are prepared by heating the latter with phenyl carbonate at about  $130^\circ$  for a short time. A homogeneous mixture of the two substances is obtained by means of phenols such as resorcinol, catechol or pyrogallol, or of acid amides such as acetamide, propionamide, or dimethylformamide. Resorcinol is an excellent solvent for mannitol, sucrose, or starch, but cannot be used for dextrose with which it condenses; for the latter sugar catechol is used as solvent.

The carbonic esters produced in this way melt either at a high temperature or not at all without decomposition. Glacial acetic acid, methyl oxalate, and formamide are the best solvents for them, whilst dextrose carbonate is also soluble in hot water. The carbonates are only very slowly saponified when boiled with water. J. C. C.

**Preparation of a Complex Copper Compound of Lecithin.** GRÄFIN VON LINDEN, F. MEISSEN, and ARTUR STRAUSS (Swiss Patent 62969).—A copper compound of lecithin is obtained by mixing alcoholic solutions of copper chloride (1 part) and lecithin (2 parts). It is an amorphous, brownish-green mass, containing about 3% of phosphorus and 6% of copper, soluble in ether or olive oil, and is of use in the treatment of tuberculosis. J. C. C.

**Platinum Compounds of Organic Sulphides, Analogous to the Salts of Reiset's First Base.** L. TSCHUGAEV and W. CHLOPIN (*Zeitsch. anorg. Chem.*, 1914, 86, 241—256).—The complex compounds of platinum with organic sulphides include representatives of the highest type,  $[\text{Pt}2\text{S}']\text{X}_2$  and  $[\text{Pt}4\text{S}']\text{X}_2$ , analogous to the salts of Reiset's first base. The soluble picrates are very suitable as reagents for these ions, yielding very crystalline, sparingly soluble salts.

The compound,  $[\text{Pt}2(\text{SEt}\cdot\text{C}_2\text{H}_4\cdot\text{SEt})]\text{Fe}(\text{CN})_5\text{NO}$ , is prepared by boiling the salt  $[\text{PtSEt}\cdot\text{C}_2\text{H}_4\cdot\text{SEtCl}_2]$  with excess of the disulphide, and adding an excess of solid sodium nitroprusside to the filtrate. The precipitate may be recrystallised from hot water. The solution in hydrochloric acid or aqua regia gives the reactions for iron, but not for platinum. The corresponding compound,



is similar. The conductivity in aqueous solution corresponds with two complex ions. The compound containing the  $\alpha$ -disulphide,

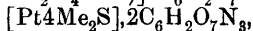
$[\text{Pt}_2(\text{SEt}\cdot\text{C}_5\text{H}_6\cdot\text{SEt})]\text{Fe}(\text{CN})_5\text{NO}$ , is less readily crystallisable, but has a similar constitution.

$[\text{Pt}_4\text{Me}_9\text{S}]\text{Fe}(\text{CN})_5\text{NO}$  is less stable.

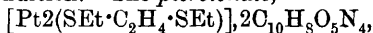
It is possible, by the action of the chloride, to obtain sparingly soluble compounds in which the nitroprusside radicle is contained in the complex. Two such compounds,  $[\text{Pt}_2\text{Me}_2\text{SFe}(\text{CN})_5\text{NO}]$  and  $[\text{PtSEt}\cdot\text{C}_2\text{H}_4\cdot\text{SEtFe}(\text{CN})_5\text{NO}]$ , have been obtained.

Selenides have also been prepared.

The *picrates*;  $[\text{Pt}_2(\text{SEt}\cdot\text{C}_2\text{H}_4\cdot\text{SEt})]2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$  and



are insoluble in cold water and highly crystalline. *Picrates* of many other bases of the types  $[\text{M}\cdot 6\text{A}]$  and  $[\text{M}\cdot 4\text{A}]$  have also been prepared in a crystalline condition. The *picrolonate*,



is also insoluble in cold water. Additive compounds with other complex acids are under investigation. C. H. D.

**Decomposition of Formates in Relation to the Industrial Preparation of Hydrogen.** M. G. LEVI and A. PIVA (*Ann. Chim. Applicata*, 1914, 1, 1—24).—The authors have investigated the decomposition of sodium and calcium formates at various temperatures in an atmosphere either of nitrogen or of carbon monoxide, the formate being introduced rapidly into the decomposition vessel previously heated to the desired temperature; more particularly the gaseous products were examined (compare Echsner de Coninck and Raynaud, A., 1913, i, 440).

In nitrogen, the decomposition of sodium formate with appreciable velocity begins at  $300\text{--}310^\circ$ , and at  $550^\circ$  the action is extremely rapid. Between  $330^\circ$  and  $600^\circ$ , the products are sodium oxalate and carbonate, carbonaceous residue, carbon monoxide, hydrogen, carbon dioxide, and certain volatile secondary products. The small proportion of carbon, like that of the carbonaceous residue, increases markedly with rise of temperature, and is doubtless due to the secondary reactions,  $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$  and  $\text{CO} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{C}$ . The proportion of carbonate in the residue remains virtually constant up to  $500^\circ$ , and then increases appreciably; the oxalate, however, decomposes into carbonate and carbon monoxide with increasing rapidity as the temperature rises, and thus raises the proportion of the monoxide in the gaseous products, whereas the hydrogen-content of the latter remains sensibly constant at all temperatures. The decomposition of the oxalate appears to be a reversible reaction,  $\text{C}_2\text{O}_4\text{Na}_2 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{CO}$ , which has a maximum velocity from right to left at about  $400^\circ$ , whilst above  $550^\circ$  it proceeds mainly in the opposite sense. Between the quantities of total gas, carbon monoxide, hydrogen, carbonate, and oxalate no numerical relations are apparent. The maximum yield of hydrogen is obtained at  $330\text{--}370^\circ$ , the highest amount obtained being 156 c.c. per gram of formate instead of 165 c.c.

Calcium formate decomposes on heating principally according to the equation,  $(\text{H}\cdot\text{CO}_2)_2\text{Ca} = \text{CaCO}_3 + \text{H}_2 + \text{CO}$ , and since no intermediate formation of oxalate was observed, the temperature of decomposition is higher for the formate than for the oxalate (compare Merz and Weith,

A., 1881, 18; 1882, 1049). In an atmosphere of nitrogen, the decomposition assumes appreciable velocity at about 400–410°, and becomes very rapid at 550°. At 400–600°, the products, apart from condensable, volatile compounds, such as methyl alcohol and formaldehyde, are calcium carbonate, carbonaceous residue, carbon monoxide and dioxide, hydrogen, and methane. The carbon dioxide and carbonaceous matter increase with rise of temperature, and the same occurs with the methane up to 500°, beyond which it diminishes in amount; the methane is probably formed by a reversible reduction of the carbon monoxide,  $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$  (compare Gautier, A., 1910, ii, 708; Vournasos, A., 1910, ii, 549; Vignon, A., 1913, ii, 700). The proportion of carbon monoxide predominates over that of hydrogen, but diminishes and tends to approach the latter as the temperature rises; the maximum amount of hydrogen is about 25% of the theoretical yield.

In an atmosphere of carbon monoxide, sodium formate yields methane, and at as low a temperature as 360° gives carbon dioxide in appreciable amount. For both sodium and calcium formates, the yield of hydrogen is less than in nitrogen, owing to the formation of secondary hydrogenated products in increased quantity.

Attempts to detect the presence of unsaturated hydrocarbons in the gases generated on heating these formates, by repeated agitation with bromine or fuming sulphuric acid and subsequent washing with potassium hydroxide, gave indefinite results. It was found, indeed, that mixtures of nitrogen and carbon monoxide, when treated in this way, showed a slight diminution in volume after each operation. This diminution may be due to absorption of the carbon monoxide either by the bromine or sulphuric acid or by the potassium hydroxide solution.

T. H. P.

**The Preparation and Properties of the Normal Ammonium Salts of Organic Acids.** LEROY McMASTER (*J. Amer. Chem. Soc.*, 1914, 36, 742–747. Compare McMaster, A., 1913, i, 444; Keiser and McMaster, *loc. cit.*, i, 248).—A description of several normal ammonium salts prepared by passing ammonia into an alcoholic or ethereal solution of the corresponding acids. The following acids were treated in this way: butyric, *isovaleric*, hexoic, ethylmalonic, itaconic, crotonic, glutaric, adipic, pimelic, sebacic, tartronic, and racemic. In the case of the first five acids the salts obtained were deliquescent, and in all cases fresh aqueous solutions of the salts were neutral to litmus.

Aconitic, *isosuccinic*, and pyrotartaric acids gave products which could not be crystallised.

D. F. T.

**The Saturated Acids of Linseed Oil.** R. S. MORRELL (*J. Soc. Chem. Ind.*, 1913, 32, 1091–1092).—The author has investigated the solid which separates when linseed oil is heated with lead oxide. It was found to consist chiefly of the lead salts of saturated aliphatic acids and was of the same composition as the lead salts obtained from linseed oil by saponification and by extraction of the lead salts of the unsaturated acids by light petroleum and ether. The yield of

lead salts was 8.2% of the oil taken, corresponding with 6% of saturated acids. The acids were investigated, the method of Kreis and Hafner (A. 1903, i, 788) being the one which gave the best results for their separation, and their composition (in percentages) found to be as follows: stearic acid, actually separated, 51.7, stearic acid present in eutectic mixture, 12.7, palmitic acid present in eutectic mixture, 20, residual eutectic mixture, 8, oleic acid, 4. No daturic, myristic, or arachidic acids were detected. T. S. P.

**Catalytic Reduction of Unsaturated Fatty Acids by means of Nickel and Nickel Oxide.** W. MEIGEN and G. BARTELS (*J. pr. Chem.*, 1914, [ii], 89, 290—301).—According to Bedford and Erdmann (A., 1913, i, 701) the catalytic reduction of unsaturated fats and fatty acids proceeds more rapidly in the presence of nickelic oxide than when metallic nickel is employed as catalyst. The authors show, however, that not only nickelic oxide but other metallic oxides such as silver and cupric oxides can only act as catalysts after they have been reduced to the corresponding metals. Moreover, when metallic nickel is used, the reduction proceeds with greater rapidity and at a lower temperature than is the case when the oxide is employed; with metallic nickel the reduction takes place at 180°, whilst with the oxide a temperature of 250° is necessary.

Although nickelic oxide is reduced by hydrogen to the metal at 250°, Bedford and Erdmann maintain that in the presence of unsaturated fats and fatty acids, a nickel suboxide is produced, which is considered to possess a much greater catalytic activity than metallic nickel itself. The conclusion that a suboxide is formed during the reduction and not metallic nickel was drawn from the behaviour of the nickelic oxide after use as a catalyst. It was found that the oxide then had a composition varying between that of NiO and Ni<sub>3</sub>O, was a non-conductor of electricity, and on treatment with carbon monoxide did not yield nickel carbonyl.

The authors point out, however, that these observations are incorrect, and show that nickelic oxide when employed as a catalyst is undoubtedly reduced to metallic nickel. After use the catalyst contains a much higher percentage of nickel than could correspond with a suboxide, and, provided that oxidation by exposure to air is prevented, not only yields nickel carbonyl on treatment with carbon monoxide, but is also a good electrical conductor. F. B.

**Rancidity of Olive Oil and Oxidation of Oleic Acid in Presence of Sunlight.** F. CANZONERI and G. BIANCHINI (*Ann. Chim. Applicata*, 1914, 1, 24—32).—The results of the authors' experiments show that, as regards olive oil, rancidity is due, not to the action of micro-organisms or of enzymes, but to the oxidising influence of the air, the simultaneous action of light having an accelerating, if not a determining effect. Rancidity of oils is not always accompanied by, and is hence independent of, marked increase in the free acidity. Certain metals and also water exert a decided catalytic action in the production of rancidity, so that, in order to preserve olive oil, the latter should be kept in the dark and out of contact with air, moisture or metal.

By causing hydrolysis of fats, the presence of moisture accelerates oxidation and increases the acidity.

The action of air or oxygen in presence of sunlight on oleic acid has been studied (compare Harries and Thieme, A., 1906, i, 793; Harries, A., 1909, i, 131; Molinari and Soncini, A., 1906, i, 792; Molinari and Barosi, A., 1908, i, 849; Molinari and Fenaroli, A., 1908, i, 849). The action of ozone on oleic acid is not so simple as Molinari states, but the typical decomposition of the acid, when treated by either ozone or oxygen, is characterised by attack of the double linking and by the tendency to form peroxides, aldehydes and acids of the nonoic type and also their oxidation products, which increase in complexity with the slowness of the oxidation. The acid,  $C_{18}H_{32}O_6$ , obtained by Molinari and Barosi (*loc. cit.*) is probably formed by the condensation of two molecules of the semialdehyde of azelaic acid,

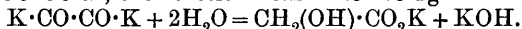
$$\begin{array}{l} O \cdot \underset{|}{CH} \cdot [CH_2]_7 \cdot CO_2H \\ O \cdot \underset{|}{CH} \cdot [CH_2]_7 \cdot CO_2H \end{array}$$

T. H. P.

**Preparation of Ethyl Di-iodobrassidate.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (Swiss Patent 62968).—Ethyl di-iodobrassidate,  $C_{21}H_{39}I_2 \cdot CO_2Et$ , is prepared by treating a solution of ethyl behenolate,  $C_{21}H_{39} \cdot CO_2Et$  (30 parts), in carbon tetrachloride (60 parts) at 30–40° with iodine (22 parts) and aluminium powder (0.05 part) and finally warming the mixture to 50° for one to two hours.

J. C. C.

**The Constitution of Potassium Carbonyl.** A. JOANNIS (*Compt. rend.*, 1914, 158, 874–876).—A study of the action of water on potassium carbonyl prepared as formerly described (compare A., 1893, ii, 520). Attacked by water vapour at a pressure of a few millimetres or by water diluted with liquid ammonia, and added drop by drop to a solution of the carbonyl in liquid ammonia, a reddish-yellow liquid is obtained on evaporating off the ammonia, in which one half of the potassium is present as a neutral salt and the other half as the free base. A quantity of sulphuric acid is added just sufficient to convert the whole of the potassium into sulphate, and this is precipitated by the addition of a mixture of alcohol and ether and filtered off. The filtrate on evaporation gives a syrupy liquid, from which crystals of glycollic acid are obtained. The carbonyl should thus be represented by the formula  $K \cdot CO \cdot CO \cdot K$ , the reaction with water being



If exactly one molecule of water is added, the intermediate reaction  $K \cdot CO \cdot CO \cdot K + H_2O = CH_2(OK) \cdot CO_2K$  is obtained.

W. G.

**Keto-enolic Tautomerism. XI. Acetoacetic Ester (Keto-form).** KURT H. MEYER and FRANCIS G. WILLSON (*Ber.*, 1914, 47, 837–841).—The results obtained by Meyer (A., 1911, i, 350, 832) and Knorr, Rothe and Auerbeck (A., 1911, i, 516) for the composition of the equilibrium mixture of ethyl acetoacetate being so different, the authors have further investigated the question.

The molecular refractivity of the equilibrium ester was determined and found to be in accordance with the measurements of Auwers (A.,



1912, ii, 4), namely,  $D_4^{10}$  1.0357,  $n_D^{10}$  1.4235,  $M_D$  32.02. The keto-ester was then obtained by Meyer's method (*loc. cit.*) by extracting the enol-ester with light petroleum. In this method it is absolutely necessary to get rid of all traces of alkali, which acts as a strong catalyst in restoring the equilibrium; this was done by shaking both the light petroleum and the ester with oxalic acid before the extraction was carried out. The keto-ester thus obtained was found to contain 1—3% of the enol-ester, the amount differing with the preparation; the refractive index varied with the enol-content, and was 1.4222 for 1.56% of enol-ester. The extraction method can also be used with methyl benzoylacetate, the equilibrium ester containing 17% of the enol-form, the extracted ester (two extractions) containing only 9.8%.

Using Knorr's method (*loc. cit.*) of freezing out, keto-ester containing only 0.4% of the enol-ester was obtained. In this method it is also necessary to remove all traces of alkali from the substances used. The ester had  $D_4^{10}$  1.0368,  $n$  1.42177. These figures are in accordance with those obtained for the keto-ester prepared by the extraction method, and the refractive index of the pure keto-ester is calculated to be 1.4217. From the results of the refractive index measurements the equilibrium ester is calculated to contain 7% of the enol-ester, which is in agreement with the result obtained by the titration method, namely, 7.4%. From his results Knorr (*loc. cit.*) concluded that 2% of the enol-ester is present in the equilibrium mixture; in all probability he prepared the pure keto-ester, but it had undergone enolisation to some extent before the refractive index was measured.

T. S. P.

**Preparation of Oxalates by Heating the Corresponding Formates.** CHEMISCHE FABRIK GRÜNAU LANDSHOFF & MEYER, AKT.-GES., EMIL FRANKE, AND WALTER KIRCHNER (D.R.-P. 269833).—Oxalates are produced in almost quantitative yield by heating formates at 385—400°.

J. C. C.

**Oxalacetic Ester.** H. GAULT (*Compt. rend.*, 1914, 158, 711—714. Compare this vol., i, 384).—Oxalacetic ester undergoes lactonisation with formation of oxalocitrolactone under various conditions, apart from the action of potassium acetate or amines, namely: (1) prolonged keeping, the rate of lactonisation varying with the initial purity of the ester. (2) Under the influence of heat, 80% being converted on heating at 150° for four hours. (3) Complete lactonisation occurs in contact with solutions of potassium carbonate, or hydrogen carbonate, sufficiently dilute so that the potassium salt of the original ester does not separate out. (4) On acidification of the sodium salt of the ester.

From this it follows that in the preparation of oxalacetic ester the washing of the ethereal solution with a saturated solution of potassium hydrogen carbonate must be as rapid as possible. The ester is best purified and kept by conversion into its potassium salt by means of a concentrated solution of potassium carbonate. When required it is obtained in the pure state by the acidification in the cold of the potassium salt.

W. G.

**Direct Rupture of the Benzene Ring without Degradation.** H. PAULY, R. GILMOUR, and G. WILL (*Annalen*, 1914, 403, 119—167).—The compound obtained by the action of concentrated or fuming sulphuric acid on 3-nitro-*p*-cresol is not acetylacrylic acid as stated by Schultz and Löw (A., 1909, i, 222), but has the formula  $C_7H_8O_4$  originally assigned to it by Schultz (A., 1907, i, 1030). It cannot be transformed into acetylacrylic acid, and this acid is not obtained as a by-product in the decomposition of 3-nitro-*p*-cresol by sulphuric acid.

On account of its importance in connexion with the rupture of a benzene nucleus without degradation, the acid  $C_7H_8O_4$  has been fully and carefully compared with acetylacrylic acid. Essential differences between the two acids are the following: (i) the acid  $C_7H_8O_4$  has m. p.  $130^\circ$ , and depresses the m. p.,  $125^\circ$ , of acetylacrylic acid; (ii) the acid,  $C_7H_8O_4$ , unlike acetylacrylic acid, does not form a phenylhydrazone in ether, but it readily decomposes, yielding a ketonic acid from which a phenylhydrazone can be prepared; (iii) the acid  $C_7H_8O_4$  does not react additively with hydrogen bromide or with bromine in chloroform or glacial acetic acid, but does so with hydrogen, yielding an acid,  $C_7H_{10}O_4$ ; (iv) acetylacrylic acid is three times as soluble as the acid  $C_7H_8O_4$  in chloroform at the ordinary temperature; (v) the ethyl ester, b. p.  $206^\circ$ , described by Schultz and Löw, is not ethyl acetylacrylate, but the ester of the ketonic acid produced by the decomposition of the acid  $C_7H_8O_4$ ; (vi) the formula  $C_7H_8O_4$ , as against  $C_5H_6O_3$ , is confirmed by a determination of the molecular weight by the ebullioscopic method in ethyl alcohol.

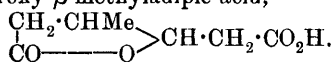
The acid  $C_7H_8O_4$  is definitely proved to be  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid,  $\begin{array}{c} \text{CH}:\text{CMe} \\ \text{CO} \text{---} \text{O} \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , by the following evidence.

The lactonic character is shown by titration, the acid  $C_7H_8O_4$  reacting as monobasic or dibasic according as it is rapidly titrated or kept for some time with an excess of sodium hydroxide. The *silver* salt,  $C_7H_7O_4\text{Ag}$ , and ethyl iodide yield the *ethyl* ester,  $C_9H_{12}O_4$ , b. p.  $183\text{--}185^\circ/13$  mm.,  $D_4^{20}$  1.153, which can also be obtained by boiling the acid  $C_7H_8O_4$  with 0.5% alcoholic hydrogen chloride for not more than two hours; the *methyl* ester,  $C_8H_{10}O_4$ , has m. p.  $36\text{--}37^\circ$ , and b. p.  $180^\circ/13$  mm. The dibasic acid  $C_7H_{10}O_5$  obtained by the rupture of the lactone ring in  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid has not been isolated; its *silver* salt,  $C_7H_8O_5\text{Ag}_2$ , prepared by keeping the lactonic acid in an excess of alkali, neutralising, and adding silver nitrate, reacts with methyl and ethyl iodides to form the *methyl* ester,  $C_9H_{14}O_5$ , b. p.  $146\text{--}148^\circ/12$  mm.,  $D_4^{20}$  1.145, and *ethyl* ester,  $C_{11}H_{18}O_5$ , b. p.  $152\text{--}154^\circ/10$  mm.,  $D_4^{20}$  1.077 respectively. These esters are more conveniently obtained by boiling methyl or ethyl methylcrotonolactone-acetate with 10% methyl- or ethyl-alcoholic hydrogen chloride.

During esterification with alcohol and concentrated sulphuric acid or by warming with aqueous alkalis or mineral acids,  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid combines with water and loses carbon dioxide, thereby yielding  $\beta$ -methyl-lævulic acid. The constitution of the  $\beta$ -methyl-lævulic acid is proved by the formation of bromoform and

methylsuccinic acid by treatment with alkaline potassium hypobromite and by direct comparison with synthetic  $\beta$ -methyl-lævulic acid (m. p.  $31.5^\circ$ , not  $-12^\circ$  as stated in the literature). It forms a *phenylhydrazone*, m. p.  $125^\circ$ , colourless leaflets, *nitrophenylhydrazone*, m. p.  $168-169^\circ$ , golden-yellow needles, *semicarbazone*, m. p.  $178-179^\circ$  (Blaise gives  $197^\circ$ ), *ethyl ester*, b. p.  $206^\circ$ ,  $D_4^{20}$  0.989, and *methyl ester*, b. p.  $199.7-200.2^\circ$  or  $82-83^\circ/10$  mm.,  $D_4^{20}$  1.022,  $D_4^{25}$  0.9786,  $n_D^{25}$  1.40518 (*phenylhydrazone*, m. p.  $88^\circ$ , colourless, rhombic crystals, *p-nitrophenylhydrazone*, m. p.  $147^\circ$ , golden-yellow prisms), and yields by distillation a mixture of two isomeric *methylangelicolactones*, b. p.  $87-89^\circ/13$  mm., m. p.  $-12^\circ$ ,  $D_4^{20}$  1.0563,  $n_D^{20}$  1.45452, and b. p.  $114-115^\circ/13$  mm.,  $D_4^{20}$  1.0613,  $n_D^{20}$  1.46439 respectively.

The dibasic acid produced in the form of its sodium salt by the rupture of the lactone ring in  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid by an excess of sodium hydroxide contains an unbranched chain of carbon atoms (excepting that of the methyl group). This is proved by reducing  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid in the presence of an excess of alkali with sodium amalgam, whereby  *$\beta$ -methyl dihydromuconic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $140^\circ$  (the position of the double linking has not been established), is obtained, which in its turn is reduced by hydrogen (1.5 atmos.) and colloidal palladium to  $\beta$ -methyladipic acid. The reduction of sodium  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetate in neutral aqueous solution by sodium amalgam in an atmosphere of carbon dioxide leads to the formation of the *lactone*, m. p.  $72^\circ$ , of  $\gamma$ -hydroxy- $\beta$ -methyladipic acid,



The production of  $\beta$ -methyl dihydromuconic acid from  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid is quite parallel to that of  $\beta\gamma$ -diphenyl dihydromuconic acid from  $\beta\gamma$ -diphenyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid (Beschke, A., 1912, i, 889), and gives the clue to the constitution of the acid  $\text{C}_7\text{H}_8\text{O}_4$ . For the complete proof of the constitution, however, the following three facts are necessary. The position of the double linking is proved as follows. By oxidation with potassium permanganate and aqueous sodium carbonate in an atmosphere of carbon dioxide,  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid yields oxalic acid and  $\beta$ -hydroxylævulic acid; the latter has not been isolated as such, but its presence is proved by the isolation, in the form of the osazone, of its product of decomposition, diacetyl. Confirmatory proof is obtained by treating methyl  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetate with 10% ozone in chloroform and decomposing the viscous *ozonide* with warm water, whereby hydrogen peroxide, oxalic acid, and methyl  $\beta$ -hydroxylævulate are formed; the last substance has been detected by means of phenylhydrazine, with which it reacts to form the *phenylhydrazone*, m. p.  $210-211^\circ$  (corr.), colourless leaflets, of 3-acetyl-1-phenyl-5-pyrazolone,

$\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{C} \begin{array}{c} \text{N} \text{---} \text{NPh} \\ \text{CH}_2 \cdot \text{CO} \end{array}$ . The same phenylhydrazone, which

exhibits all the reactions typical of pyrazolones, is obtained by heating methyl  $\beta$ -bromolævulate with aqueous methyl alcohol and magnesium carbonate at  $70^\circ$  and treating the resulting syrup of methyl  $\beta$ -hydroxylævulate with phenylhydrazine and 50% acetic acid.

The proof that  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid is a  $\gamma$ -lactone with the double linking in the  $\alpha\beta$ -position follows, in accordance with Thiele's researches on unsaturated lactones, from the facts that the lactic acid reduces ammoniacal silver oxide and Fehling's solution, develops a yellow coloration with alcoholic potassium hydroxide, does not react additively with bromine, and condenses with benzaldehyde in the presence of a few drops of piperidine, but not of aniline, to form *ad*-dibenzylidene- $\beta$ -methylangelicolactone,  $\text{CHPh}:\text{CH}\cdot\text{C}\begin{smallmatrix} \text{CMe}\cdot\text{C}:\text{CHPh} \\ \text{O} \cdots \text{CO} \end{smallmatrix}$ ,

m. p.  $130^\circ$ , orange-red needles, carbon dioxide being evolved and the double linking shifting from the  $\alpha\beta$ - to the  $\beta\gamma$ -position, which is characteristic of  $\alpha\beta$ -unsaturated lactones during their condensation with benzaldehyde in the presence of piperidine.

The course of the reaction whereby 3-nitro-*p*-cresol is converted into  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid has been studied quantitatively so far as the volatile products of the decomposition are concerned. Carbon dioxide and sulphur dioxide are produced only in traces (compare Schultz and Löw, *loc. cit.*); also, ammonia is not a primary product of the decomposition, but hydroxylamine is formed in appreciable quantities. The function of the sulphuric acid is merely hydrolytic. 3-Nitro-*p*-cresol, reacting in the isomeric form of the nitronic acid, undergoes fissive hydrolysis yielding ultimately the hydroxamic acid,  $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{CMe}:\text{CH}\cdot\text{C}(\text{OH})\cdot\text{NOH}$ ; the latter is hydrolysed to hydroxylamine and  $\beta$ -methylmuconic acid which lactonises to  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid.

The authors have obtained in larger quantity the nitrogenous acid by-product formed during the decomposition of 3-nitro-*p*-cresol by concentrated sulphuric acid (Schultz and Löw, *loc. cit.*). It has the formula  $\text{C}_7\text{H}_7\text{O}_3\text{N}$ , m. p.  $207^\circ$  (decomp.), forms a *methyl* ester, m. p.  $114^\circ$ , b. p. about  $150^\circ/12$  mm., colourless leaflets, does not exhibit reducing properties, gives precipitates with metallic salt solutions, and develops a yellowish-red coloration with alcoholic ferric chloride. Most probably it is 2-hydroxy-4-methylpyridine-6-carboxylic acid, produced from the hypothetical hydroxamic acid (see above) by loss of water and ring closure. C. S.

**Cholic Acid. IV. Rearrangement in the Oximes of Derivatives of Cholic Acid.** MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1914, 89, 360—366. Compare A., 1913, i, 1042).—When the trioxime of dehydrocholic acid is heated for fifteen to twenty minutes on a steam-bath with 90% sulphuric acid, rearrangement occurs. The *isotrioxime*,  $\text{C}_{24}\text{H}_{37}\text{O}_5\text{N}_3$ , is a colourless, crystalline substance, which on heating becomes brown at about  $187^\circ$  and decomposes at about  $210^\circ$ . When its solution in hydrochloric acid is boiled for some time, it remains clear, whilst a similar solution of the original trioxime deposits a precipitate of dehydrochloric acid.

The dioxime of bilianic acid undergoes rearrangement when treated with sulphuric acid in the manner described. The *isodioxime*  $\text{C}_{24}\text{H}_{36}\text{O}_8\text{N}_2$ , crystallises in needles, which become brown at about  $250^\circ$  and decompose at about  $258^\circ$ . Its solution in hydrochloric acid remains clear on boiling, whilst that of the original dioxime does not. R. V. S.

**Formaldehyde. IV. The Vapours of Formaldehyde and its Polymerides.** FRIEDRICH AUERBACH and WERNER PLÜDDERMANN (*Arb. Kais. Gesund. Amt.*, 1914, **47**, 116—132. Compare *ibid.*, 1909, **30**, 195; A., 1905, i, 859; 1908, i, 131).—Pure anhydrous formaldehyde vapour, diluted only with nitrogen, can be obtained by the vaporisation of  $\alpha$ -polyoxymethylene in a current of warm nitrogen, the vapours being first heated to 220—230° in order to depolymerise them, and then cooled to -25° to -30° in order to bring about the deposition of any residual polymeride. Formaldehyde vapour prepared in this way shows no appreciable tendency to polymerise at temperatures up to 100°. This result made it possible to investigate the vapours obtained from polyoxymethylenes at temperatures up to 100°; the vapours were first cooled to -25° to -30° in order to condense the polymerides, and then passed through water to dissolve the formaldehyde; the quantities of the polymerides and of formaldehyde were then determined by analysis.

$\alpha$ -Polyoxymethylene, when vaporised in a current of dry air at 40—100°, gives only vapours of polyoxymethylene; the same is true for  $\beta$ -polyoxymethylene at 40—60°, except that the vapours change partly into the more stable  $\alpha$ -polymeride. In neither case is any appreciable quantity of simple formaldehyde contained in the vapours.

Water and aqueous vapour cause depolymerisation of the polyoxymethylenes and their vapours, but the process is slow and incomplete.

These results are of importance in connexion with the use of the solid polymerides of formaldehyde for disinfecting purposes, since only the unimolecular formaldehyde is a disinfectant. Larger quantities of the solids must be used in the presence of water than of aqueous formaldehyde solution.

In the iodometric estimation of solutions of formaldehyde, iodine and alkali should not be mixed before the addition of formaldehyde, otherwise the iodate formed will not oxidise the formaldehyde. In the estimation in alkaline solutions, the solution should be neutralised before the addition of iodine, and only then made alkaline once more. The excess of iodine should be at least 50% of the iodine used up in the oxidation.

T. S. P.

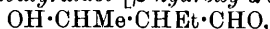
**Preparation of Acetaldehyde and its Condensation and Polymerisation Products from Acetylene.** NATHAN GRÜNSTEIN (D.R.-P. 270049).—Acetylene is led into a mixture of mercuric oxide and 25% sulphuric acid at 40—45°, and the acetaldehyde which is formed is immediately distilled off at 30°/400 mm. The last fractions, consisting of crotonaldehyde and paracetaldehyde, are distilled at 40°/10—15 mm.

J. C. C.

**Some Organic Preparations.** L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1914, **36**, 530—537).—Aldols are best prepared by means of Grignard and Abelmann's method, which consists in treating an ethereal solution of the aldehyde with alkali hydroxide. Condensation can be effected in this way even in the case of aldehydes which are very sensitive towards alkali hydroxide.

Aldols and ketonic alcohols can be converted into the corresponding dihydroxy-compounds by electrolytic reduction in sulphuric acid

solution, preferably with a lead cathode. Aldols are also easily reduced to the glycols by Zelinski and Ujedinov's method (A., 1912, i, 16). *Acetbutyraldol* [ $\beta$ -hydroxy- $\alpha$ -ethylbutaldehyde],



has b. p. 102—104°/20 mm.

Pinacone can be prepared by reducing acetone with calcium amalgam.

Crotonaldehyde can be readily prepared by heating acetaldoal in presence of powdered aluminium phosphate; the yield amounts to about 60% of the theoretical.

Ethylideneacetone can be prepared by heating hydracetylacetone (pentan- $\delta$ -ol- $\beta$ -one) with a few drops of concentrated sulphuric acid. Mesityl oxide can be obtained in a similar manner from diacetone alcohol [isohexan- $\delta$ -ol- $\beta$ -one].

E. G.

The Catalysts of Acids. A. MAILHE (*Bull. Soc. chim.*, 1914, [iv], 15, 321—324).—Polemical. A reply to Senderens (compare this vol., i, 251).

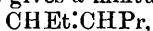
W. G.

Some Applications of Catalytic Methods. A. MAILHE (*Bull. Soc. chim.*, 1914, [iv], 15, 327—329).—Methods of utilising ketones prepared by catalysis of acids by means of the oxides of cadmium, iron, or manganese (compare A., 1913, i, 700, and this vol., i, 548) by catalytic means employing finely divided nickel and metallic oxides.

Propionone passed over divided nickel at 140—150° yields diethylcarbinol,  $\text{CHEt}_2\cdot\text{OH}$ , b. p. 116°, which when passed with ammonia over thorium oxide at 350—380° yields diethylcarbinylamine [ $\gamma$ -aminopentane],  $\text{CHEt}_2\cdot\text{NH}_2$ , b. p. 90°. With hydrogen sulphide in the presence of thorium oxide it gives the *mercaptan*,  $\text{CHEt}_2\cdot\text{SH}$ , b. p. 105°.

Propiononeoxime, b. p. 165°, when passed with hydrogen over finely divided nickel yields  $\gamma$ -aminopentane, b. p. 90—91°, and the secondary *amine*,  $\text{NH}(\text{CHEt}_2)_2$ , b. p. 170°, giving a *phenylurethane*, m. p. 177°.

Direct hydrogenation of butyryl in the presence of finely divided nickel at 150° gives dipropylcarbinol,  $\text{CHPr}_2\cdot\text{OH}$ , b. p. 152—154°. In the presence of thorium oxide at 350° with ammonia this alcohol gives dipropylcarbinylamine, b. p. 140°, whilst with hydrogen sulphide under the same conditions it gives a mixture of  $\Delta^7$ -heptene,



b. p. 97—98°, *dipropylcarbinyl mercaptan*,  $\text{CHPr}_2\cdot\text{SH}$ , b. p. 135—138°, which yields a white precipitate with mercuric chloride, and a small quantity of a *sulphide*,  $(\text{CHPr}_2)_2\cdot\text{S}$ , b. p. 210°. Butyroxime, b. p. 195°, on hydrogenation by means of finely divided nickel at 200°, gives a mixture of dipropylcarbinylamine, b. p. 140°, and the secondary *amine*,  $\text{NH}(\text{CHPr}_2)_2$ , b. p. 230°.

*iso*Butyryl by a similar series of reactions has given the following compounds: *diisopropylcarbinol*,  $\text{CHPr}_2^\beta\cdot\text{OH}$ , b. p. 130—133°;  $\alpha\delta$ -dimethyl- $\Delta^\beta$ -pentene, b. p. 82—84°; *diisopropylcarbinyl mercaptan*,  $\text{CHPr}_2^\beta\cdot\text{SH}$ , b. p. 110—113°; *diisopropylcarbinylamine*,  $\text{CHPr}_2^\beta\cdot\text{NH}_2$ , b. p. 125°, and the secondary *amine*,  $\text{NH}(\text{CHPr}_2^\beta)_2$ , b. p. 210—213°.

*iso*Valerone yields the following derivatives: diisobutylcarbinol,  $\text{CH}(\text{CH}_2\cdot\text{CHMe}_2)_2\cdot\text{OH}$ , b. p. 173—175°;  $\beta\zeta$ -dimethyl- $\Delta^7$ -heptene, b. p. 132—134°; diisobutylcarbinyl mercaptan,  $\text{CH}(\text{CH}\cdot\text{CHMe}_2)_2\cdot\text{SH}$ , b. p. 155—158°, giving a yellow precipitate with mercury salts; diisobutylmethylamine, b. p. 164—166°, and the secondary amine,  $\text{NH}[\text{CH}(\text{CH}_2\cdot\text{CHMe}_2)_2]_2$ , b. p. 248—251°, giving a phenylurethane, m. p. 183°.

W. G.

**Dissociation Processes in the Sugar Group. III.** J. U. NEF (*Annalen*, 1914, 403, 204—383. Compare A., 1908, i, 5; 1910, i, 711).—A complete and very simple explanation can now be given of the behaviour of any carbohydrate in aqueous alkali hydroxides towards oxidising agents such as air, hydrogen peroxide, or the oxides of mercury, silver, and copper. The necessary preliminary work on the behaviour of carbohydrates in aqueous alkali hydroxides in the absence of an oxidising agent (*loc. cit.*) has yielded as its most important result the proof that in weak alkaline solution any carbohydrate exists eventually as an equilibrium mixture of, theoretically, 116, actually, only 93 different substances (see below). The equilibrium is disturbed, in the absence of an oxidising agent, by the conversion of the different sugars into  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$ , and  $\text{C}_6$  saccharinic acids; in the presence of air or other oxidising agents, the oxidation of the 47 sugars present results in the formation of carbon dioxide, formic, glycollic, oxalic, and *dl*-glyceric acids, four trihydroxybutyric acids, eight tetrahydroxyvaleric acids, and eight pentahydroxyhexoic acids, the separation and quantitative isolation of which has occupied the author during the last nine years. Some errors in the previous researches have been corrected.

I. *Fission of hexoses in all three theoretically possible directions.*—By the spontaneous decomposition of the  $\alpha\beta$ -,  $\beta\gamma$ -, and  $\gamma\delta$ -dienols produced in alkaline solution, any hexose may yield (a) formaldehyde and aldopentoses, (b) diose and aldotetroses, (c) *dl*-glyceraldehyde. Examples of (b) and (c) have been recorded (*loc. cit.*), but the author has repeatedly been unable to verify (a) experimentally. It has now been shown that this decomposition actually occurs to a considerable extent. The oxidation of dextrose and of *d*-galactose in weak alkaline solution by air, hydrogen peroxide, or Fehling's solution yields *d*-arabonic acid and *d*-lyxonic acid respectively. These two acids, which have erroneously been described as  $\alpha$ -hydroxymethyl-*d*-arabonic acid and  $\alpha$ -hydroxymethyl-*d*-lyxonic acid (Spoehr, A., 1910, i, 221; Nef and Lucas, *ibid.*, i, 711), are evidently produced by the oxidation of *d*-arabinose and *d*-lyxose resulting from the dissociation of dextrose- $\alpha\beta$ -dienol and *d*-galactose- $\alpha\beta$ -dienol.

A 1% aqueous solution of *d*-galactose containing sodium hydroxide (6 equiv.) is oxidised for forty-eight hours at 30—40° by a rapid current of purified air, and the completely colourless solution yields thereby 1.27 grams of carbon dioxide, 12.81 of formic acid, and 40.95 of non-volatile hydroxy-acids (from 50 grams of the sugar). The isolation and separation of the individual acids was only possible after a thorough study had been made of all obtainable, optically active hexonic, pentonic, and tetronic acids,  $\text{C}_n\text{H}_{2n+1}\text{O}_{n+1}$ . The conditions of lactone formation have been especially studied, and have led to the

remarkable result that hydroxy-acids,  $C_nH_{2n+1}O_{n+1}$ , can yield quite generally bimolecular  $\alpha$ -lactones and unimolecular  $\beta$ - and  $\gamma$ -lactones. With the information thus gained, the author has been able to ascertain that the mixture of non-volatile acids obtained by the oxidation of *d*-galactose contains only glycollic acid, traces of oxalic acid, *d*- and *l*-glyceric acids, *l*-threono- $\gamma$ -(and  $\beta$ l)-lactone, *d*-erythrono- $\gamma$ -lactone, *d*-lyxono- $\gamma$ -lactone, a little *l*-xylono- $\gamma$ -lactone, and a resin. (The formation of this resin in varying amounts during oxidation explains why the different sugars of the *d*-glucose and *d*-galactose series do not give exactly the same results by titration with Fehling's solution.)

*d*-Lyxono- $\gamma$ -lactone when quite pure has m. p. 113—114° and  $[\alpha]_D^{20} + 82.4^\circ$  in 4% aqueous solution. It is most conveniently isolated as the phenylhydrazide, which forms a crystalline *quinine* salt, m. p. 169°,  $[\alpha]_D^{20} - 109.8^\circ$ , and yields by oxidation with nitric acid, D 1.21, the same *d*- $\alpha\beta\gamma$ -trihydroxyglutaric acid, m. p. 128°,  $[\alpha]_D^{20} + 22.8^\circ$ , as does *d*-arabonic acid.

The physical constants of *l*-xylono- $\gamma$ -lactone and of its derivatives given in the literature are frequently incorrect. The oxidation of *l*-xylose by aqueous bromine yields a mixture probably of  $\beta$ - and  $\gamma$ -lactones of *l*-xylonic acid, from which only the latter has been isolated in a pure state. *l*-Xylono- $\gamma$ -lactone has m. p. 99—103°,  $[\alpha]_D^{20} + 89.56^\circ$  (all specific rotations in the paper are calculated from the rotations in 4% aqueous solution unless otherwise stated), and forms a cinchonine salt, m. p. 170°,  $[\alpha]_D^{20} + 126.2^\circ$ , and brucine salt, m. p. 176° (anhydrous),  $[\alpha]_D^{20} - 18.7^\circ$ .

Glycollic acid can be completely removed from a mixture of non-volatile hydroxy-acids by evaporating a concentrated aqueous solution of the mixture to dryness on the water-bath.

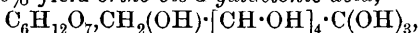
*l*-Threonolactone yields *strychnine l-threonate*, m. p. 115—120°,  $[\alpha]_D^{20} - 28.5^\circ$ , and the corresponding *quinine* salt, m. p. 168°,  $[\alpha]_D^{20} - 116.99^\circ$ , and *brucine* salt, m. p. 214°,  $[\alpha]_D^{20} - 32.4^\circ$ ; the last is by far the most suitable alkaloid salt for the isolation of *l*-threonolactone.

The reaction between *l*-xylose and 10% hydrogen cyanide in the presence of a few drops of 30% ammonia yields *l*-gulonic acid and a little *l*-idonic acid; the original paper must be consulted for details of the separation of the former as *l*-gulono- $\gamma$ -lactone and of the latter as brucine idonate.

*l*-Gulonic acid forms a *brucine* salt, m. p. 162—164°,  $[\alpha]_D^{20} - 18.67^\circ$ , flattened needles, *quinine* salt, m. p. 155°,  $[\alpha]_D^{20} - 94.4^\circ$ , *strychnine*, decomp. 120—125°,  $[\alpha]_D^{20} - 17.24^\circ$ , and *cinchonine* salt, which is a syrup.

*l*-Idonic acid forms a *quinine* salt, m. p. 158°,  $[\alpha]_D^{20} - 103.1^\circ$ , *strychnine* salt, decomp. 120—125°,  $[\alpha]_D^{20} - 26^\circ$ , and unstable *phenylhydrazide*, m. p. 100—110°,  $[\alpha]_D^{20} - 12.42^\circ$ .

When a very dilute aqueous solution of calcium *d*-galactonate is shaken at 50° with the calculated amount of oxalic acid, rapidly cooled and filtered, and the filtrate is rapidly evaporated under 20 mm. pressure, or when the cadmium salt, suspended in cold water, is treated with hydrogen sulphide and the filtrate is similarly evaporated, there is produced in 50% yield *ortho-bis-d-galactonic acid*,



m. p. 140—142°,  $[\alpha]_D^{20} - 11.69^\circ$ , clusters of transparent needles. The



ortho-acid in the solid state is bimolecular and very stable, and does not lose a trace of water by keeping over sulphuric acid in a vacuum; in aqueous solution it is unimolecular. By heating the ortho-acid at its m. p. and under 20 mm. pressure, it loses water very rapidly, but immediately, by intramolecular addition, there is produced from the primarily formed, unimolecular *d*-galactonic acid an equilibrium mixture of *d*-galactono- $\gamma$ -lactone hydrate, *d*-galactono- $\gamma$ -lactone, and *d*-galactonic acid. Exactly the same changes occur to the extent of 70% when a cold 4% aqueous solution of the ortho-acid is kept for three weeks; the change is more rapid and more complete when the solution is heated at 100°. The solution finally contains at 20° about 70% of *d*-galactono- $\gamma$ -lactone hydrate, about 29% of *d*-galactonic acid, and a little *d*-galactono- $\gamma$ -lactone; by evaporating the water completely under 15 mm. pressure and heating the resulting syrup for a long time at 100°/15 mm., the solid residue consists entirely of *d*-galactono- $\gamma$ -lactone. Crystals of *d*-galactono- $\gamma$ -lactone hydrate change smoothly to the  $\gamma$ -lactone by keeping for two days over sulphuric acid in a vacuum; conversely, the  $\gamma$ -lactone changes to the  $\gamma$ -lactone hydrate by keeping in a powdered state for two days in a closed vessel containing water.

*d*-Galactonic acid forms a *brucine* salt, m. p. 141—143°,  $[\alpha]_D^{20} - 23.39^\circ$ , *cinchonine* salt, a syrup, and a very sparingly soluble *quinine* salt, m. p. 160°,  $[\alpha]_D^{20} - 98.7^\circ$ .

Anderson's experiments on the oxidation of *d*-galactose in weak alkaline solution by Fehling's solution (A., 1909, i, 881) have been repeated with substantially the same results. A larger amount of *d*-talonic acid has been found, the absence of *l*-gulonic and *l*-idonic acids has been proved with a considerable degree of certainty, and Anderson's  $\alpha$ -hydroxymethyl-*d*-arabonic acid and  $\alpha$ -hydroxymethyl-*d*-lyxonic acid are shown to be *d*-arabonic acid and *d*-lyxonic acid respectively.

Spoehr's experiments (*loc. cit.*) on the oxidation of *d*-galactose by 3% hydrogen peroxide in alkaline solution are somewhat superficial and therefore have been repeated by the author with great thoroughness. It has been found that a much more concentrated solution of hydrogen peroxide can be used without causing an alteration in the relative quantities of the oxidation products, and that a larger amount of non-volatile hydroxy-acids is produced when the sodium hydroxide is added gradually. In addition to a large quantity of formic acid and traces of oxalic acid, the author has identified glycollic, *dl*-glyceric, *l*-threonic, *d*-erythronic, *d*-lyxonic, *l*-xylonic, *d*-galactonic, and *d*-talonic acids; the quantity of the C<sub>5</sub>-acids is very much less than that obtained when air is the oxidising agent, but, in contrast to the results of oxidation with Fehling's solution, still exceeds the amount of the C<sub>6</sub>-acids produced.

The oxidation of *l*-xylose or *l*-arabinose by 3% hydrogen peroxide in aqueous sodium hydroxide yields an amount of formic acid which shows that under the conditions of the experiment about 80% of the sugar has dissociated to hydroxymethylene. The non-volatile hydroxy-acids, about 23% in amount, consist most probably of *d*-lyxonic, *l*-xylonic, *l*-threonic, *dl*-glyceric, and glycollic acids, together with traces of *d*-erythronic and oxalic acids; in accordance with expectation,

*l*-erythronic acid (and *l*-glyceric acid) has been isolated from the mixture of hydroxy-acids obtained by the oxidation of *l*-arabinose.

*d*-Gluconic acid forms a calcium salt, voluminous anhydrous crystals,  $[\alpha]_D^{20} + 10.5^\circ$ , *cinchonine* salt, m. p.  $189^\circ$ ,  $[\alpha]_D^{20} + 124.6^\circ$ , plates (by far the most suitable derivative for the isolation of *d*-gluconic acid), *brucine* salt, m. p.  $120-125^\circ$  ( $150-155^\circ$ , anhydrous),  $[\alpha]_D^{20} - 18.76^\circ$ , *quinine* salt, m. p.  $140^\circ$ ,  $[\alpha]_D^{20} - 94.6^\circ$ , and *strychnine* salt, decomp.  $110-130^\circ$ ,  $[\alpha]_D^{20} - 14.38^\circ$ . *d*-Mannonic acid forms a calcium salt, flattened needles containing  $2H_2O$ ,  $[\alpha]_D^{20} - 7.52^\circ$ , a *quinine* salt, m. p.  $165^\circ$ ,  $[\alpha]_D^{20} - 102^\circ$ , but is best isolated as the *brucine* salt, m. p.  $212^\circ$ ,  $[\alpha]_D^{20} - 26.73^\circ$ .

II. *Limited Equilibrium of Tetroses, Pentoses, or Hexoses.*—When the amount of sodium hydroxide or other alkaline hydroxide in a sugar solution is diminished from more than one equiv. to 0.5 equiv., the number of substances in the system, after equilibrium has been attained, is very much smaller; for example, dextrose or *d*-galactose yields only a mixture of the six isomeric active sugars of the corresponding series, *l*-arabinose or *l*-xylose yields the corresponding three active pentoses, and *d*- or *l*-erythrose yields *d*-erythrose, *l*-threose, and *d*- $\beta$ -ketotetrose, or the three antipodes respectively. The various hexose-, pentose-, and tetrose-dienols do not decompose under these conditions into lower aldoses according to fission (a) above.

The study of the limited equilibrium existing under such conditions shows that (i) the relative quantities of the sugars present are strikingly different after equilibrium has been established, (ii) ketoses are enolised only in quite definite directions, that is, only certain preferred olefinedienols are formed, not all those theoretically possible. Thus a 30% aqueous solution of dextrose, *d*-mannose, or *d*-fructose, in the presence of calcium hydroxide (1/20 equiv.), at  $15-20^\circ$ , attains equilibrium after three months and then contains, in addition to sugar-resin and appreciable quantities of polysaccharides, dextrose, *d*-mannose, *d*-fructose, *d*- $\psi$ -fructose, and  $\alpha$ - and  $\beta$ -*d*-glucose; the presence of these sugars and the absence of *d*-allose, *d*-latose, and other aldo- and keto-hexoses prove that the only dienols existing in the solution are  $\alpha$ -*d*-glucose- $\alpha\beta$ -dienol and *d*-glucose- $\beta\gamma$ -dienol. (A mixture of aldoses and ketoses can be sharply separated by keeping a cold 12% aqueous solution for seven days with bromine, whereby the aldoses are oxidised to the corresponding aldonic acids whilst the ketoses are scarcely affected.) The application of this method to the preceding mixture of sugars obtained from dextrose, *d*-mannose, or *d*-fructose and 1/20 equiv. of calcium hydroxide shows that aldoses and ketoses are formed in approximately equal quantities; the aldoses consist of dextrose and *d*-mannose in the ratio 5 : 1.

Quite similar results have been obtained with *d*-galactose in the presence of a little alkali hydroxide. Only the six sugars of the *d*-galactose series are formed, showing that the solution contains only two olefinedienols,  $\alpha$ -*d*-galactose- $\alpha\beta$ -dienol and *d*-galactose- $\beta\gamma$ -dienol; over 90% of the aldoses present consists of *d*-galactose. Similarly, *l*-arabinose yields an equilibrium mixture of *l*-arabinose, *l*-ribose, and *l*-erythro- $\beta$ -ketopentose (hence the only dienol is *l*-arabinose- $\alpha\beta$ -dienol), whilst *l*-xylose yields *l*-xylose, *d*-lyxose, and *l*-threo- $\beta$ -ketopentose. The tetroses being difficultly obtained, the proof of the preceding statement

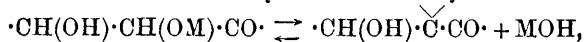
has in this case been obtained as follows. In the presence of an excess of sodium hydroxide, *l*-arabinose (in the form of its  $\alpha\beta$ -dienol) decomposes into hydroxymethylene and *l*-erythrosemethylene-enol; the latter is immediately converted into a mixture of the three active sugars of the *l*-erythrose series. Similarly, dextrose and *d*-galactose (in the form of their  $\beta\gamma$ -dienols) decompose into diose and *d*-erythrose or *l*-threose; each of the latter at once changes to one and the same mixture of the three sugars of the *d*-erythrose series. The fact that only the three, not the six possible, tetroses are formed is established by an examination of the products of oxidation of *l*-arabinose by air, hydrogen peroxide, copper oxide, or mercuric oxide in the presence of an excess of sodium hydroxide; these products contain only two active trihydroxybutyric acids, namely, *l*-erythronic and *d*-threonic acids. Similarly, the oxidation of dextrose by air in weak alkaline solution at 20—40° yields, amongst other products, only two active trihydroxybutyric acids (*d*-erythronic and *l*-threonic acids). However, when dextrose, *d*-mannose, or *d*-fructose is oxidised by copper oxide or mercuric oxide in the presence of an excess of alkali, the products contain, in addition to those formed by atmospheric oxidation, two active hexonic acids (*d*-gluconic and *d*-mannonic acids). These facts prove that (i) in spite of the presence of an excess of alkali, only the six sugars of the dextrose series are present in the solution, (ii) that not one of these sugars is oxidised by air or hydrogen peroxide (air can be passed for seventy-one hours through a solution of dextrose or *d*-fructose containing one-sixth equiv. of barium hydroxide without any appreciable oxidation occurring), (iii) that only three of the six sugars are oxidised by copper oxide and an excess of alkali, namely, dextrose, *d*-mannose, and *d*-fructose; these yield the same  $\alpha\beta$ -*d*-glucosone, which then partly changes to *d*-gluconic and *d*-mannonic acids by a "benzilic acid transformation," and partly enolises to the  $\beta\gamma$ -dienol, which then decomposes into *d*-erythrose and glyoxal.

Quite similar results are obtained by the oxidation of *d*-galactose by air at 30—40° in the presence of sodium hydroxide (6 equiv.). Only traces of hexonic acids are produced (see above), so that none of the six sugars of the *d*-galactose series are oxidised as such; the substances actually obtained are those formed by the oxidation of the fission products of  $\alpha$ -*d*-galactose- $\alpha\beta$ -dienol, *d*-galactose- $\beta\gamma$ -dienol, and *d*-galactose- $\gamma\delta$ -dienol. When hydrogen peroxide or copper oxide is employed as the oxidising agent, the products, although formed in quite different proportions in each case, are the same as those obtained by atmospheric oxidation, but in addition two hexonic acids (*d*-galactonic and *d*-talonic acids, the transformation products of ( $\alpha$ )- $\alpha\beta$ -*d*-galactosone) are formed.

III. *Conversion of Pentoses and Hexoses into the corresponding Sugar-resins and Polysaccharides.*—The study of the limited equilibrium described under II is rendered difficult by two disturbing factors, namely, the formation of resins and of polysaccharides.

The resins which are produced when a solution of a sugar is kept or warmed with the hydroxide of sodium, potassium, barium, calcium, or lead (1/30—1/6 equiv.) cannot be diose resins as previously suggested because pentoses and hexoses, as has just been shown, do not decom-

pose into smaller molecules in the presence of a little metallic hydroxide. The author now is of opinion that each individual sugar, by salt-formation and the thereby increased methylene dissociation,



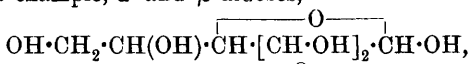
is unavoidably and irreversibly transformed partly into a mixture of methylene polymerides,  $[\cdot\text{CH}(\text{OH})\cdot\overset{\vee}{\text{C}}\cdot\text{CO}\cdot]_x$ . If this is the explanation, resin formation should diminish as the concentration of the metallic hydroxide diminishes. This is actually the case, but when the quantity of the hydroxide (best, calcium hydroxide) falls below 1/30 equiv., enolisation of the sugar no longer occurs and the sugar (dextrose, *d*-mannose, *d*-fructose, etc.) can be kept unchanged in solution for a month. When the conditions are such that enolisation can occur without simultaneous salt-formation, no trace of resin is formed (saccharinic acids, the formation of which also depends on salt-formation, are also not formed).

The mutual interconversion of the individual sugars of a definite pentose or hexose series is effected best by simply keeping for a long time at the ordinary temperature a concentrated aqueous solution of the sugar containing  $\frac{1}{2}$ —2 equiv. of sodium carbonate. In the presence of 2 equiv., there is neither the slightest decomposition of the existent dienols nor any trace of saccharinic acids formed, but only a very small amount of resin; the formation of this is completely prevented when only  $\frac{1}{2}$  equiv. of sodium carbonate is present. Concentrated solutions of individual pentoses or hexoses containing 3 equiv. of potassium hydrogen carbonate can be kept in closed vessels for two months at the ordinary temperature without undergoing the slightest change, in particular, without the formation of polysaccharides.

Polysaccharides synthesised from pentoses and hexoses belong to two classes, those which are hydrolysed only with difficulty, and those which are easily hydrolysed to simple sugars by weak acids or by a little hydrochloric acid. Disaccharides of both classes are formed when the solution of a sugar is treated with sodium carbonate or a little metallic hydroxide. Moreover, the disaccharides produced from dextrose by a little calcium hydroxide are quite different, according to the optical behaviour of their products of hydrolysis, from those formed from dextrose by sodium carbonate. In both reactions  $\alpha$ -bishexoses,  $\text{C}_{12}\text{H}_{24}\text{O}_{21}$ , are formed, but only in the presence of the metallic hydroxide are these, by salt-formation and subsequent loss of metallic hydroxide (1 or 2 mols.), converted into anhydro- $\alpha$ -bishexoses (disaccharides),  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , or bisanhydro- $\alpha$ -bishexoses,  $\text{C}_{12}\text{H}_{20}\text{O}_{10}$ .

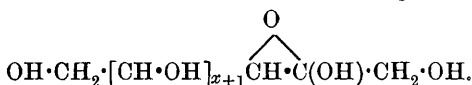
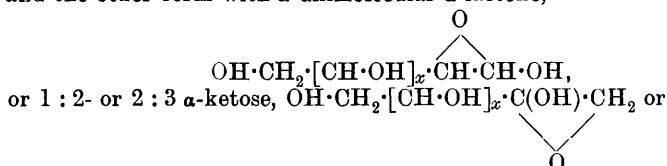
The discovery of the conditions under which any individual pentose or hexose or suitably selected mixture can be converted (i) by polymerisation into only the corresponding  $\alpha$ -bise (C<sub>n</sub>H<sub>2n</sub>O<sub>n</sub>)<sub>2</sub>, and (ii) by condensation into only the corresponding polysaccharide is very important. The first object is attained simply by keeping a concentrated aqueous solution of the sugar at the ordinary temperature in the presence of 1—3 equiv. of calcium acetate. The formation of the  $\alpha$ -bise is very slow and amounts to 25% after two months, but occurs more rapidly at 40—60°. The most favourable conditions have

only recently been discovered, and the author has not had time to isolate the individual polysaccharides as such; he has proved, however, that disaccharides like maltose and lactose, which are difficultly hydrolysed, are not formed. The author's speculations as to the constitutions of the  $\alpha$ -bis-oses, therefore, need not be recorded at present. One point in connexion with the constitution of simple sugars, however, requires mention. It is well known that each simple sugar occurs in two optically and crystallographically totally different forms which are mutually interconvertible in solution. These two forms are almost universally regarded as  $\alpha$ - and  $\beta$ -stereoisomeric modifications of a  $\gamma$ -lactone, for example,  $\alpha$ - and  $\beta$ -aldoses,



and  $\alpha$ - and  $\beta$ -ketoses,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\overbrace{[\text{CH}\cdot\text{OH}]_2}^{\text{O}}\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ . In consequence of his work on lactones (see below), the author claims that the two forms are structurally different, one form corresponding with the free aldehyde or ketone,

$\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_{x+1}\cdot\text{CHO}$  or  $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_x\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ ,  
and the other form with a unimolecular  $\alpha$ -lactone,

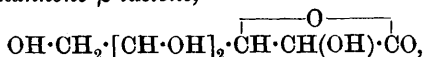


IV.  $\text{C}_8$ -,  $\text{C}_4$ -,  $\text{C}_5$ -, and  $\text{C}_6$ -ortho-Osones,  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot$ , the Intermediate Products in the Conversion of Sugars into  $\text{C}_8$ -,  $\text{C}_4$ -,  $\text{C}_5$ -, and  $\text{C}_6$ -Saccharinic Acids by Alkali Hydroxides.—The conditions under which ortho-osone formation from the various hexoses, pentoses, tetroses, and trioses may be expected are discussed. Probably salt-formation is the first occurrence. An oxidising agent should not be present. Also it is essential that alkali hydroxides be absent, otherwise the ortho-osone immediately undergoes a "benzilic acid transformation" into a saccharinic acid; moreover, the presence of an alkali promotes enolisation, polymerisation, resinification, and condensation of the sugar, so that a mixture of different osones is produced instead of one definite osone. ortho-Osone formation, therefore, must be effected in neutral or faintly acid solution, and reasons are given for the selection of lead hydroxide or chloride or basic acetate (or salts of thorium, zinc, aluminium, or ferrous iron) as the best reagent.

The original paper must be consulted for the wealth of experimental details on which are based the generalisations stated in sections I, II, III, and IV above.

The following important observations on lactone formation in the sugars are recorded. *d*-Mannonic acid, liberated from its salts at the

ordinary temperature, changes under all conditions at 20° almost entirely into *d*-mannono- $\beta$ -lactone,



m. p. 156°,  $[\alpha]_D^{20} + 111.1^\circ$ , highly refractive, octahedral crystals (Hedenburg, working under the author's directions, has recently observed, m. p. 162° and  $[\alpha]_D^{20} + 111.85^\circ$ ). The  $\beta$ -lactone, in contrast to the  $\gamma$ -lactone (below), changes within twenty-four hours in 4% aqueous solution at 20° to *d*-mannonic acid to the extent of 75%; by rapidly removing the water below 50° under reduced pressure, the residue consists almost entirely of the  $\beta$ -lactone (details for the preparation of the pure  $\beta$ -lactone are given). By heating the aqueous solution on the water-bath for four hours and evaporating in an open dish, a residue is obtained consisting of mixed crystals of chiefly the  $\gamma$ -lactone, but containing up to 10% of the  $\beta$ -lactone. The pure  $\gamma$ -lactone, m. p. 151°,  $[\alpha]_D^{20} + 51.8^\circ$ , is obtained by evaporating an aqueous solution of the mixed crystals or of *d*-mannonic acid or of the  $\beta$ -lactone or of ethyl *d*-mannonate with 10% of hydrochloric acid on the water-bath and heating the powdered residue until every trace of hydrochloric acid has been expelled. A 4% aqueous solution of the  $\gamma$ -lactone at 20° remains unchanged even after many weeks. In 4% solution, *d*-mannonic acid or its  $\beta$ -lactone undergoes an irreversible change to the  $\gamma$ -lactone which at 20° requires at least six months for its completion. The  $\beta$ -lactone, suspended in 1% alcoholic hydrogen chloride, changes quite smoothly to ethyl *d*-mannonate within twenty-four hours; the same change occurs when a mixture of *d*-mannonic acid and its  $\beta$ -lactone is dissolved in absolute alcohol. Ethyl *d*-mannonate, thus prepared, has m. p. 164°, crystallises in voluminous needles, and is optically inactive; by fusing under 15 mm., it is converted into almost pure *d*-mannono- $\gamma$ -lactone, whilst a 4% aqueous solution has  $[\alpha]_D^{20} + 28.65^\circ$  after thirty-six days, and contains *d*-mannonic acid and its  $\beta$ - and  $\gamma$ -lactones.

From the mixture of uni- and multi-molecular anhydrides obtained from *d*-gluconic acid at all temperatures between 20° and 100° (A., 1908, i, 5) or by heating ethyl *d*-gluconate at 70—80°, the author has as yet succeeded in isolating only the unimolecular *d*-glucono- $\beta$ - and - $\gamma$ -lactones. *d*-Glucono- $\beta$ -lactone, m. p. 150—152°, clusters of transparent needles, has  $[\alpha]_D^{20} + 61.7^\circ$  after it has been in solution for twelve minutes, but even in cold aqueous solution it changes with extraordinary rapidity to *d*-gluconic acid, and cannot be recovered unchanged by the evaporation of the solution. Ethyl *d*-gluconate, m. p. 60—65° (or 45—54° when containing EtOH), needles, is optically inactive. C. S.

**Some Products of the Decomposition of Dextrose in Alkaline Medium.** A. FERNBACH and M. SCHOEN (*Compt. rend.*, 1914, 158, 976—978).—On warming a 5% solution of dextrose with two parts per thousand of sodium carbonate, there is a rapid fall in the rotation and also a progressive diminution in the alkalinity. The volatile acid formed is entirely acetic acid. Working with more concentrated sodium carbonate (5%) at 100° there is an increased yield of acid.

Amongst the non-acid volatile products, the authors have isolated methylglyoxal in the form of its osazone, although they have not been able to obtain any evidence of the formation of acetaldehyde. Under the experimental conditions no lactic acid was obtained. W. G.

**Action of Acids on Lævulose and Dextrose.** M. M. HARRISON (*J. Amer. Chem. Soc.*, 1914, **36**, 586—603).—As the action of acids on lævulose and dextrose is of great importance in studies of sugar hydrolysis, it was considered desirable to investigate the effect of acids on the composition and rotatory power of a solution of invert-sugar. Experiments have therefore been made on the action of hydrochloric and formic acids on solutions of lævulose and dextrose.

In the decomposition of lævulose by hydrochloric acid at 60°, it has been found that the first change is a bimolecular reaction, and the conclusion is drawn that an unstable disaccharide is produced which changes reversibly into lævulose and lævulosin, first described by Wohl (A., 1890, 1086). The other decomposition products include hydroxymethylfurfuraldehyde, humin, and formic and lævulic acids. The first two of these are formed by the decomposition of the lævulosin, whilst the acids are produced from the hydroxymethylfurfuraldehyde.

The decomposition of dextrose by hydrochloric acid at 75° is also bimolecular in its earlier stages, giving rise to the disaccharide, *iso*-maltose. The final decomposition products, formic and lævulic acids, and humins, appear to be identical with those of lævulose, the two acids being formed from hydroxymethylfurfuraldehyde. The processes of decomposition in the case of lævulose and dextrose are thus strictly analogous. The assumption made by Koenigsfeld (A., 1912, i, 163) that dextrose is partly changed into lævuloæ seems to be without foundation.

The results of this work show that the rate of decomposition of the sugars is not rapid enough to vitiate the final polarimetric reading in ordinary sugar hydrolysis, and also indicate that in ordinary circumstances this final reading is quite trustworthy and does not need any correction. E. G.

**Heptoses.** GEORGE PEIRCE (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxxv—xxxvi).—*d*-α-Mannoheptitol and *d*-α-galaheptitol melt at 188°, and have a specific rotation in saturated borax solution of +4.85° and -4.35° respectively. They form a compound melting at 203° (uncorr.). Fischer found *d*-α-mannoheptitol and *l*-α-mannoheptitol form a compound also melting at 203°. *d*-α-Mannoheptite is therefore the antipode of *d*-α-galaheptitol. Configurative formulæ of the heptic acids are given. *d*-α-Mannopentahydroxypimelic acid is apparently the antipode of *d*-α-galapentahydroxypimelic acid. W. D. H.

**Biochemical Synthesis of α-d-Galactosides. II. α-Ethylgalactoside** H. HÉRISSEY and A. AUBRY (*J. Pharm. Chim.*, 1914, [vii], **9**, 327—331. Compare this vol., i, 253).—The authors have obtained α-ethylgalactoside in a crystalline form by the method already

described for  $\alpha$ -methylgalactoside (*loc. cit.*). The physical properties as determined by them, namely, m. p.  $140-142^\circ$  (corr.),  $[\alpha]_D + 185.47'$ , differ somewhat from those given by Fischer and Beensch (compare A., 1894, i, 565), but agree with those given for galactitol (compare this vol., i, 389). The galactoside does not reduce Fehling's solution, and is readily hydrolysed by dilute mineral acids and by  $\alpha$ -galactosidase in aqueous solution. W. G.

**Biochemical Synthesis by means of Emulsin of the  $\beta$ -Monoglucoside of Glycol.** EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1914, 158, 898—900; *J. Pharm. Chim.*, 1914, [vii], 9, 383—388. Compare Fischer and Fischer, A., 1910, i, 716).—The authors have prepared a crystalline  $\beta$ -glycolmonoglucoside,  $C_6H_{11}O_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , by the action of emulsin on an aqueous solution of glycol and dextrose containing eighty-seven grams of the former and twenty grams of the latter in 100 c.c. At the end of five months, 77% of the dextrose was converted into glucoside, which was isolated by precipitating the emulsin with alcohol, distilling off the water, alcohol, and glycol under reduced pressure, and removing the excess of dextrose by fermentation with yeast. The residue finally obtained was dissolved in alcohol and precipitated with ether as a pasty mass which slowly crystallised on keeping. The crystals so obtained were hygroscopic, had a slightly bitter taste, were very soluble in water, moderately soluble in alcohol, and had  $[\alpha]_D^{18} - 30.55^\circ$ . The glucoside was hydrolysed by emulsin in aqueous solution or by heating with 3% sulphuric acid in a sealed tube at  $100^\circ$ . W. G.

**Phytin.** C. NEUBERG (*Biochem. Zeitsch.*, 1914, 61, 187—188).—Reiteration of the view that phytin is an ester of phosphoric acid and inositol. S. B. S.

**The Properties of Phytin. II.** M. A. JEGOROV (*Biochem. Zeitsch.* 1914, 61, 41—54. Compare A., 1912, i, 676).—By heating together inositol with phosphoric acid under varying conditions, a complete synthesis of an organic phosphorus compound could not be accomplished, as has been claimed by Carré and Contardi. A reaction does, however, take place, even at a comparatively low temperature, and the unchanged phosphoric acid can be separated from the reaction product by means of ether. A product was obtained by this method containing 22.6% of combined phosphoric acid. Experiments were also carried out to account for the formation of a yellow precipitate with molybdate in acid solution, and the conclusion was drawn that in the process of precipitation a scission of phosphoric acid from the phytin takes place; the precipitate produced contains only a small quantity of organic substance. It was also found that scission of phosphoric acid takes place when phytin is kept with water under aseptic conditions. S. B. S.

**Phytin. VIII. (I). Composition of Barium Phytate and Phytic Acid. (II). Properties of Phytic Acid and Its Decomposition Products.** R. J. ANDERSON (*J. Biol. Chem.*, 1914, 17, 171—190).—The composition of phytic acid prepared from commercial



phytin agrees with that of inositol hexaphosphate obtained from cotton-seed meal, oats, and maize. The crystalline tri- and hepta-barium salts were prepared.

When the acid is dried for forty-eight hours at 105°, under diminished pressure, about 75% of the phosphoric acid is found to be present as inorganic phosphoric acid. Ten grams of the acid yielded 0.25 gram of inositol. The organic phosphoric acids remaining were isolated as barium salts, but could not be obtained in pure forms. It is probable that the different fractions represent more or less impure mixtures of the barium salts of tetra-, tri-, di-, and mono-phosphoric acid esters of inositol.

N. H. J. M.

#### The Action of the Silent Discharge on Starch and Glycine.

WALTHER LÖB (*Biochem. Zeitsch.*, 1914, **60**, 286—296).—The effect of the silent discharge on starch solutions is to produce hydrolysis. After nine hours, these solutions gave only a light reddish-violet tint with iodine solutions. A small amount of the starch was flocculated at the same time. By the action of the silent discharge on glycine solutions, a small amount of deamidisation could be produced. Traces of formaldehyde could also be detected.

S. B. S.

#### The Action of Strong Nitric Acid on Cotton Cellulose.

EDMUND KNECHT and ADOLF LIPSCHITZ (*J. Soc. Chem. Ind.*, 1914, **33**, 116—122).—The extent of the action of nitric acid on cellulose depends on the concentration of the acid, the time, and the temperature. If the concentration is kept constant, increase in temperature shortens the time required to produce a given result. For example, with an acid of D 1.415 the maximum of firmly combined nitric acid is obtained after three hours' steeping at 31°; raising the temperature to 61° resulted in the expulsion of the whole of the nitrogen and the formation of oxycellulose.

The physical and chemical properties of the treated cotton are described in detail, as also the behaviour of the cotton towards all classes of colouring matters.

T. S. P.

#### Colloidal Chemistry of the Humus Substances.

SVEN ODÉN (*Kolloid. Zeitsch.* 1914, **14**, 123—130. Compare A., 1912, i, 336).—The separation of three different substances from an aqueous extract of sphagnum peat is described. Two of these substances are colloidal, whilst the third gives solutions which are non-colloidal in character. If the peat is extracted by treatment with 4*N*-ammonia solution at 50°, other products are obtained when the extract is fractionally coagulated by the addition of sodium chloride or acidified by means of hydrochloric acid.

The substance precipitated by hydrochloric acid yields an aqueous suspension, the conductivity of which is  $8 \times 10^{-6}$  mho., and if measured quantities of ammonia are added to the suspension on the one hand, and to an equal volume of distilled water on the other, it is found that the electrical conductivity of the first series of solutions is very much greater than that of the pure ammonia solutions. If the added ammonia is sufficient in quantity, the difference in the two conductivi-

ties is practically constant, and this is supposed to be due to the formation of ammonium humate.

Observations made directly with the aqueous extract of sphagnum peat are similar in character and afford evidence of the presence of an acid in the aqueous suspension of the natural peat substance. If the purified acid is dried at  $100^{\circ}$ , it is transformed into a hard brittle substance which is insoluble both in water and in alkalis. By long-continued treatment with a solution of alkali, the insoluble form appears to be reconverted into the soluble modification, and this transformation can be followed by means of conductivity measurements. H. M. D.

**The Hydrates of Primary Amines.** FÉLIX BIDET (*Compt. rend.*, 1914, 158, 876—878).—*iso*Amylamine, amylamine and *iso*-butylamine form hydrates on exposure to atmospheric moisture in long, vertical tubes, sealed at the bottom end, and loosely plugged at the top with glass wool. Crystals begin to form just below the glass wool and gradually spread down the tube. The crystals are very sensitive to variations in atmospheric moisture, and gradually liquefy on removing the glass wool plug. Similarly, they liquefy owing to the presence of excess of vapour of the base, if the tube is warmed slightly. *iso*Amylamine yields a definite hydrate,  $C_5H_{11}\cdot NH_2\cdot 2H_2O$ , which on heating in a sealed tube begins to sublime at  $70^{\circ}$  and melts at  $95$ — $96^{\circ}$ . In the case of this base a hydrate is also obtained by passing dry ammonia gas through a suspension of *iso*amylamine hydrochloride in dry ether at  $0^{\circ}$  for two hours, filtering the liquid, and allowing it to evaporate in the air. The crystals obtained in this way are much larger, but contain a trace of ether and have m. p.  $82^{\circ}$ , subliming. The constitution of the hydrates of the other two amines has not been determined, but that of amylamine has m. p.  $78^{\circ}$ , and that of *isobutylamine* has m. p.  $74^{\circ}$ . All these hydrates are very soluble in water and ether, and are strongly alkaline to litmus and phenolphthalein. W. G.

**Reactions under High Pressures. III. Reactions with Compressed Ammonia.** ARTHUR STÄHLER (*Ber.*, 1914, 47, 909—913. Compare this vol., i, 378).—The author has investigated the action of highly compressed ammonia on certain carbonaceous substances. The material was placed in a glass vessel contained in an autoclave, liquid ammonia was added, and the autoclave quickly closed. Attack of the iron of the latter by substances containing halogens was avoided by silver-plating the inside.

Carbon tetrachloride gives, at  $140^{\circ}$  and in the presence of iodine and copper, guanidine, and a small amount of either cyanogen or hydrogen cyanide. Ethyl chloride at  $220^{\circ}$  and 220 atmos. gives a mixture of ethylamine (80%), diethylamine (15%), and triethylamine (5%) (compare Vincent and Chappuis, A., 1886, 438). Ethylene chloride furnishes ethylenediamine hydrochloride; the free base was obtained from the hydrate by heating with sodium in a sealed tube. Chlorobenzene could not be decomposed, whilst bromobenzene, using ammonium and aluminium iodides as catalysts, gave only a small amount of aniline. The product obtained from tetrachloroethylene

was mostly ammonium chloride, together with a black mass, and a similar black mass was furnished by hexachloroethane. Dichloroethylene reacts only to a slight extent, giving apparently monochloroacetylene. Absolute ether and ammonia do not interact at 250° and 270 atmos., nor was the amide produced from ethyl diethylmalonate at 150° and 70 atmos. Aqueous ammonia and compressed carbon monoxide in the presence of iron did not yield ammonium formate, but the formation of carbamide and hydrogen cyanide was observed, together with a little violet Prussian blue.

Methyldichloroamine, which might have been expected to give the hitherto unknown methyldi-imide,  $\text{CH}_3 \cdot \text{N}_2 \cdot \text{H}$ , was completely decomposed, giving a substance which reduced ammoniacal silver solution feebly, but Fehling's solution not at all, and had a burning taste. The explosions which caused the experiments with this substance to be discontinued were possibly due to the presence of nitrogen chloride.

J. C. C.

**Hexahalogenotellurates [Tellurihaloids].** A. GUTBIER and F. FLURY [with V. WEINZIERL (*Zeitsch. anorg. Chem.*, 1914, **86**, 169—195. Compare A., 1912, i, 241, 689).—The salts described below have all the composition  $(\text{R} \cdot \text{NH}_3)_2 \text{TeX}_6$ , where R is the organic radicle and X the halogen. They are anhydrous, and form glistening crystals, the chlorides being yellow and the bromides red. Most of the crystals are monoclinic or rhombic, and the chlorides and bromides crystallise in different systems, but the tetramethylammonium chloro- and bromo-compounds are regular, both crystallising in combinations of the cube and octahedron.

The following tellurichlorides are described: *Tetramethylammonium*, *tripropylammonium*, *di-* and *tri-isobutylammonium*, *allylammonium*, *tri-iso-amylammonium*, *guanidinium*, *m-* and *p-chloro-anilinium*, *iso-amylanilinium*, *benzylideneanilinium*, *benzylethylanilinium*, *dimethyl-o-* and *-p-toluidinium*,  *$\psi$ -cumidinium*, *3-methylpyridinium*, *lutidinium*, *collidinium*, *isoquinolinium*, *piperidinium*, *benzylmethylammonium*, *benzylidenemethylammonium*, and *benzylidene-ethylammonium*.

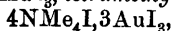
The telluribromides described include the above, together with the *mono-* and *di-isoamylammonium*, *aminoguanidinium*, *o-chloro-anilinium*, *2:4-dichloroanilinium*, *o-*, *m-*, and *p-bromoanilinium*, *m-nitroanilinium*, *benzylanilinium*, *benzylmethylanilinium*, *diphenylammonium*, *2:4-* and *3:4-tolylenediammonium*, *o-* and *p-phenetidinum*, and *benzoylpiperidinium* salts.

C. H. D.

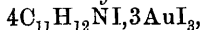
**The Double Auric Iodides of Substituted Ammonium Bases.** SATYARANJAN DAS GUPTA (*J. Amer. Chem. Soc.*, 1914, **36**, 747—751).—An attempt to prepare double auric iodides of the alkali metals by the addition of auric chloride to solutions of the corresponding iodides was unsuccessful, except in the case of caesium, on account of the great solubility of the expected compounds. It was found that alkylammonium auri-iodides could be readily obtained by this method.

*Caesium auri-iodide*,  $\text{CsAuI}_4$ , forms lustrous, black crystals.

*Methylammonium auri-iodide*,  $\text{NH}_2\text{Me} \cdot \text{HI} \cdot \text{AuI}_3$ , *butylammonium auri-iodide*,  $\text{C}_4\text{H}_9 \cdot \text{NH}_2 \cdot \text{HI} \cdot \text{AuI}_3$ , *tetramethylammonium auri-iodide*.



*tetraethylammonium auri-iodide*,  $4\text{NEt}_4\text{I}, 3\text{AuI}_3$ , *quinolinium auri-iodide*,  $2\text{C}_9\text{H}_8\text{NI}, \text{AuI}_3$ , *quinoline-ethylammonium auri-iodide*,



and *pyridinium auri-iodide*,  $4\text{C}_5\text{H}_6\text{NI}, 3\text{AuI}_3$ , were black solids. *Dipropylammonium auri-iodide*,  $3\text{NPr}_2\text{H}_2\text{I}, \text{AuI}_3$ , and *tripropylammonium auri-iodide*,  $4\text{NPr}_3\text{HI}, \text{AuI}_3$ , were obtainable only of pasty consistency.

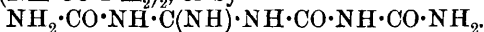
D. F. T.

**Preparation of Hexamethylenetetramine Methyl Thiocyanate.** KARL HEINRICH SCHMITZ (D.R.-P. 269746. Compare this vol., i, 20).—Instead of using hexamethylenetetramine as described in the chief patent (*loc. cit.*) for the preparation of the methyl thiocyanate, a mixture of concentrated solutions of formaldehyde (6 mols.) (or its polymerides) and ammonia (4 mols.) may be used.

J. C. C.

**Preparation of Cyanuric Acid by means of Carbamide and Chlorine.** A. BÉHAL (*Bull. Soc. chim.*, 1914, [iv], 15, 149—159).—Various experiments designed to determine the best conditions for the formation of cyanuric acid are described, and finally a detailed account is given of the method of preparation recommended. The crude cyanuric acid is purified by conversion into the ammoniacal copper derivative, then into the ammonium salt from which the acid is regenerated by means of nitric acid. In the course of the purification a small quantity of *caluret*,  $\text{C}_4\text{H}_8\text{O}_3\text{N}_6$ , a colourless, amorphous substance, is obtained, along with some biuret. Caluret is insoluble in water, but dissolves in sodium hydroxide solution, being reprecipitated by carbon dioxide; it closely resembles ammeline in properties.

The solution of caluret in sodium hydroxide solution gives white precipitates of *argentic* derivatives with ammoniacal silver nitrate. Caluret appears to be formed when guanidine carbonate is heated with carbamide at  $120^\circ$ , whence it may be represented by the formula  $\text{NH}_2\cdot\text{CO}\cdot\text{N}:\text{C}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$ , or by



The mode of formation of cyanuric acid from carbamide is discussed.

T. A. H.

**Presence of Nitrides in Calcium Cyanamide.** C. MANUELLI (*Ann. Chim. Applicata*, 1914, 1, 110—114).—That commercial calcium carbide contains metallic calcium is shown by the presence of hydrogen in the acetylene obtained on treatment with water. In the conversion of the carbide into calcium cyanamide, it may be expected that this calcium will be transformed into calcium nitride. The proportion of the latter in samples of commercial calcium cyanamide has been estimated by distillation with water in a reflux apparatus at  $35\text{--}40^\circ$  and under a pressure not exceeding 30 mm., the ammonia liberated being absorbed by standard sulphuric acid. Under these conditions, it is found that the nitrogen of the cyanamide itself yields no ammonia. The maximum proportion of nitrogen as calcium nitride in five different samples of calcium cyanamide amounted to 0.56%

T. H. P.

**Prussian Blue and Turnbull's Blue.** ERICH MÜLLER (*Chem. Zeit.*, 1914, 38, 281—282, 328—330).—The author calls attention to his own publications on the subject of Prussian Blue and Turnbull's Blue (A., 1909, i, 142, 705, 706; 1911, i, 844) and criticises the statements and results of Woringer (A., 1912, i, 170) and Eibner and Gerstaecker (A., 1913, i, 254).  
T. S. P.

**Composition of Prussian Blue.** P. WORINGER (*J. pr. Chem.*, 1914, [ii], 89, 51—68. Compare A., 1912, i, 170).—By methods similar to those employed by Müller (A., 1911, i, 844), the author has determined the composition of the precipitates formed by the interaction of potassium and sodium ferrocyanide with ferric chloride in various proportions in decinormal solution, and finds that in the case of potassium ferrocyanide the precipitate has the composition  $\text{Fe}_7(\text{CN})_{18}$ , only when a considerable excess of ferric chloride is employed. Diminution in the amount of ferric chloride results in the formation of precipitates containing potassium, the percentage of which progressively increases as the excess of ferric salt is gradually diminished. It is probable that the first stage in the action consists in the formation of a soluble potassium salt,  $\text{KFe}[\text{Fe}(\text{CN})_6]$ , and that the potassium is then partly replaced by iron, the extent of this replacement depending on the amount of ferric chloride present.

On the other hand, the interaction of ferric chloride and sodium ferrocyanide even in molecular proportions yields a precipitate of the composition  $\text{Fe}_7(\text{CN})_{18}$ , whilst excess of ferric chloride gives rise to a basic salt which approximates to the composition  $\text{Fe}_5(\text{OH})_3[\text{Fe}(\text{CN})_6]_3$ .

If potassium ferrocyanide and ferric chloride are allowed to interact in molecular proportions, or if the ferrocyanide is in excess, the cyanide remaining in the solution after filtration is not present as ferrocyanide but as ferricyanide.

In view of this result the author considers that the formation of Prussian blue is preceded by the simultaneous oxidation and reduction of the ferrocyanide and ferric salt respectively, thus:  $[\text{Fe}''(\text{CN})_6]''' + \text{Fe}''' = [\text{Fe}'''(\text{CN})_6]''' + \text{Fe}''$ ; the precipitates formed by the interaction of alkali ferrocyanides and ferric chloride are, therefore, ferricyanides and not ferrocyanides as stated by Müller. In support of this conclusion it is found that samples of Prussian blue derived from various sources, on decomposition with ammonium carbonate, gave 90% of ammonium ferricyanide and 10% of ammonium ferrocyanide.

Soluble Prussian blue is thus a potassium ferrous ferricyanide,  $\text{KFe}''[\text{Fe}(\text{CN})_6]'''$ , whilst insoluble Prussian blue has the composition  $\text{Fe}''' \text{Fe}_3''[\text{Fe}(\text{CN})_6]_3'''$ .  
F. B.

**Composition of Prussian Blue.** ERICH MÜLLER (*J. pr. Chem.*, 1914, [ii], 89, 68—69. Compare A., 1909, i, 142, 705; 1911, i, 844).—A reply to Woringer (preceding abstract).  
F. B.

**A New Type of Complex Tungsten and Molybdenum Cyanides (Preliminary Notice).** OSCAR OLSSON (*Ber.*, 1914, 47, 917—923).—By the action of potassium cyanide on a solution of potassium tungsten chloride,  $\text{K}_3\text{W}_2\text{Cl}_9$  (compare A., 1913, ii, 328),

a complex tungsten cyanide of the composition  $K_4W(CN)_8 \cdot 2H_2O$  is obtained (compare Rosenheim and Dehn, this vol., i, 260). By the conversion of this compound into the corresponding *silver* salt, and then double decomposition with various chlorides, as well as by direct interaction of the potassium salt with metal salts, a series of complex tungsten cyanides, all of the type  $M_4W(CN)_8 \cdot xH_2O$ , has been obtained. The potassium, *sodium*, *ammonium*, *rubidium*, *cæsium*, *barium*, *strontium*, and *calcium* salts are all easily soluble in water; the *thallium* salt is more sparingly and the *cadmium* salt much more sparingly, soluble; the crystalline *manganese* and *zinc* salts are insoluble in water. By the action of hydrochloric acid on the amorphous, light yellow silver salt, the *acid*,  $H_4W(CN)_8 \cdot 6H_2O$ , was obtained as slender, yellow needles, which are readily soluble in both water and alcohol; the concentrated aqueous solutions are red, the dilute yellow, and neutral to litmus. In agreement with the results of Rosenheim and Dehn (*loc. cit.*), titration with permanganate indicates that the tungsten is in the quinquevalent condition, whereas according to the formula it should be quadrivalent. This abnormality is shown not to be real, but to be due to the fact that the permanganate oxidises the compounds, not to tungstic acid, but to complex tungsten cyanides of the type  $M_3W(CN)_8 \cdot xH_2O$ , in which the tungsten is really quinquevalent. The valency of the tungsten in both these classes of compounds was determined by heating them for ten to twelve hours at  $140-160^\circ$  with ammoniacal silver nitrate in a sealed tube, when reaction takes place according to the equation:  $W^{vi-x} + n_1Ag^+ = W^{vi} + xAg + (n_1 - x)Ag^+$ . From the amount of silver deposited, the valency of the tungsten can be determined.

*Potassium tungsten cyanide*,  $K_3W(CN)_8 \cdot 2.5H_2O$ , is obtained by oxidising a solution of the salt,  $K_4W(CN)_8 \cdot 2H_2O$ , with potassium permanganate, precipitation of the corresponding silver salt from solution, and then double decomposition with potassium chloride. It forms light yellow crystals, which undergo decomposition when exposed to moist air in daylight; in dry air it is fairly stable. It readily forms *additive* compounds, the one with potassium chloride crystallising in red, slender prisms, and having the formula  $K_3W(CN)_8 \cdot KCl \cdot 5H_2O$ . The following *salts* have also been obtained:  $Na_3W(CN)_8 \cdot 4H_2O$ ,  $Rb_3W(CN)_8 \cdot 2H_2O$ ,  $Cs_3W(CN)_8 \cdot 2H_2O$ ,  $Ba_3[W(CN)_8]_2 \cdot 10H_2O$ , and  $Sr_3[W(CN)_8]_2 \cdot 11H_2O$ . The corresponding *acid*, prepared from the silver salt and hydrochloric acid, forms orange-yellow crystals of the composition  $H_3W(CN)_8 \cdot 6H_2O$ .

Experiments showed that the anomalies observed by Rosenheim with the corresponding molybdenum compounds (A., 1910, i, 101, 231) can be explained in a similar manner to the above, although the compounds containing quinquevalent molybdenum could not be isolated.

T. S. P.

**Oximinocarbonic Esters and Related Compounds.** LAUDER WILLIAM JONES and RALPH E. OESPER (*J. Amer. Chem. Soc.*, 1914, 36, 725—732).—When an ethereal solution of ethyl iodide is kept with the silver salt,  $CO_2Et \cdot NAg \cdot OBz$ , of the benzoyl derivative of hydroxyurethane for two weeks in the dark, interaction occurs with formation

of the corresponding *N-ethyl* derivative,  $\text{CO}_2\text{Et}\cdot\text{NEt}\cdot\text{OBz}$ , an oil, b. p. 188—190°/25 mm. (slight decomp.), of spicy odour; the constitution of this substance is indicated by the production of  $\beta$ -ethylhydroxylamine,  $\text{NH}\cdot\text{Et}\cdot\text{OH}$ , on hydrolysis with concentrated hydrochloric acid at 105°.

The action of ethyl iodide on an alcoholic solution of the benzoyl derivative of hydroxyurethane to which sodium ethoxide had been added gave a mixture of ethyl benzoate with ethoxyurethane,  $\text{OEt}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$  (Jones, A., 1898, i, 174).

The action of an ethereal solution of *isoamyl* iodide on the silver salt of the benzoyl derivative of hydroxyurethane in the manner described above yielded the *N-isoamyl* derivative,  $\text{CO}_2\text{Et}\cdot\text{N}(\text{C}_5\text{H}_{11})\cdot\text{OBz}$ , a yellow oil, b. p. 203—205°/30 mm. (slight decomp.), which gave  $\beta$ -*isoamyl*hydroxylamine on treatment with hydrochloric acid at 110°.

By the gradual addition of benzoyl chloride to a cooled, aqueous solution of sodium hydrogen carbonate and ethyl oximinocarbonate (Houben and Schmidt, A., 1913, i, 958), the last named is converted into the *benzoyl* derivative,  $\text{OBz}\cdot\text{N}\cdot\text{C}(\text{OEt})_2$ , colourless needles, m. p. 148°.

Interaction between ethyl cyanoiminocarbonate and a suspension of sodium *isoamyl*oxide in ether, aided by heating, gave rise to *ethyl isoamyl iminocarbonate*,  $\text{NH}\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$ , a yellow oil which decomposed when distilled under a pressure of 25 mm. Its identity was demonstrated by its conversion by hydroxylamine into *ethyl isoamyl oximinocarbonate*,  $\text{OH}\cdot\text{N}\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$ , colourless crystals which melt at the ordinary temperature. D. F. T.

**Ether Scission and Replacement of Alkoxy by Alkyl by means of Magnesium Alkyl Haloids.** ERNST SPÄTH (*Ber.*, 1914, 47, 766—767).—In order to sustain a claim for priority over Tschitschibabin and Jeglasin (this vol., i, 276) and Simonis and Remmert (this vol., i, 270), the author gives a summary of his results in this field (compare this vol., i, 1). In addition, he shows that the "currents of propane" which the latter authors obtained in the action of magnesium methyl iodide on phenetole really consisted of a mixture of hydrocarbons. J. C. W.

**Observations on Some Barbier-Grignard Reactions.** L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1914, 36, 657—663).—In effecting the interaction of aliphatic ketones and aldehydes with organo-magnesium compounds it is advisable to work with low temperatures; vigorous shaking is necessary to prevent local heating. It is found that ethyl chloride, as a starting point for an organo-magnesium compound, possesses the advantage over ethyl bromide of giving more soluble condensation products with ketones.

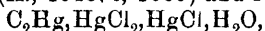
When chloroacetone is gradually introduced into an ethereal solution of magnesium ethyl bromide at -10°, and, after keeping cold by ice for one to two hours, the mixture is successively treated with ice and acetic acid, extracted with ether, the extract then separated from the ether by distillation of the latter, and finally shaken with aqueous potassium hydroxide solution,  $\alpha\beta$ -oxido- $\beta$ -methylbutane,  $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , is obtained

in a yield of 65% calculated on the magnesium taken (compare Fournneau and Tiffeneau, A., 1907, i, 818). The formation of this substance is due to the elimination of the elements of hydrogen chloride from the  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ -methylbutane primarily produced.

*Magnesium ethyl chloride* was obtained by keeping a mixture of magnesium and an ethereal solution of ethyl chloride, with a little methyl iodide and a trace of iodine in a stoppered bottle at the b. p. of ether. After heating for some time, the bottle was periodically cooled and a further quantity of ethyl chloride passed in until the necessary quantity of ethyl chloride had been introduced. The solution reacted with chloroacetone in the manner described above, and on account of the solubility of the primary condensation product, the danger of local heating was greatly reduced. It also reacted with acetone, giving a 70% yield of tertiary amyl alcohol.

The interaction of ethylideneacetone ( $\Delta^2$ -penten- $\delta$ -one) and magnesium methyl iodide in ethereal solution at  $-10^\circ$  gave an almost 80% yield (calculated on the ketone) of *aa*-dimethyl- $\Delta^2$ -butenol (compare Gry, A., 1908, i, 307), which was identified by its dehydration (Kyriakides, this vol., i, 473) to a hexadiene of which the structure is probably  $\text{CHMe}:\text{CH}:\text{CMe}:\text{CH}_2$  (compare Gry, *loc. cit.*). The quantity of methyl isobutyl ketone produced was very small. D. F. T.

**Trichloromercuriacetaldehyde.** HEINRICH BILTZ and KURT REINKOBER (*Annalen*, 1914, **404**, 219—236).—The white substance obtained by passing acetylene into a solution of mercuric chloride has been shown to be trichloromercuriacetaldehyde,  $\text{C}(\text{HgCl})_3 \cdot \text{CHO}$ , by Biltz and Mumm (A., 1905, i, 2, 165). The formula has been rejected by Manchot and Haas (A., 1913, i, 1009) and replaced by



chiefly because the substance exhibits the reactions of mercurous as well as of mercuric salts. The authors' interpretation of their observation, however, is erroneous. When the white substance is covered with aqueous sodium hydroxide, only yellow mercuric oxide is at first formed, but after a few seconds it is reduced by the acetaldehyde also liberated and gradually darkens. Experimentally it is shown that acetaldehyde reduces mercuric oxide in the presence of sodium hydroxide.

The action of aqueous ammonia on trichloromercuriacetaldehyde is much more rapid than that of sodium hydroxide, and the separation of yellow mercuric oxide cannot be detected.

The other arguments of Manchot and Haas in favour of their formula are adversely criticised. A powerful argument in favour of the trichloromercuriacetaldehyde formula and against Manchot and Haas' formula is the fact that the white substance reacts with iodine and aqueous sodium hydroxide to form iodoform. It is known that the acetylene derivatives of mercury, silver, and copper react readily with iodine to form di-iodoacetylene and tetra-iodoethylene, never iodoform, whereas the last is known to be produced from acetaldehyde. The formation of chloral by the action of chlorine water is also in harmony with the trichloromercuriacetaldehyde formula.



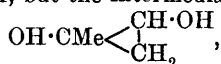
The authors are of opinion that the two substances obtained by Manchot and Haas from phenylacetylene and mercuric chloride and mercuric bromide respectively (*loc. cit.*) are, according to the evidence recorded by them, *trichloromercuriacetophenone*,  $C(HgCl)_3 \cdot CPh$ , and *tribromomercuriacetophenone*,  $CH(HgBr)_2 \cdot CPh$ , respectively. In view of this opinion, it becomes of interest to ascertain whether acetylene itself reacts with two or with three molecules of mercuric bromide. The latter is the case. Aqueous mercuric bromide and acetylene yield *tribromomercuriacetaldehyde*,  $C(HgBr)_3 \cdot CHO$ , pale yellow, amorphous powder, which resembles trichloromercuriacetaldehyde in its behaviour.

C. S.

**Relations between Organic Rings and Unsaturation.** I. B. K. MERESHKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 97—123).—The author discusses the statics and dynamics of molecules in labile equilibrium, more especially as regards cyclic compounds. In cases where the removal of hydrogen bromide, chloride or iodide or water from a molecule may give rise to an acetylenic or an allenic or conjugated linking, the reaction should proceed in the direction which yields the conjugated linking. There should, however, exist conditions in which compounds of all these types should be obtained and the period of their existence protracted.

Tribromo- $\beta$ -methylpropane (compare Pogorshelski, A., 1905, i, 315) has  $n_D^{14}$  1.57012, and when treated with solid potassium hydroxide at 145—150° and 100 mm. pressure yields  $\alpha\gamma$ -dibromo- $\beta$ -methylpropene,  $CH_2Br \cdot CMe \cdot CHBr$ , which is an unstable, caustic liquid, b. p. 102°/100 mm.,  $D_4^{20}$  1.8942,  $D_4^{15.1}$  1.8691,  $n_D^{15.1}$  1.53958. The action on this hydrocarbon of zinc dust (or wool) and 85% aqueous alcohol gives  $\beta$ -methylpropene and another compound which gives the liquid tetrabromide,  $CMeBr_2 \cdot CH_2 \cdot CHBr_2$ , undergoes isomeric change to divinyl when heated with alumina, and is shown to be  $\alpha$ -methyl- $\Delta^2$ -cyclopropene,  $CMe \leq \begin{smallmatrix} CH \\ CH_2 \end{smallmatrix}$ . On gentle oxidation, the latter yields aceto-

acetic acid,  $CH_2Ac \cdot CO_2H$ , but the intermediate glycol,



could not be obtained. Hydrogenation in presence of reduced nickel at 170—180°, or of palladium at 80°, yields pure  $\beta$ -methylpropane, methylcyclopropane being formed as an intermediate product. This result is in agreement with Kishner's rule (A., 1912, i, 245) that, when cyclopropane derivatives are ruptured and at the same time hydrogenated, the hydrogen combines with the most highly hydrogenated carbon atoms of the ring.

T. H. P.

**Constitution of the Benzene Nucleus with Reference to the Phenomenon of Di-substitution.** CECIL L. HORTON (*Chem. News*, 1914, **109**, 157).—An attempt to account for the phenomena generalised in Crum Brown's rule by considerations of the distribution of the valency in the nucleus. The author claims that the atoms or radicles, the presence of which in the benzene molecule determines the

formation of ortho- and para-disubstituted derivatives, are unsaturated, whilst the groups such as  $\text{CO}_2\text{H}$ ,  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{SO}_3\text{H}$ , which determine the production of meta-disubstituted derivatives, are saturated. The assertion is made that an unsaturated atom or group attached to carbon atom 1 of the nucleus has the effect of rendering carbon atoms 2 and 4 more reactive than 3, whilst a saturated group attached to 1 causes a distribution of the valency such that carbon atoms 3 and 5 are exceptionally reactive. Special hypotheses are advanced to bring into harmony with the author's theory radicals such as alkyl groups which are apparently saturated and yet determine the production of ortho- and para-disubstituted derivatives, and also the aldehyde group, which is essentially unsaturated and yet determines the formation of meta-disubstituted derivatives. C. S.

**Nitro-substituted Benzenes Obtained from the Corresponding Amino-derivatives.** W. KÖRNER and A. CONTARDI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 281—286. Compare this vol., i, 263).—Further use of the method (*loc. cit.*) of preparing nitro-compounds from amino-compounds by the spontaneous decomposition of the nitrites of the corresponding diazo-compounds has shown that aniline, and *o*-, *m*-, and *p*-nitroaniline only give traces of the nitro-derivatives when treated in this way. 2:6-Dibromosulphanilic acid, however, yields 1-nitro-2:6-dibromobenzene-4-sulphonic acid quantitatively, and 2-substituted dinitrobenzenes can also be prepared from the corresponding nitroanilines.

In the cases above-mentioned where the method is not applicable, the nitro-derivatives may be prepared, however, by employing a mixture of copper sulphate (1 mol.) and sodium or potassium nitrite (2 mols.) instead of the solution of sodium or potassium nitrite alone. In this way, *o*- and *p*-dinitrobenzene are readily obtained. The substitution of the  $\text{NH}_2$ -group of *m*-nitroaniline cannot be so effected, but occurs when *m*-nitroaniline is treated with enough nitric acid (D 1.38) to convert it into nitrate, and then treated with a cold solution of copper sulphate and sodium nitrite. After some hours the *m*-dinitrobenzene formed can be distilled with steam.

2-Chloro-1:4-dinitrobenzene,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{Cl}$ , forms almost colourless prisms, m. p.  $64^\circ$ . When heated for ten hours with alcoholic ammonia, it yields (1) 2:5-dinitroaniline (m. p.  $137^\circ$ ); (2) 4-nitro-*m*-phenylenediamine (orange-yellow needles, m. p.  $161^\circ$ ); (3) 2-chloro-4-nitroaniline.

2-Bromo-1:4-dinitrobenzene,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{Br}$ , crystallises in almost colourless needles or prisms, m. p.  $70^\circ$ , and with alcoholic ammonia behaves like the chloro-derivative.

2-Bromo-4-nitroaniline is conveniently prepared by acting on *p*-nitroaniline with bromine in glacial acetic acid solution.

2-Iodo-1:4-dinitrobenzene,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{I}$ , forms almost colourless needles or prisms, m. p.  $117.4^\circ$ . Alcoholic ammonia does not react with this substance at  $100^\circ$ . R. V. S.

**The Nitro-compounds of Toluene and Benzene.** W. WILL (*Ber.*, 1914, 47, 704—717).—In order to obtain some information on

the possible sources of danger in the manufacture of trinitrotoluenes for explosive purposes, a thorough investigation of the technical products, of nitrations under all possible conditions, and of the intermediate compounds has been undertaken. A full account of the work will appear in another place, but in the present communication an interesting review of this branch of the explosives industry is given, and the constitution of the nitro-derivatives of benzene and toluene is discussed.

Of the six possible trinitrotoluenes only three are known. The pure article of commerce, the so-called  $\alpha$ -trinitrotoluene, m. p.  $80.6^\circ$ , has been shown, by a number of syntheses and transformations, which are reviewed in this paper, to be 2:4:6-trinitrotoluene. The other derivatives are usually obtained by nitrating *m*-nitrotoluene. The  $\gamma$ -compound, m. p.  $104^\circ$ , has already been shown to be 2:4:5-trinitrotoluene, and this has now been confirmed by the nitration of 2:5- and of 3:4-dinitrotoluenes. The constitution of the remaining  $\beta$ -isomeride, m. p.  $112^\circ$ , was hitherto uncertain. The compound has now been obtained by nitrating 2:3-dinitrotoluene, and to the extent of 25% in the nitration of 3:4-dinitrotoluene. It has also been reduced to a dinitrotoluidine and then transformed into 2:4-dinitrotoluene. The compound is therefore 2:3:4-trinitrotoluene. These  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomerides are of practically the same value as explosives. They may be detected by means of acetone and ammonia, with which they give deep red, greenish-yellow, and blue colorations, respectively. The  $\alpha$ -compound is not so sensitive towards alkalis as the others. In alkaline, alcoholic solution it forms coloured salts (compare Hantzsch and Kissel, A., 1900, i, 89) which, under the simultaneous action of oxidising agents, give a hexanitrodiphenylethane, m. p.  $212^\circ$ . The  $\beta$ - and  $\gamma$ -compounds react even with 1% sodium carbonate or lead oxide and alcohol with the formation of dinitrotoloxides. In all three cases the salts are very explosive.

Numerous searches were made for other trinitrotoluenes or even higher nitro-derivatives in the products of nitration under all possible conditions, but without success. If the reaction is promoted by heat or pressure, either trinitrobenzoic acid or even tetranitromethane is obtained. The intense odour of the latter is sometimes observed in the factory, but the former, owing to its solubility, has escaped detection, but must be taken into account as the salts may be very dangerous. All the possible dinitrotoluenes are known, but only the 3:5-derivative could possibly give a fourth trinitrotoluene by nitration. The author has failed to obtain any trinitro-derivative from this source.

It is now also doubtful whether anything higher than a trinitro-derivative exists in the case of benzene. Nietzki (A., 1901, i, 196) described a tetranitrobenzene, m. p.  $116^\circ$ , which he obtained by oxidising a dinitrodinitrosobenzene, m. p.  $133^\circ$ . The latter compound was prepared by condensing picryl chloride with hydroxylamine in presence of sodium acetate. Drost (A., 1899, i, 751) nitrated *o*-dinitrosobenzene, and obtained a dinitro-derivative with m. p.  $172^\circ$ . These preparations have now been examined. Drost's compound is confirmed, whereas it is shown that Nietzki only used half the

required amount of sodium acetate, and that the product was impure, being Drost's compound mixed with picric acid.

Many attempts were made to oxidise the pure compound, but it was always recovered unchanged or destroyed. Nietzki's trinitrophenyl-hydroxylamine (*loc. cit.*) was also oxidised, but picric acid and trinitronitrosobenzene (*ibid.*) and not tetranitrobenzene were the products. Dinitrodinitrosobenzene gives the reactions which were assigned to tetranitrobenzene, and therefore this compound is to be cancelled.

J. C. W.

**Nitration of Toluene and of its Derivatives Chlorinated in the Side-chain.** A. F. HOLLEMAN [with J. VERMEULEN and W. J. DE MOOR] (*Rec. trav. chim.*, 1914, 33, 1—34).—The type of substitution caused by a complex group can be predicted if that which is caused by its component parts is known. Two cases can be distinguished in which the components direct a new substituent in the same or in the contrary sense. Thus the groups  $\text{-OAlk}$  and  $\text{-NAlk}_2$  direct the nitro-group or the halogen atom towards the ortho-para-position, as do the  $\text{-OH}$  and  $\text{-NH}_2$  groups on the one hand and the alkyl groups on the other. In the second case, the velocities of substitution caused by the different groups are rendered evident. Thus the carboxyl group is composed of  $\text{-CO}$  directing towards the meta-position and  $\text{-OH}$  directing to the ortho-para-positions; the velocity of substitution caused by  $\text{-OH}$  is greater than that caused by other groups directing to the same positions, and thus, when  $\text{-OH}$  is replaced by  $\text{-NH}_2$ ,  $\text{-OAlk}$ ,  $\text{-Cl}$ ,  $\text{-H}$ ,  $\text{-CH}_3$ , the new complex groups should direct new substituents to the meta-position, as is found to be the case.

In order further to study the directive action of complex groups, the author has investigated the nitration of toluene and of its derivatives chlorinated in the side-chain. On the one hand, it is to be expected that the groups  $\text{-CH}_2\text{Cl}$ ,  $\text{-CHCl}_2$  and  $\text{-CCl}_3$  would direct the nitro-group to the ortho-para-positions, as do  $\text{-CH}_3$  and  $\text{-Cl}$ , whilst on the other hand the close relationship of benzylidene chloride and benzotrichloride to benzaldehyde and benzoic acid respectively might lead to the supposition that meta-derivatives would be formed.

The nitration of toluene itself has already been studied by van den Arend (*Rec. trav. chim.*, 1909, 28, 408). A repetition of the work has disclosed certain errors which have been corrected. Further, it has been found that nitration of the compounds  $\text{Ph}\cdot\text{CHCl}_2$  and  $\text{Ph}\cdot\text{CCl}_3$  can only be satisfactorily accomplished in the presence of acetic anhydride. Toluene has therefore been nitrated under the same conditions. *p*-Nitrotoluene has m.p.  $51\cdot4^\circ$  instead of  $54^\circ$  recorded in the literature and  $54\cdot4^\circ$  given by van den Arend (*loc. cit.*). *o*-Nitrotoluene has  $n^{21}_{\text{D}}$   $1\cdot5462$ , whilst under the same conditions the meta- and para-isomerides have  $1\cdot5470$  and  $1\cdot5554$  respectively, the latter value being calculated from the refraction of a mixture of the ortho- and para-isomerides.

For the nitration of toluene, nitric acid ( $D_{1\cdot475}$ ) is gradually added to toluene at  $30^\circ$ , and the product is distilled. Determination of the index of refraction of the first and last portions of the distillate shows the absence of unchanged toluene and of dinitrotoluenes respectively.

The relative amounts of the isomeric nitrotoluenes are in close agreement with those found by van den Arend.

When a mixture of pure nitric acid and acetic anhydride is gradually added to toluene at 30°, a violent reaction occurs; the product contains 37.3% *p*-, 57.7% *o*-, and 4.4% *m*-nitrotoluene, so that the proportions of the isomerides are not sensibly modified by the presence of acetic anhydride. The ortho-, meta- and para-isomerides have  $n^{62.5}$  1.5271, 1.5275 and 1.5346 respectively.

*o*-Nitrobenzyl chloride, prepared by the method of Gabriel and Borgmann (A., 1883, 1121), has m. p. 47.9°,  $n^{61.5}$  1.5557. The meta-isomeride has m. p. 44.8°,  $n^{61.5}$  1.5577, whilst the para-compound has m. p. 72.4°,  $n^{61.5}$  1.5647, the latter value being deduced by extrapolation from the index of refraction of a mixture of the meta- and para-isomerides.

A carefully purified commercial specimen of benzyl chloride is treated with nitric acid in the manner described for toluene, the product poured into water, extracted with benzene, and the extract washed until free from acid and then dried over sodium sulphate. The benzene is distilled and the residue heated for several hours on the water-bath under diminished pressure in a current of carbon dioxide to remove the last traces of benzene and any unchanged benzyl chloride. It is finally distilled under about 1 mm. pressure. (Experiments with synthetic mixtures of the three nitrobenzyl chlorides have shown that an alteration in composition is not affected by this treatment.) Determination of the index of refraction of the first and last portions of the distillate shows the absence of unchanged benzyl chloride and of polynitro-compounds. Thermal analysis of the product shows the proportions, 54.9% of the para-, 40.9% of the ortho-, and 4.2% of the meta-isomeride.

*o*-Nitrobenzylidene chloride (compare Kliegl, A., 1908, i, 82) has m. p. 25.7°. *m*-Nitrobenzylidene chloride (Widman, A., 1880, 635; Ehrlich, A., 1883, 54) melts at 64.5°, whilst the para-isomeride (Zimmermann and Miller, A., 1885, 771) has m. p. 42.8°.

Benzylidene chloride, m. p. -16.4°, is nitrated in the manner described for benzyl chloride. During the process, a small proportion of the chlorine is eliminated. Thermal analyses of the product by the methods of Valetton and van der Linden give as mean results, 42.9% of the para-, 23.3% of the ortho-, and 33.8% of the meta-isomeride.

Since the presence of *o*-nitrobenzylidene chloride in the product of the nitration of benzylidene chloride has not previously been proved, a special search has been made for it in the following manner: the oily nitration product is kept, when a small quantity of the meta-isomeride crystallises. After separation, the liquid portion is heated with concentrated sulphuric acid until hydrogen chloride ceases to be evolved, and the product poured into water and oxidised by boiling permanganate. For the separation of the three nitrobenzoic acids, the crude mixture is treated with chloroform, when the bulk of the para-acid remains undissolved. The soluble acids are converted into their barium salts, and after separation of the sparingly soluble barium *m*-nitrobenzoate, a small amount of a readily soluble barium salt is obtained, from which mineral acids liberate *o*-nitrobenzoic acid.

Nitro-derivatives of benzotrichloride have not previously been described. Since preliminary experiments indicated that their isolation would be a matter of difficulty, the author has attempted to analyse the nitration product of benzotrichloride by converting it into the corresponding mixture of acids and investigation of the latter.

Commercial specimens of benzotrichloride contain a varying amount of chlorine in the nucleus. By repeated solidification and partial melting of such products, however, a pure material is obtained. Nitration is effected in the manner already described. Saponification of the nitro-compounds is very difficult, owing to the formation of resinous products. The best method consists in boiling the nitro-compound under reflux with hydrochloric acid, the mixture being very vigorously agitated, followed by purification by sublimation under 1 mm. pressure. Qualitative analysis of the mixed nitrobenzoic acids is effected in the manner described above. In this manner, *p*- and *m*-nitrobenzoic acids are readily identified. In place of *o*-nitrobenzoic acid expected, however, *o*-chlorobenzoic acid, m. p.  $137^{\circ}$ , is obtained, replacement of the  $-\text{NO}_2$  group by Cl taking place during saponification, since *o*-nitrobenzoic acid itself is found to be practically unaffected by boiling hydrochloric acid under the experimental conditions adopted. The quantitative, thermal analysis of the mixture of acids is therefore carried out on the assumption that the *o*-nitrobenzoic acid has been quantitatively converted into *o*-chlorobenzoic acid, and the proportions thus found are: 28.7% of the para-, 6.8% of the ortho-, and 64.5% of the meta-isomeride.

The introduction of the first chlorine atom into the methyl group does not thus change the type of substitution, the quantity of the para-isomeride being, however, increased at the expense of the ortho-isomeride. When a second chlorine atom is present, the type of substitution is completely altered, the quantity of meta-isomeride being greatly increased, whilst in the presence of a third chlorine atom, the increase is yet more marked. On comparison of the nitration products under investigation with those of benzaldehyde and benzoic acid, the directing action of the chlorine atom towards the ortho-para-positions is marked, since although the relative amount of *m*-nitrobenzaldehyde formed in the nitration of benzaldehyde is not exactly known, it is certainly greater than 70%.  
H. W.

**Direct Formation of Isomeric Nitrobenzenesulphonic Acids. Auto-orientation of Entering Substituents.** JUL. OBERMILLER (*J. pr. Chem.*, 1914, [ii], 89, 70—86).—According to Limpricht (this Journ., 1875, 1027) both the sulphonation of nitrobenzene and the nitration of benzenesulphonic acid gives rise to small amounts of *o*- and *p*-nitrobenzenesulphonic acids, the main product consisting of the meta-isomeride.

The author finds, however, that in the sulphonation of nitrobenzene no ortho-acid is formed, whilst the para-isomeride is produced to the extent of only 2%. On the other hand, the nitration of benzenesulphonic acid in sulphuric acid solution yields considerable amounts (up to 50%) of the ortho- and para-compounds, the former being

produced in far larger amount than the para-isomeride; the proportion of *m*-nitrobenzenesulphonic acid formed in the reaction diminishes with rise of temperature and with the amount of sulphuric acid employed.

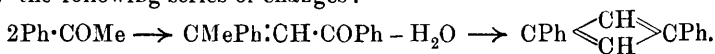
The formation of such a large amount of the ortho-isomeride in the nitration of benzenesulphonic acid is ascribed to the tendency of the nitro-group to take up the nearest possible position to a substituent already present in the benzene nucleus, a tendency which the author refers to a kind of "auto-orientation" and is not shared with the sulphonic acid group.

The position occupied by an entering group is thus dependent on the nature of the group, and is not determined solely by the nature of the substituents already present in the nucleus as maintained by Holleman.

The separation of the three nitrobenzenesulphonic acids is effected by a complicated fractionation of their *calcium*, *barium*, *ammonium* and *potassium* salts. In addition to the above, the *magnesium* and *zinc* salts are described.

The chlorides of the *o*-, *m*-, and *p*-nitrobenzenesulphonic acids have m. p. 68—69°, 63—64°, and 80° respectively, the amides, m. p. 193°, 167—168°, 179—180° (compare Ekbohm, A., 1902, i, 274). F. B.

*s*-Diphenylcyclobutadiene. I. C. GASTALDI and F. CHERCHI (*Gazzetta*, 1914, **44**, i, 282—286).—Claisen (A., 1887, 575) has shown that the condensation of equimolecular proportions of ethyl benzoate and acetophenone in presence of sodium ethoxide yields the sodium derivative of enolic dibenzoylmethane. The authors find that the latter is not the sole product, but that it is accompanied by a hydrocarbon,  $C_{16}H_{12}$ , which is also obtained by heating acetophenone with sodium ethoxide in absence of ethyl benzoate and is apparently formed by the following series of changes:



Phenylmethylcarbinol is also formed.

*Diphenylcyclobutadiene*, thus obtained, crystallises in large, stable, prismatic plates, m. p. 130°, exhibits normal cryoscopic behaviour in benzene, and resists attack when fused with a mixture of sodium and potassium hydroxides. It is readily oxidised by nitric acid, giving principally *p*-nitrobenzoic acid and carbon dioxide. It yields (1) a *disulphonic acid*, the *sodium*,  $C_{16}H_{10}(SO_3Na)_2 \cdot 2H_2O$ , and insoluble *barium* salts of which were prepared, and (2) an isomeric *disulphonic acid*, giving a readily soluble *barium* salt and the *sodium* salt,  $C_{16}H_{10}(SO_3Na)_2 \cdot 6H_2O$ . T. H. P.

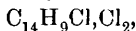
**Some Chloro-substitution and Additive Products of Anthracene.** C. LIEBERMANN and M. BEUDET (*Ber.*, 1914, **47**, 1011—1015).—The authors have examined the action of chlorine on 1- and 2-mono- and 1:5- and 1:8-di-chloroanthracenes, and find that anthracenes substituted in the  $\alpha$ -position yield additive products, whereas, in the  $\beta$ -chloroanthracenes, substitution of the hydrogen in the *meso*-position appears to be facilitated, so that the isolation of

pure additive products is difficult. Addition of the chlorine atoms is shown to take place in the positions 9 and 10, since the products, when boiled with alcohol or dilute alcoholic potassium hydroxide, lose a half of the added chlorine and are converted into mono-*meso*-substituted compounds. Further, on oxidation with an excess of chromic acid in acetic acid solution, they are converted into the same chloroanthraquinones, which serve as original material for the chloroanthracenes.

The products are prepared by leading a current of dry chlorine into a cooled solution of the requisite chloroanthracene in chloroform or carbon tetrachloride, or, preferably, by the addition of a freshly saturated solution of chlorine in carbon tetrachloride (containing 7—8% free chlorine) to the chloroanthracene previously moistened with the same solvent. The solutions are preserved in the dark until the desired products have separated. The mother liquors contain additive products, mixed, however, with some substitution products; since the separation of these is difficult, it is preferable to add an excess of chlorine, and to allow the mixture to remain for twenty-four hours. In this process, the hydrogen atoms in the positions 9 and 10 only are replaced.

Anthraquinones, chlorinated in the positions 1-, 2-, 1:5-, 1:8-, are reduced to the corresponding anthracenes by the action of zinc dust and ammonia (Schilling, A., 1913, i, 494) and the products freed from anthranols by boiling with dilute aqueous alcoholic potassium hydroxide. The additive products are pure white, give non-fluorescent solutions, and melt with evolution of gas. Of the chloroanthracenes substituted in the benzene nucleus, the  $\beta$ -compound is white, the  $\alpha$ -compound pale yellowish-white; their solutions do not fluoresce. On the other hand, when substitution has also occurred in the *meso*-groups, the compounds are strongly coloured, and their solutions strongly fluorescent.

1-Chloroanthracene yields 1-chloroanthracene 9:10-dichloride,



m. p. 128° (decomp.), which is transformed into 1:9- or 1:10-dichloroanthracene, yellow needles, m. p. 127—128°, by protracted boiling, and is oxidised by chromium trioxide in glacial acetic acid solution to 1-chloroanthraquinone, m. p. 162°. 1:9:10-Trichloroanthracene,  $\text{C}_{14}\text{H}_7\text{Cl}_3$ , yellow needles, m. p. 147°, is obtained from the mother liquors, and yields 1-chloroanthraquinone on oxidation.

1:5-Dichloroanthracene gives rise to 1:5-dichloroanthracene 9:10-dichloride, m. p. 205—223° (decomp.). Alcoholic potassium hydroxide converts it into 1:5:9-trichloroanthracene, yellow needles, m. p. 162°, which is oxidised to 1:5-dichloroanthraquinone, m. p. 246°.

1:5-Dichloroanthracene 9:10-dibromide,  $\text{C}_{14}\text{H}_7\text{Cl}_2\text{Br}_2$ , m. p. 186° (decomp.), is obtained by the action of a large excess of bromine in carbon tetrachloride solution, and is readily oxidised to 1:5-dichloroanthraquinone.

1:8-Dichloroanthracene 9:10-dichloride is a white, crystalline powder, m. p. 183—185° (decomp.). Alcoholic potassium hydroxide transforms it into 1:8:10- or 1:8:9-trichloroanthracene, yellow needles, m. p. 190°.



1:8-Dichloroanthracene 9:10-dibromide forms white crystals, which soften with slow evolution of gas at 165—180°.

2-Chloroanthracene 9:10-dichloride has not been obtained free form substitution products. On the other hand, 2:9:10-trichloroanthracene, lemon-yellow needles, m. p. 178°, is readily obtained by the use of a large excess of chlorine. It is converted by oxidation into 2-chloro-anthraquinone, m. p. 208°.

Comparison of results obtained with the chlorinated anthracenes and anthraquinones shows that here, as in the naphthalene series, the  $\alpha$ -compounds have lower m. p.'s than the corresponding  $\beta$ -compounds, whilst the 1:8-products melt at lower temperatures than the more symmetrical 1:5-products.

On account of its high m. p., the above 1:8:9- or 1:8:10-trichloro-anthracene probably has the latter constitution. H. W.

Carbamates as Intermediate Products in the Hofmann Degradation of Amides. ERNST MOHR (*J. pr. Chem.*, 1914, [ii], 89, 208. Compare A., 1906, i, 357).—That carbamates are formed as intermediate products in the conversion of amides into amines by the Hofmann reaction was first shown by Hoogewerff and van Dorp (A., 1889, 981). F. B.

Methyltrimethyleneamine [ $\alpha$ -cycloPropylethylamine] and its Behaviour towards Nitrous Acid. N. J. DEMJANOV and S. A. PINEGIN (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 58—61).— $\alpha$ -cyclo-

Propylethylamine,  $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CHMe} \cdot \text{NH}_2$ , obtained by the reduction

of cyclopropyl methyl ketoxime with sodium and absolute alcohol, is a colourless, mobile liquid with an ammoniacal odour, b. p. 94.2—94.8°/745 mm.,  $D_4^{20}$  0.8229,  $D_4^{25}$  0.8019,  $D_4^{30}$  0.8032,  $n_D^{25}$  1.4265, optical exaltation 0.68. Its hydrochloride and platinichloride were prepared. When heated, the nitrite of the amine is converted into cyclopropylmethylcarbinol. T. H. P.

Iodo-compounds obtained with *o*-Nitroaniline and *o*-Nitrosulphanilic Acid. PAUL BRENANS (*Compt. rend.*, 1914, 158, 717—720 \*).—The author has repeated the work of Körner and Contardi (compare A., 1907, i, 117) and has shown, by similarity in properties and the method of mixed melting points, that the iodo-derivatives of nitroaniline and nitrobenzene obtained by them are identical with those previously obtained by him (compare A., 1902, i, 673) and have the constitution assigned to them by him, rather than that given by Körner and Contardi. In support of this he has converted his 4-iodo-2-nitroaniline into 2:5-di-iodoaniline, and this in turn into 1:4-di-iodobenzene, m. p. 129°, obtaining in the last reaction some di-iodophenetole, m. p. 46°. An iodonitroaniline having the constitution assigned to it by Körner and Contardi (*loc. cit.*) would have yielded 1:2-di-iodobenzene by this process. Finally he has obtained 1:2:4-tri-iodobenzene from his 2:5-di-iodoaniline, identical

\* and *Bull. Soc. chim.*, 1914, [iv], 15, 375—384.

in every respect with that tri-iodobenzene already prepared by Körner and Belasio (compare A., 1908, i, 778). W. G.

**Preparation of a Sparingly Soluble Compound of Dimethylaniline, Benzyl Chloride, and Zinc Chloride.** CHEMISCHE FABRIK ROHNER & Co. (Swiss Patent 64016).—*Phenylbenzyl dimethylammonium zincchloride*,  $(\text{CH}_2\text{Ph}\cdot\text{NMe}_2\text{Ph})_2\text{ZnCl}_4$ , is obtained by mixing molecular quantities of benzyl chloride and dimethylaniline with an aqueous solution of zinc chloride containing at least half a molecule of the salt. It forms compact crystals, which are very sparingly soluble in water. J. C. C.

**Action of Acid Anhydrides and Chlorides on Tertiary Benzylamines [Fission at the Nitrogen Atom].** M. TIFFENEAU and K. FUHRER (*Bull. Soc. chim.*, 1914, [iv], 15, 162—175).—The authors have examined the action of a number of acid anhydrides and chlorides on amines and find that fission at the nitrogen atom can be effected by these reagents solely in those cases in which the amine has the structure  $\text{Ar}\cdot\text{CH}_2\cdot\text{NRR}'$ . This is in general agreement with the experiments of von Braun (A., 1900, i, 430, 641, 657) on the fission of bases by cyanogen bromide, since, although the latter substance seems universally applicable, its reaction is most marked when the amine contains the benzyl group. The action is attributed to the intermediate formation

of compounds of the type 
$$\begin{array}{c} \text{Ar}\cdot\text{CH}_2 \\ \text{Me}\cdot\text{CO}\cdot\text{O} \end{array} \rangle \text{NAcRR}'$$
, which are

subsequently decomposed by heat in the manner indicated by the dotted lines.

The reagents usually employed are acetic anhydride, benzoic anhydride, and benzoyl chloride, but equally favourable results have been obtained with butyric anhydride. Succinic anhydride reacts energetically, evolving carbon dioxide and yielding a charred mass which has not been completely investigated. Mixed anhydrides, such as acetic butyric anhydride, react as if they consisted of a mixture of the simple anhydrides; formic acetic anhydride (compare Béhal (*Ann. Chim. Phys.*, 1908, [vii], 19, 274) reacts in the cold with formation of carbon monoxide and the acetate of the base just as in the case of other tertiary bases.

Benzyl dimethylamine (compare Jackson and Wing, A., 1887, 721; Baillie and Tafel, A., 1899, i, 268; Emde, 1909, i, 707) has b. p. about  $67\text{--}68^\circ/14\text{ mm.}$ ,  $178^\circ/\text{ordinary pressure}$ ,  $D_0\ 0.915$ . Its hydrochloride has m. p.  $175^\circ$ , methiodide, m. p.  $178\text{--}179^\circ$ , and methochloride, m. p.  $243^\circ$ , whereas Emde (*loc. cit.*) gives  $235^\circ$ . When heated with acetic anhydride and sodium acetate during fifteen hours at  $200^\circ$ , the base yields dimethylacetamide and benzyl acetate; with benzoyl chloride it gives benzyl chloride, benzyl dimethylamine hydrochloride, and dimethylbenzamide.

*p*-Methylbenzyl dimethylamine, b. p.  $197\text{--}198^\circ$  (methiodide, m. p.  $208^\circ$ ), yields dimethylacetamide and *p*-methylbenzyl acetate, b. p.  $220^\circ$ , after prolonged treatment at  $100^\circ$ .

*p*-Methoxybenzyl dimethylamine (compare Tiffeneau, A., 1911, i,

778) is transformed by acetic anhydride into dimethylacetamide and anisyl acetate, b. p. about 137—139°/12 mm.,  $D^{20}$  1.1014; butyric anhydride converts it into dimethylbutyramide and anisyl butyrate, whilst, with benzoic anhydride at 180°, it yields dimethylbenzamide, m. p. 41°, and anisyl benzoate, m. p. 38°.

2-*p*-Methoxybenzyl-1:3-dihydroisoindole is converted by acetic anhydride into anisyl acetate and 2-acetyl-1:3-dihydroisoindole (A., 1911, i, 810).

When *p*-hydroxybenzyl dimethylamine is heated under reflux with acetic anhydride, it gives dimethylacetamide and *p*-acetoxybenzylacetate, b. p. 155—157°/11 mm.,  $D^{19}$  1.156.

$\alpha$ -Dimethylamino-*a-p*-methoxyphenylpropane,  
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt}\cdot\text{NMe}_2$   
 (Tiffeneau, Thèse, Paris, 1910), has b. p. 133—135°/15 mm.,  $D^0$  0.9834 (methiodide, m. p. 164.5°). With boiling acetic anhydride, it yields methoxyphenylpropyl acetate, dimethylacetamide, and small quantities of anethole.

Boiling acetic anhydride converts 2:3-dimethoxybenzyl dimethylamine into dimethylacetamide and 2:3-dimethoxybenzyl acetate, b. p. 278—280°/760 mm. (compare Douetteau, A., 1912, i, 620).

2:4-Dimethoxybenzyl dimethylamine gives dimethylacetamide and veratryl acetate with acetic anhydride; with benzoic anhydride it yields dimethylbenzamide and veratryl benzoate, which, however, could not be induced to crystallise.

3:4-Methylenedioxybenzyl dimethylamine is almost quantitatively converted by acetic anhydride into dimethylacetamide and piperonyl acetate, m. p. 21°.

Ethyl  $\alpha$ -dimethylaminophenylacetate,  $\text{NMe}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  (Tiffeneau and Fournau, A., 1913, i, 1338), is unchanged by treatment with acetic anhydride for seven hours at 200°; fission could be effected by benzoyl chloride, but the bulk of the ester remained unchanged after eight hours' heating at 100°.

*Bases with which acid anhydrides and chlorides do not cause fission at the nitrogen atom.*—*p*-Methoxybenzylamine, anisylamine, and *p*-methoxybenzylmethylamine are converted by prolonged boiling with acetic anhydride into the corresponding acetamides.

Acetic anhydride does not react with dimethylaniline at 250°.

$\beta$ -Phenylethyl dimethylamine (compare Barger, T., 1909, 95, 2193; von Braun, A., 1911, i, 35) has b. p. 203—205°,  $D^0$  0.914 (hydrochloride, m. p. 171°; hydriodide, m. p. 108°; methiodide, m. p. 232°). It is scarcely affected by acetic anhydride at 235°. Nevertheless, a small fraction, b. p. 170—173°/15 mm., can be isolated from the product of the reaction, which contains nitrogen, and in which the acetyl group has possibly entered the nucleus. The presence of phenylethyl acetate or of dimethylacetamide could not be detected.

$\gamma$ -Phenylpropyl dimethylamine, b. p. 222—224°/760 mm., 117—118°/26 mm. (methiodide, m. p. 178°, hydrochloride, m. p. 146°) (compare von Braun, A., 1911, i, 35), is not acted on by acetic anhydride below 200°; at 220—230°, the fission characteristic of benzylamines is not observed, but, as in the preceding case, small quantities of a fraction,

b. p. 160—210°/27 mm., can be obtained, in which one or more acetyl groups have probably entered the nucleus.

isoAmyldihydroisoinsole,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > N \cdot C_5H_{11}$ , b. p. 262—263°/756 mm., 144—146°/14 mm.,  $D_0$  0.9503 (hydrobromide, m. p. 208°, methiodide, m. p. 138°), is obtained by the action of *o*-xylylene bromide on isoamylamine in alcoholic solution. It is mainly recovered unchanged after treatment with acetic anhydride for six hours at 180°, but a small fraction, b. p. 160—280°/14 mm., is also obtained, the composition of which is uncertain.

Horde-nine,  $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_3$ , when heated with acetic anhydride for eight hours at 150°, yields acetylhorde-nine, b. p. 175—176°/32 mm.,  $D_0$  1.037 (hydriodide, m. p. 177—178°, methiodide, m. p. 273°). Treatment at 200° yields a practically identical result.

$\beta$ -Dimethylamino- $\alpha$ -phenylethanol,  $OH \cdot CHPh \cdot CH_2 \cdot NMe_3$  (compare Tiffeneau and Fourneau, A., 1913, i, 1337), b. p. 132—133°/15 mm., yields the corresponding acetate (methiodide, m. p. 194°) when boiled with acetic anhydride.

H. W.

**Catalytic Action of Iodine.** F. KNOEVENAGEL [and, in part, with HASKEL ITZKO BERLIN, DANIEL SAKOM, HERMANN DIETERICH, and I. MOSES] (*J. pr. Chem.*, 1914, [ii], 89, 1—50).—In the preparation of thiodiarylamines by the action of sulphur on diarylamines, the addition of 0.05—2% iodine not only lowers the temperature at which the reaction takes place and considerably shortens the time necessary for its completion, but also yields a much purer product. A similar effect has also been observed in the following reactions: (1) the formation of aryl-naphthylamines by the condensation of aromatic amines with the naphthols and naphthylamines; (2) the alkylation of aniline and  $\alpha$ -naphthylamine by the direct action of alcohols; (3) anil formation with ketones and aromatic amines; (4) sulphonation; (5) oxidation.

Thiodiphenylamine is obtained in almost quantitative yield by heating diphenylamine and sulphur at 180—190° for ten minutes with 1% iodine. Of the thiodiarylamines prepared in this manner, the following are new: *thio-m-chlorophenyl- $\beta$ -naphthylamine*, m. p. 163°, from *m-chlorophenyl- $\beta$ -naphthylamine*; *thio-m-chlorophenyl- $\alpha$ -naphthylamine*, m. p. 172°; *thio-m-tolyl- $\beta$ -naphthylamine*, m. p. 168—169°.

The preparation of the aryl-naphthylamines described below was accomplished by heating  $\alpha$ - or  $\beta$ -naphthol with the requisite aromatic amine for several hours at 180—200°, in the presence of 1% iodine: *o-chlorophenyl- $\beta$ -naphthylamine*, b. p. 236—238°/13.5 mm., m. p. 89°; *m-chlorophenyl- $\beta$ -naphthylamine*, b. p. 250—253°/11 mm., m. p. 101°; *m-chlorophenyl- $\alpha$ -naphthylamine*, b. p. 245—248°/13 mm.; *p-chlorophenyl- $\beta$ -naphthylamine*, b. p. 251.5°/13 mm., m. p. 101°; *p-chloro-o-tolyl- $\beta$ -naphthylamine*, b. p. 262—264°/15.5 mm., m. p. 75°. Attempts to condense *o*- and *p*-chloroaniline with  $\alpha$ -naphthol, and  $\alpha$ -chloro- $\beta$ -naphthol with aniline resulted in the formation of phenyl- $\alpha$ - and - $\beta$ -naphthylamines respectively, the chlorine being eliminated during the reaction. The aryl- $\alpha$ -naphthylamines are also readily formed by heating  $\alpha$ -naphthylamine with aniline and its derivatives at 240—250°

in the presence of iodine: *o*-methoxyphenyl- $\alpha$ -naphthylamine from *o*-anisidine has b. p. 226—228°/11 mm., m. p. 99·5°; *m*-chlorophenyl- $\alpha$ -naphthylamine, b. p. 238—241°/12 mm., m. p. 72·5°; *p*-chlorophenyl- $\alpha$ -naphthylamine, m. p. 102—103°. *o*-Tolyl- $\alpha$ -naphthylamine has b. p. 198—202°/9 mm., and does not solidify even at a low temperature (Friedländer, A., 1884, 80, gives m. p. 94—95°). *m*-Tolyl- $\alpha$ -naphthylamine has b. p. 234—237°/11 mm.; *p*-tolyl- $\alpha$ -naphthylamine, b. p. 230°/10 mm., m. p. 78°; *m*-xylyl- $\alpha$ -naphthylamine, b. p. 227—232°/9 mm.

When heated alone with iodine,  $\beta$ -naphthylamine yields  $\beta\beta$ -dinaphthylamine, whilst *p*-aminophenol gives rise to di-*p*-hydroxydiphenylamine, which has m. p. 169°, and forms a triacetyl derivative, m. p. 132·5° (compare Schneider, A., 1899, i, 499).

On treatment with iodine (2 atoms) in alcoholic solution, *o*-phenylenediamine is converted into 2:3-diaminophenazine.

*m*- and *p*-Phenylenediamines react with  $\alpha$ - and  $\beta$ -naphthols to form the corresponding dinaphthylphenylenediamines.

The preparation of methyl-, dimethyl-, ethyl-, diethyl-, *iso*amyl-, di*iso*amyl-, benzyl-, and dibenzyl-aniline by heating aniline with the necessary alcohol and a little iodine at 230—240° is also described.

$\alpha$ -Naphthylamine and methyl or ethyl alcohol yield only the monoalkyl derivative.  $\beta$ -Naphthylamine and ethyl alcohol give rise to naphthalene and  $\beta\beta$ -dinaphthyl, the alcohol being reduced to acetaldehyde; if the alcohol is in considerable excess or if methyl alcohol is employed, only  $\beta\beta$ -dinaphthylamine is produced.

2:3-Diphenyldiaminonaphthalene, prepared from 2:3-dihydroxynaphthalene and aniline, crystallises in lustrous, silvery needles, m. p. 143°.

Of the large number of anils obtained by the condensation of aromatic ketones and amines in the presence of iodine, the following have not hitherto been described: *Benzildi-o-tolil*, yellow plates, m. p. 143°. *Benzilmono-m-tolil*, yellow plates, m. p. 91°. *Benzildi-m-tolil*, yellow leaflets, m. p. 106°. *Benzil-p-hydroxyanil*, lustrous, yellow leaflets, m. p. 185°. *Benzoin-m-tolil*, yellow cubes, m. p. 129°. *Benzoin-o-chloroanil*, white needles, m. p. 120°. *Benzoin-m-chloroanil*, white needles, m. p. 127°. *Benzoin-p-chloroanil*, white needles, m. p. 136°. *Benzoin- $\alpha$ -naphthil*, light yellow cubes, m. p. 101°.  $\beta$ -*Isatin-o-tolil*, lustrous, yellow leaflets, m. p. 178—179°.  $\beta$ -*Isatin-m-tolil*, yellow needles, m. p. 238°.  $\beta$ -*Isatin-p-tolil*, yellow needles, m. p. 217—218°.  $\beta$ -*Isatin-o-nitroanil*, reddish-yellow needles, m. p. 146—147°.  $\beta$ -*Isatin- $\alpha$ -naphthil*, dark red, lustrous needles, m. p. 243°.  $\beta$ -*Isatin- $\beta$ -naphthil*, brownish-yellow needles, m. p. 216°.

Benzophenoneanil as obtained by the above method has m. p. 112°, and is converted into an isomeride of m. p. 117° by heating to 130° and then cooling in liquid air. The reverse transformation is effected by heating the less fusible isomeride at 130° and allowing it to cool slowly.

Benzilmonoanil has m. p. 96°, and slowly passes into a modification of m. p. 105° when kept.

*p*-Nitrosodimethylaniline condenses with aniline in the presence of iodine, yielding *p*-dimethylaminoazobenzene, which forms dark yellow

leaflets, m. p. 117°. The condensation of the nitroso-compound with 2 : 4-dinitrotoluene is also described. F. B.

**Action of Nitric Acid on the Phenylcarbamides.** J. F. L. REUDLER (*Rec. trav. chim.*, 1914, 33, 35—84).—The author has examined the action of nitric acid alone and in conjunction with sulphuric acid on phenylcarbamide, *as*-diphenylcarbamide, *s*-diphenylcarbamide, triphenylcarbamide, and tetraphenylcarbamide. In general, nitric acid, D<sup>15</sup> 1·5204, containing 99·7% HNO<sub>3</sub> has been employed.

2 : 4-Dinitrophenylnitrocarbamide,  $C_6H_3(NO_2)_2 \cdot NH \cdot CO \cdot NH \cdot NO_2$ , pale yellow needles, which commence to decompose with the formation of a red sublimate at 142° and disengage gas copiously at 12° or 15° higher according to the rate of heating, is obtained by the gradual addition of finely divided phenylcarbamide to twelve times its weight of nitric acid cooled in a mixture of ice and salt. When heated with water, it evolves equal volumes of nitrous oxide and carbon dioxide and yields 2 : 4-dinitroaniline, m. p. 179°, in accordance with the equation:  $C_7H_5O_7N_5 = C_6H_5O_4N_3 + CO_2 + N_2O$  (compare Griess, *Ber.*, 1869, 2, 434). Treatment with aqueous ammonia gives the same product, but when suspended in ether at 0° and treated with a current of dry ammonia, 2 : 4-dinitrophenylcarbamide, softening at 176° and decomposing with evolution of gas at about 200°, is formed. It dissolves in hot alcohol without evolution of nitrous oxide, and, on cooling, 2 : 4-dinitrophenylethylurethane, pale yellow needles, m. p. 109°, is obtained, the constitution of which follows from its identity with the substance prepared by the action of ethyl chloroformate on *p*-nitroaniline and subsequent nitration of the product so obtained (compare Hager, A., 1885, 149; Rudolph, A., 1879, 921).

2 : 4-Dinitrophenylnitrocarbamide is also obtained when a cooled solution of phenylcarbamide in concentrated sulphuric acid is added to a well-cooled mixture of pure nitric and concentrated sulphuric acids.

Further confirmation of the constitution of 2 : 4-dinitrophenylnitrocarbamide has been obtained by a study of the nitration of the nitrophenylcarbamides. These are obtained by the interaction of carbonyl chloride and the requisite nitroaniline in toluene solution and treatment of the resulting product with ammonia (compare Vittenet, A., 1899, i, 692). The *o*-, *m*- and *p*-nitrophenylcarbamides have m. p. 181°, 196°, and 238° respectively. The latter, when nitrated in the manner previously described, gives an almost quantitative yield of 2 : 4-dinitrophenylnitrocarbamide without formation of isomerides. The ortho-compound, on the other hand, gives the same product in 65—70% yield, whilst, in addition, 2 : 6-dinitroaniline (Bamberger and Hoff, A., 1900, i, 435), m. p. 138°, can be obtained from the mother-liquors. The latter is probably formed by the action of water on 2 : 6-dinitrophenylnitrocarbamide, but this substance could not be isolated. The nitration of *m*-nitrophenylcarbamide gives a mixture of products which could not be separated from one another; however, by boiling the crude substance with water and converting the nitroanilines so formed into their acetyl derivatives, it has been found possible to isolate 2 : 3-dinitro-

acetanilide, m. p. 186°, and 2:5-dinitroacetanilide, m. p. 121°. A third substance, possibly 3:4-dinitroacetanilide, is also present but in amount insufficient for its isolation.

When *as*-diphenylcarbamide is treated with ten times its weight of pure nitric acid and the product immediately, or after regaining the ordinary temperature, is poured into water a mixture of substances is obtained which cannot be purified. Nitric acid (D 1·48) or a mixture of nitric and acetic acids does not give a better result. If, however, the weight of pure nitric acid is reduced to five times that of the diphenylcarbamide, nitration takes place quietly and *as*-4:4'-dinitrodiphenylcarbamide,  $[\text{C}_6\text{H}_4(\text{NO}_2)]_2\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , pale yellow needles decomposing at 182—186° according to the rate of heating, is formed. The same product is obtained by the addition of a mixture of sulphuric and pure nitric acids to a solution of *as*-diphenylcarbamide in concentrated sulphuric acid. Its constitution is proved by its conversion by dilute alcoholic alkali at the ordinary temperature into 4:4'-dinitrodiphenylamine (Bamberger, A., 1898, i, 366). Indications of the presence of the isomeric *as*-2:4'-dinitrodiphenylcarbamide in the crude product of nitration were also observed.

The nitration of *as*-diphenylcarbamide by a large excess of pure nitric acid in the presence of sulphuric acid has also been investigated. At the temperature of a freezing mixture of ice and salt, reaction proceeds quietly, but if the mixture is allowed to attain the ordinary temperature, a vigorous disengagement of gas occurs. If the product is now poured into water and crystallised from dilute acetic acid, *as*-2:4:2':4'-tetranitrodiphenylcarbamide, intensely yellow needles, m. p. 188—189° (decomp.) (which are transformed by alcoholic alkali into 2:4:2':4'-tetranitrodiphenylamine, yellow needles, m. p. 199°: compare Juillard, A., 1906, i, 12), and 2:4:6:2':4':6'-hexanitrodiphenylamine are obtained. The latter substance has also been prepared by nitration of diphenylamine. It is the sole product of the nitration of *as*-diphenylcarbamide if the reaction product is heated on the water-bath. The mechanism of its formation has not been definitely decided, but it has been shown that equal volumes of carbon dioxide and nitrous oxide are evolved during the nitration.

*s*-Diphenylcarbamide reacts very vigorously with pure nitric acid cooled in a mixture of ice and salt, giving *s*-2:4:2':4'-tetranitrodiphenylcarbamide (compare Losanitsch, A., 1879, 67). This is not decomposed by hydrochloric acid even at 125°; boiling alcoholic potassium hydroxide converts it into 2:4-dinitrophenol, m. p. 112·5°, although 2:4-dinitroaniline is unaffected by a similar treatment; aqueous ammonia transforms it quantitatively into 2:4-dinitroaniline, m. p. 176°. A more dilute nitric acid (D 1·48) converts *s*-diphenylcarbamide into the same tetranitro-derivative at a higher temperature, and, by the action of concentrated sulphuric acid and pure nitric acid, this can be further nitrated to *s*-2:4:6:2':4':6'-hexanitrodiphenylcarbamide, prisms, m. p. 206—209° (decomp.) after commencing to decompose at 140° (Perkin, T., 1893, 63, 1068, gives m. p. 203°).

The symmetrically substituted dinitrodiphenylcarbamides have been prepared by the action of carbonyl chloride on the corresponding

nitroanilines (compare Vittenet, *loc. cit.*). *s*-4:4'-Dinitrodiphenylcarbamide sublimes without melting at about 300°; *s*-3:3'-dinitrodiphenylcarbamide, m. p. 242°, forms almost colourless needles and yellow crystals; *s*-2:2'-dinitrodiphenylcarbamide, yellow needles, m. p. 225°, is only formed in 10–15% yield by this method, the *o*-nitrodiphenylcarbamide reacting with difficulty with *o*-nitroaniline hydrochloride. If, however, a further quantity of *o*-nitroaniline is added, the yield becomes quantitative. Nitration of these derivatives is effected by well-cooled pure nitric acid. In these circumstances, the di-*para*-derivative gives a 90% yield of 2:4:2':4'-tetranitrodiphenylcarbamide; the di-*ortho*-derivative gives a product, m. p. 190° (decomp.), which appears to be a hexanitro-compound containing possibly a small amount of a tetranitro-derivative, and which is converted by a mixture of nitric and sulphuric acids into *s*-2:4:6:2':4':6'-hexanitrodiphenylcarbamide; the di-*meta*-derivative appears to yield a mixture of several nitro-compounds (compare Struve and Radenhausen, A., 1896, i, 35).

Triphenylcarbamide, m. p. 136°, is readily obtained in the pure state by the action of diphenylcarbamy chloride on aniline in the presence of alcohol (compare Steindorff, *Ber.*, 1876, 9, 398). It is violently attacked by well-cooled, pure nitric acid and, after treatment of the product with water, yields 2:4:2':4'-tetranitrodiphenylamine. The formation of this substance is shown to be due to the decomposition of the primary product of nitration by water. Various attempts to isolate the latter were unsuccessful, but an indication as to its nature was obtained by boiling the crude product, separated by means of water, with alcohol, when 2:4:2':4'-tetranitrodiphenylamine and 2:4-dinitrophenylurethane, m. p. 109–110°, were obtained. The initial product thus appears to be *hexanitrotriphenylcarbamide*:  $[C_6H_5(NO_2)_2]_2N \cdot CO \cdot NH \cdot C_6H_5(NO_2)_2 + EtOH = [C_6H_5(NO_2)_2]_2NH + C_6H_5(NO_2)_2 \cdot NH \cdot CO_2Et$ . A mixture of nitric and sulphuric acids reacts still more violently with triphenylcarbamide. After decomposition of the product by boiling water, 2:4:2':4'-tetranitrodiphenylamine and 2:4:6-trinitroaniline are obtained, whilst the former substance and 2:4:6-trinitrophenylurethane, m. p. 147° (van Romburgh, A., 1892, 711, gives m. p. 144°), are obtained when alcohol is used. Probably, 2:4:6:2':4':2'':4'-*heptanitrotriphenylcarbamide* is initially formed, but it has not been isolated.

The determination of the constitution of the products obtained by nitrating tetraphenylcarbamide is rendered exceptionally difficult by the stability of the latter substance. Ammonia, alcoholic potassium hydroxide, boiling aqueous potassium hydroxide (10% or 30%) and hydrochloric acid (D 1.2) at 250° are without action, although the latter (D 1.12) causes a quantitative decomposition into diphenylamine and carbon dioxide (compare Michler, *Ber.*, 1876, 9, 711). Aniline at 200° is without action. Sulphuric acid (80%) at 250° yields carbonised products, whilst at 110–150° the greater part of the diphenylamine which is formed is sulphonated.

Treatment of tetraphenylcarbamide with pure nitric acid, at first at the temperature of a mixture of ice and salt and subsequently at the ordinary temperature, yields a *hexanitrotetraphenylcarbamide*, m. p.



245—246° (decomp.) after darkening at 240°. The constitution of this product has not been established by reason of its instability.

*Octanitrotetraphenylcarbamide*, decomposing at about 310°, is obtained by the action of a mixture of pure nitric and concentrated sulphuric acids on tetraphenylcarbamide. In view of the general behaviour of the phenylcarbamides during nitration, the author is inclined to regard the two last-mentioned products as  $\alpha$ -2:4:2':4'-tetranitrodiphenyl- $\beta$ -4:4'-dinitrodiphenylcarbamide (possibly containing some of the  $\alpha$ -2:4:2':4'- $\beta$ -2:4'-isomeride) and 2:4:2':4':2'':4'':2'':4'''-octanitrotetraphenylcarbamide respectively.

It is worthy of note that in the series of compounds studied, nitro-groups are never introduced into the meta-position by means of nitric acid. This is in agreement with other experiments on the nitration of substances containing the group  $\text{NHPh}\cdot\text{CO}-$ . H. W.

**The Action of Halogen on 4-Nitro-*m*-cresol.** L. CHAS. RAIFORD (*J. Amer. Chem. Soc.*, 1914, **36**, 670—680).—When 4-nitro-*m*-cresol is treated in acetic acid solution with free chlorine, a small amount of 6-chloro-4-nitro-*m*-cresol, m. p. 143—144°, is obtained (compare Kehrman and Tichvinski, A., 1899, i, 129), although the main product is the 2-chloro-4-nitro-*m*-cresol (compare Raiford, A., 1911, i, 993).

The action of potassium chlorate on a suspension of 4-nitro-*m*-cresol in concentrated hydrochloric acid (compare Kollrepp, A., 1886, 1018) gave only a substance, colourless prisms, m. p. 143°, which was identified as 2:6-dichloro-4-nitro-*m*-cresol. This was reducible to 2:6-dichloro-4-amino-*m*-cresol, needles, m. p. 175—176 (decomp.); *hydrochloride*, decomp. about 250°; *mono-acetyl* derivative, needles, m. p. 204—207°. Oxidation of the dichloroaminocresol by sodium dichromate and dilute sulphuric acid gave rise to 2:6-dichlorotoluquinone, m. p. 103° (Claus and Schweitzer, A., 1886, 614).

By the addition of an aqueous solution of 2:6-dichloro-4-amino-*m*-cresol hydrochloride to an ice-cold solution of sodium hypochlorite and hydrochloric acid, 2:6-dichloro-4-chloroiminotoluquinone,  $\text{NCl}\cdot\text{C}_6\text{HMeCl}_2\cdot\text{O}$ , yellow prisms, m. p. 87°, was obtained.

When treated with bromine in acetic acid solution, 2-chloro-4-nitro-*m*-cresol was easily converted into 2-chloro-6-bromo-4-nitro-*m*-cresol, almost colourless prisms, m. p. 150°, which on reduction passed into 2-chloro-6-bromo-4-amino-*m*-cresol, colourless, rhombic crystals, m. p. 187° (decomp.); *hydrochloride*. Oxidation of the hydrochloride by sodium dichromate and sulphuric acid solution gave a 97% yield of 2-chloro-6-bromo-3-toluquinone,  $\text{O}\cdot\text{C}_6\text{HClBrMe}\cdot\text{O}$ , irregular scales, m. p. 119°, which could be reduced by sulphurous acid to 2-chloro-6-bromo-3-toluquinol,  $\text{C}_6\text{HClBrMe}(\text{OH})_2$ , colourless crystals, m. p. 163°. When an aqueous solution of the hydrochloride of 2-chloro-6-bromo-4-amino-*m*-cresol is introduced into an ice-cold solution of hypochlorous acid an almost quantitative yield of 2-chloro-6-bromo-4-chloroimino-3-toluquinone,  $\text{NCl}\cdot\text{C}_6\text{HClBrMe}\cdot\text{O}$ , square prisms, m. p. 93—94°, decomp. above 176°, is obtained, accompanied by a very small quantity of the corresponding chlorobromotoluquinone described above. D. F. T.

**Polymerides of *iso*Safrole.** MARIO MAYER (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 358—363).— $\beta$ -*iso*Safrole forms a *picrate*, which is a red substance, m. p. about  $75^\circ$ , and can be used for the preparation of pure  $\beta$ -*isosa*frole.

Both the polymerides of  $\beta$ -*isosa*frole can be prepared by means of the same polymeriser (hydrochloric acid or ferric chloride), employing the ordinary temperature if Puxeddu's dimeride is required (compare Puxeddu, A., 1913, i, 460) or a temperature of  $150^\circ$  if that of Angeli and Mola (compare A., 1895, i, 24) is wanted. The latter compound (m. p.  $145^\circ$ ) can be obtained also by distilling the former (m. p.  $95^\circ$ ); both boil at  $380^\circ$ .

The spectra of acetone solutions of the two compounds in the ultra-violet region are identical.

The *disosa*frole of m. p.  $145^\circ$  when oxidised by dilute permanganate yields a small quantity of an oily compound,  $C_{10}H_{10}O_3$  (probably identical with the ketone of Balbiano and Paolini, A., 1904, i, 72), as well as piperonylic acid and acetic acid.

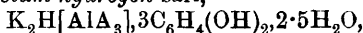
R. V. S.

**Some Aluminium Compounds and Alkali Salts of Catechol.** R. F. WEINLAND and WILHELM DENZEL (*Ber.*, 1914, 47, 737—750).—Catechol inhibits the precipitation of aluminium by alkali hydroxides owing to the formation of two colourless acids,  $H_3[Al(C_6H_4O_2)_3]$  and  $H[Al(C_6H_4O_2)_2]$ , which correspond with the ferri-acids previously described (A., 1912, i, 184, 445). The alkali salts of the former acid crystallise from solutions containing aluminium chloride, catechol, and alkali hydroxide in the proportion 1 : 4 : 10 to 18. The solutions, even of the ammonium salt, may be boiled without hydrolysis, but ferric hydroxide causes an exchange of the metals. The salts of the second acid crystallise from less alkaline solutions, for example, aluminium chloride : catechol : alkali = 1 : 2.2 : 4.5. These are also unaffected by ammonia, even on heating, both series being more stable towards alkalis than the corresponding iron compounds.

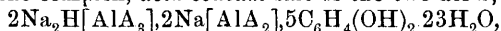
In addition, some very complicated salts were obtained by employing still less alkali hydroxide or by adding acetic acid to the solutions of the salts of the tribasic acid. Some of these contained combined catechol and the possibility of the formation of "per-acid" salts of catechol was therefore investigated, and some of the alkaline salts were indeed prepared.

[In the following formulæ, A = the catechol residue,  $C_6H_4O_2$ .] The *sodium* salt,  $Na_3[AlA_3] \cdot 7H_2O$ , separates when 12 grams of sodium hydroxide are added to a solution of 7.2 grams of aluminium chloride and 13.2 grams of catechol in 30 c.c. of water. It must be filtered from the hot solution as it passes into the *hydrate* with  $10H_2O$ , which crystallises in large octahedra when the solution is diluted and then evaporated in vacuum. Both salts are white, but soon become brown in the air. The corresponding *potassium* and *ammonium* salts crystallise with  $1.5H_2O$ . The *sodium* salt,  $Na[AlA_2] \cdot 4H_2O$ , and the corresponding *potassium* and *ammonium* salts with  $5H_2O$ , are less alkaline and less soluble than the salts of the tribasic acid.

The *acid dipotassium hydrogen* salt,



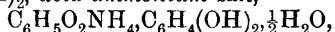
crystallises from a solution containing 4.8 grams of aluminium chloride, 8.8 grams of catechol, and 6.7 grams of potassium hydroxide in 30 c.c. of water. The complex, *acid sodium* salt of the two acids,



crystallises from a solution of 6 grams of the above tertiary salt in 20 c.c. of *N*-acetic acid. Under similar conditions, the complex *ammonium* salt,  $(\text{NH}_4)_3[\text{AlA}_3], (\text{NH}_4)_2\text{H}[\text{AlA}_3], 4\text{NH}_4[\text{AlA}_2], 24\text{H}_2\text{O}$  (compare the corresponding iron compound, *ibid.*), is deposited, whereas from a solution containing relatively twice as much acetic acid, the *acid ammonium* salt,

$(\text{NH}_4)_3[\text{AlA}_3], (\text{NH}_4)_2\text{H}[\text{AlA}_3], 4\text{NH}_4[\text{AlA}_2], 2\text{C}_6\text{H}_4(\text{OH})_2, 29\text{H}_2\text{O}$ , separates out.

The following crystalline salts of catechol were prepared by evaporating solutions containing the theoretical amounts of the phenol and alkali hydroxide: *monopotassium* salt,  $\text{C}_6\text{H}_5\text{O}_2\text{K}, \frac{1}{2}\text{H}_2\text{O}$ , *mono-acid potassium* salt,  $\text{C}_6\text{H}_5\text{O}_2\text{K}, \text{C}_6\text{H}_4(\text{OH})_2, \frac{1}{2}\text{H}_2\text{O}$ , *di-acid* salt,  $\text{C}_6\text{H}_5\text{O}_2\text{K}, 2\text{C}_6\text{H}_4(\text{OH})_2$ , *acid ammonium* salt,



and *acid sodium* salt,  $2\text{C}_6\text{H}_5\text{O}_2\text{Na}, \text{C}_6\text{H}_4(\text{OH})_2, 8\text{H}_2\text{O}$ .

J. C. W.

**1-Phenol-3-mercaptan** [*m*-Hydroxyphenyl Mercaptan]. TH. ZINCKE and C. EBEL (*Ber.*, 1914, **47**, 923—933).—*m*-Hydroxyphenyl mercaptan (Szathmáry, A., 1910, i, 733) is prepared by the following series of reactions. Sodium phenol-*m*-sulphonate is converted into *sodium m-ethylcarbonatobenzenesulphonate*,  $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO}_2\text{Et}$ , white, asbestos-like needles, and the *chloride*, m. p. 30—31° (*sulphanilide*, colourless prisms, m. p. 89—90°), is reduced to the corresponding *mercaptan*, an almost colourless oil with an unpleasant odour (*benzoyl* derivative, white needles, m. p. 60—61°), which on hydrolysis yields *m*-hydroxyphenyl mercaptan,  $\text{SH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , a colourless, strongly refracting oil, of unpleasant odour, b. p. 168°/35 mm., m. p. 16—17°; the *dibenzoyl* derivative forms white leaflets, m. p. 78°. The mercaptan is easily oxidised in alkaline solution to *m*-hydroxyphenyl disulphide, small, white needles, m. p. 94—95°. The ethylcarbonato-derivative of *m*-hydroxyphenyl mercaptan, on methylation, furnishes the corresponding methyl sulphide, which on hydrolysis yields *m*-hydroxyphenyl methyl sulphide, a colourless, highly refractive oil having a faint odour, b. p. 148—151°/14 mm., 224°/760 mm.; on strongly cooling, it solidifies to a crystalline mass, m. p. 15°. The *benzoyl* derivative forms colourless, matted needles, m. p. 56—57°.

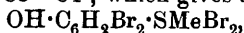
With methyl iodide, *m*-hydroxyphenyl methyl sulphide gives *m*-hydroxyphenyldimethylsulphonium iodide,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SMe}_2\text{I}$ , colourless needles, m. p. 97—98° (decomp.); the *hydroxide* is a colourless syrup, the *chloride* could not be obtained crystalline, and the *platinichloride* forms yellow spikes, m. p. 148—149° (decomp.).

*m*-Hydroxyphenyl methyl sulfoxide,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SMeO}$ , prepared by hydrolysing the corresponding ethylcarbonato-derivative (from the sulphide and hydrogen peroxide), is a colourless oil, the *benzoyl* derivative of which forms small, white crystals, m. p. 83—84°.

*m*-Hydroxyphenylmethylsulphone,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Me}$ , prepared from

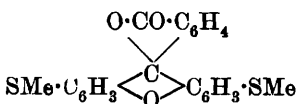
the corresponding *ethylcarbonato*-derivative (colourless leaflets, m. p. 59°) forms white, pointed needles, m. p. 84—85°.

With bromine, *m*-hydroxyphenyl methyl sulphide forms an oily *monobromo*-derivative (*benzoyl* derivative, small, white crystals, m. p. 112—113°), and 4:6-*dibromo-3-hydroxyphenyl methyl sulphide*, white, glistening leaflets, m. p. 83—84°, which gives a *dibromide*,



reddish-brown, unstable tablets or leaflets.

With nitrous acid, *m*-hydroxyphenyl methyl sulphide yields 4-nitroso-3-methylthiolphenol (Zincke and Müller, A., 1913, i, 735).



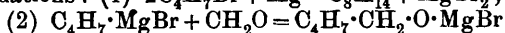
Condensation of *m*-hydroxyphenyl methyl sulphide with phthalic anhydride furnishes 3:6-*dimethylthiolfluorescein* (annexed formula), white leaflets, m. p. 179°, which

gives red oxonium salts (*nitrate*, *sulphate*, *chloride*), but these could not be isolated in a pure state.

J. C. C.

**Isomerisation in the Transformations of Trimethylcarbinol [*cyclo*Propylcarbinol].** I. N. J. DEMJANOV and J. N. DEMJANOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 42—53).—With the object of obtaining  $\beta$ -*cyclopropylethyl* alcohol, ethyl *cyclopropane*-carboxylate was reduced to *cyclopropylcarbinol*, the latter converted into bromide, and the corresponding organo-magnesium compound treated with paraformaldehyde. Although this reaction takes place at a low temperature, it follows a complicated course. An alcohol,  $\text{C}_5\text{H}_9\cdot\text{OH}$ , is formed, but never in more than 30% yield, and is found to consist of a mixture of the cyclic alcohol with an isomeric one containing a double linking; other products are a hydrocarbon,  $\text{C}_8\text{H}_{14}$ , and the acetals of formaldehyde and the alcohol,  $\text{C}_5\text{H}_9\cdot\text{OH}$ .

The action of hydrobromic acid on *cyclopropylcarbinol* yields a mixture, b. p. 108—109°/746 mm., of bromomethyl*cyclopropane* and bromo*cyclobutane*. The action of magnesium and paraformaldehyde on this mixture of isomeric bromides may be represented by the following equations: (1)  $2\text{C}_4\text{H}_7\text{Br} + \text{Mg} = \text{C}_8\text{H}_{14} + \text{MgBr}_2$ ;



and this  $+ \text{H}_2\text{O} = \text{C}_5\text{H}_9 \cdot \text{OH} + \text{MgBr} \cdot \text{OH}$ ; (3)  $2\text{C}_5\text{H}_9 \cdot \text{OH} + \text{CH}_2\text{O} = \text{C}_5\text{H}_9 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_5\text{H}_9 + \text{H}_2\text{O}$ . These reactions are similar to those obtained with allyl bromide (compare Pariselle, A., 1911, i, 940).

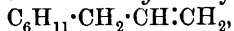
The hydrocarbon,  $\text{C}_8\text{H}_{14}$ , is a mobile liquid with a characteristic odour, b. p. 114—116°. The cyclic alcohol present in the mixture,  $\text{C}_5\text{H}_9\cdot\text{OH}$ , is *cyclobutylcarbinol*, and the accompanying unsaturated alcohol gives the trihydric alcohol,  $\text{C}_5\text{H}_{12}\text{O}_3$ , as a colourless, viscous liquid, b. p. 180—182°/15 mm.

T. H. P.

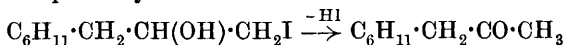
**Trimethylenemethylcarbinol [*cyclo*Propylmethylcarbinol]** and certain of its Transformations. I. N. J. DEMJANOV and S. A. PINEGIN (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 54—58).—*cyclo*-Propylmethylcarbinol, prepared as described by Michiels (A., 1912, i, 259), has b. p. 122—122.4°/755 mm.,  $D_4^{20}$  0.9010,  $D_4^{25}$  0.8856,  $D_4^{30}$  0.8866,  $n_D^{20}$  1.4285. When treated with hydriodic acid, the alcohol

yields (1) a mixture of  $\beta$ -cyclopropyl- $\beta$ -iodoethane and  $\delta$ -iodo- $\Delta^a$ -pentene, b. p.  $68^\circ/35$  mm.,  $D_0^0$  1.6083,  $D_0^{15}$  1.586,  $D_0^{20}$  1.579,  $n_D^{20}$  1.521, and (2) the di-iodo-compound, consisting principally of  $\beta\delta$ -di-iodo-pentane, b. p.  $147^\circ/35$  mm.,  $D_0^0$  2.1957,  $D_0^{15}$  2.172,  $D_0^{20}$  2.163,  $n_D^{20}$  1.600. Thus, the action of hydriodic acid is similar to that of hydrobromic acid (compare Michiels, *loc. cit.*). T. H. P.

**Iodohydrins and Alkyliodohydrins derived from cycloHexylpropene.** B. DE RESSÉGUIER (*Bull. Soc. chim.*, 1914, [iv], 15, 175—182).—Up to the present, very little work has been done on the mode of fixation of hypoiodous acid and its esters at double bonds. In the cases of styrene,  $\alpha$ -phenylpropene,  $\beta$ -phenylpropene and allylbenzene, Tiffeneau (A., 1906, i, 965; 1908, i, 19) has shown that the hydroxyl group attaches itself to the carbon atom nearest the benzene nucleus, whilst the iodine atom occupies the more distant position. The author has therefore studied the addition of hypoiodous acid and its esters to cyclohexylpropene,



and finds that addition occurs in each of the two possible manners. Attempts to prove the composition of the additive product by an investigation of its action towards dimethylamine were unsuccessful, since an intermediate oxide, common to the two isomerides, is first formed (compare Tiffeneau and Fourneau, A., 1913, i, 1337). The action of silver nitrate, however, furnishes the required information, the products of the change being cyclohexylpropaldehyde and cyclohexylpropanone respectively :



and  $C_6H_{11} \cdot CH_2 \cdot CHI \cdot CH_2 \cdot OH \xrightarrow{-HI} C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot CHO$ . Addition of the esters of hypoiodous acid occurs in a similar manner and the nature of the product is deduced by removal of hydrogen iodide by means of alcoholic potassium hydroxide followed by hydrolysis with acid.

The mixture of cyclohexylpropene iodohydrins,  $D_0^0$  1.4653, is obtained as a pale yellow, somewhat syrupy liquid, which decomposes on exposure to air and light by the addition of iodine to a suspension of yellow mercuric oxide in a solution of cyclohexylpropene in wet ether. When dissolved in anhydrous ether and shaken with solid potassium hydroxide, it yields the corresponding oxide, b. p.  $182$ — $185^\circ$ ,  $D_0^0$  1.003, which, when treated with sulphuric acid, is converted into an aldehyde, the semicarbazone of which has m. p.  $137^\circ$ .

An ethereal solution of the iodohydrin is treated with an aqueous solution of silver nitrate and the product distilled, whereby the following fractions are obtained: (1) b. p.  $70$ — $90^\circ/25$  mm.; (2)  $175$ — $195^\circ/25$  mm., and (3)  $220$ — $225^\circ/25$  mm. The second fraction is probably a mixture of the two nitric esters,  $C_6H_{11} \cdot CH_2 \cdot CH(NO_3) \cdot CH_2 \cdot OH$  and  $C_6H_{11} \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot NO_3$ . The first fraction yields two semicarbazones, m. p.  $137^\circ$  and  $183^\circ$  respectively, of which the latter is identical with the semicarbazone of cyclohexylacetone (compare Freundler, A., 1906, i, 283). From the former, a liquid,  $C_9H_{16}O$ , can be regenerated, which gives Schiff's reaction, and, on oxidation with

silver oxide, is converted into an acid having the properties of *cyclohexylpropionic acid*. The structure of the aldehyde is confirmed by the identity of its semicarbazone with that derived by isomerisation of *cyclohexylpropeneoxide* (see above). On treatment with dimethylamine in benzene solution, the mixture of iodohydrins yields  $\gamma$ -*dimethylamino- $\alpha$ -cyclohexylpropan- $\beta$ -ol*,  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p. 133—134°/19 mm.,  $D_0$  0.9340, (*methiodide*, m. p. 175°, *hydrochloride* of *benzoyl* derivative, m. p. 182°).

The mixture of *cyclohexylpropene methyl iodohydrins*, b. p. 140—145°/13 mm.,  $D_0$  1.4116, is prepared by the addition of iodine to a methylalcoholic solution of *cyclohexylpropene* in the presence of mercuric oxide. It is unaffected by solid or aqueous potassium hydroxide; alcoholic potassium hydroxide converts it into a mixture of ethers,  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{C}(\text{OMe})\cdot\text{CH}_2$  and  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2\cdot\text{OMe}$ , b. p. 195—200°, from which, by successive treatment with acid and semicarbazide, two semicarbazones, m. p. 182—183° and 136—137° respectively, are obtained, identical with the semicarbazones of *cyclohexylacetone* and *cyclohexylpropaldehyde*.

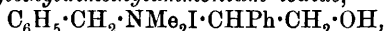
The mixture of *cyclohexylpropene ethyl iodohydrins* is obtained as a colourless liquid, practically stable to air and light, in the manner described for the lower homologue. Alcoholic potassium hydroxide converts it into a mixture of the ethers,  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{CH}_2$  and  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{OEt}$ , b. p. 215—220°, from which, by successive action of acid and semicarbazide, two semicarbazones, m. p. 137° and 183° respectively, are prepared. H. W.

**Determination of the Constitution of Iodohydrins by the Action of Tertiary Amines.** Iodohydrins Derived from Styrene. TIFFENEAU and FOURNEAU (*Bull. Soc. chim.*, 1914, [iv], 15, 275—281. Compare A., 1913, i, 1337).—The action of tertiary amines on the two iodohydrins of styrene has been studied. It was expected that, on the one hand, the bases would act as eliminators of hydrogen iodide, and on the other, would simply be attached to the hydrins with the production of quaternary salts. Both reactions take place simultaneously in the cold with trimethylamine or benzyl-dimethylamine. Substituted choline iodides are the additive compounds obtained, but the hydrogen atom involved in the elimination of hydrogen iodide is not that of the hydroxyl group and therefore the product is not styrene oxide but a vinyl alcohol, which undergoes rearrangement into a ketone or aldehyde. Thus the action of tertiary amines affords a double indication of the constitution of these iodohydrins. Quantitatively the two substances behave differently, for with the primary iodide,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\text{I}$ , the elimination of the hydracid is the preponderating reaction, whereas the isomeride gives more of the choline derivative.

Phenyl iodomethylcarbinol was left for a day with a 20% solution of trimethylamine in benzene, when the hydriodide of the base which separated was filtered, and the solution was heated at 100° in a sealed tube for a day. Acetophenone, to the extent of 80% of the products, was isolated from the liquid, and the further deposit of crystals contained the salt of the base and the hydriodide of secondary

phenylcholine,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$  (*ibid.*). Similarly, benzyl-dimethylamine gave acetophenone and a solid which was separated by water into the very soluble iodide of the base and a small amount of the sparingly soluble *quaternary ammonium iodide*, m. p.  $198^\circ$  (Maquenne block).

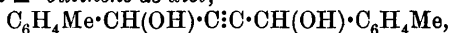
$\alpha$ -Iodobenzylcarbinol was left with trimethylamine for several days, when a crystalline mass separated. The product was extracted with very dilute hydrochloric acid and then ether. The ethereal extract contained phenylacetaldehyde, and the viscous residue, insoluble in either solvent, was probably a polymeric of this. The acid extract was treated with silver oxide, filtered, freed from trimethylamine by warming in a vacuum, and acidified with hydrochloric acid. Primary phenylcholine hydrochloride (*ibid.*) was obtained on evaporation. Similarly, benzyldimethylamine yielded acetophenone and *benzyl- $\beta$ -hydroxy- $\alpha$ -phenylethyl-dimethylammonium iodide*,



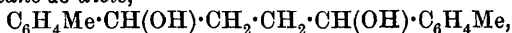
which forms colourless rhombohedra, m. p.  $142^\circ$  (Maquenne block); the *chloride* has m. p.  $168^\circ$ . J. C. W.

**The Stereochemical Isomerides of Some  $\gamma$ -Glycols.** GEORGES DUPONT (*Compt. rend.*, 1914, 158, 714—716).—Of the two series of stereoisomeric acetylenic  $\gamma$ -glycols and saturated  $\gamma$ -glycols already prepared (compare A., 1909, i, 545; 1910, i, 85) theory indicates that the members of one series should be separable into optical isomerides. In the study of two new acetylenic  $\gamma$ -glycols the author has unsuccessfully endeavoured to solve this problem.

*$\alpha\delta$ -Di-*p*-tolyl- $\Delta^8$ -butinene- $\alpha\delta$ -diol,*

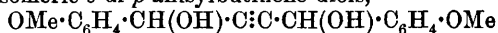


obtained by the action of tolualdehyde on magnesium diacetylene dibromide, is easily separable by repeated washing with cold ether into its two isomerides. The fraction insoluble in ether crystallises from alcohol in small, monoclinic prisms, m. p.  $173^\circ$ , exhibiting antihemihedrism having [ $a:b:c=1.242:1:1.307$ ;  $\gamma=80^\circ57'$ ]. This crystalline form is superposable on its optical opposite. The fraction obtained by evaporating the ether crystallises in triclinic prisms, m. p.  $127^\circ$ , having [ $a:b:c=1.066:1:0.7455$ ;  $\alpha=87^\circ30'$ ,  $\beta=112^\circ22'$ ,  $\gamma=80^\circ24'$ ], all the crystals obtained being superposable. The first of these isomerides on heating with benzoyl chloride in pyridine yields a *dibenzoyl* derivative, m. p.  $125^\circ$ , whilst the second gave non-crystallisable products. The two isomerides on hydrogenation in alcoholic solution in the presence of platinum black gave two isomeric *di-*p*-tolylbutane- $\alpha\delta$ -diols*,



having respectively m. p.  $133$ — $134^\circ$  and  $103$ — $104^\circ$ .

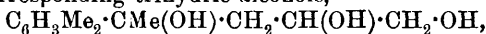
The two isomeric *s*-di-*p*-anisylbutinene-diols,



(compare Iocitsch, this vol., i, 376), have respectively m. p.  $131$ — $132^\circ$  and  $112$ — $113^\circ$ , the former crystallising in minute prisms and the latter in slender needles. The first isomeride on hydrogenation gave the corresponding saturated glycol, m. p.  $115$ — $116^\circ$ , whilst in the case of the second isomeride the benzene nucleus was apparently attacked.

Finally, the author has found that the acetylenic and saturated  $\gamma$ -glycols give colour reactions with sulphuric acid, the colour varying with the nature of the glycol. W. G.

**Properties of Tertiary Allyl Aromatic and Hydroaromatic Alcohols.** IPPOLIT MACUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 13—38).—Gentle oxidation of the xylylmethylallylcarbinols previously described (A., 1911, i, 961) by means of permanganate yields the corresponding trihydric alcohols,



whilst if the oxidation is more energetic, the molecule is ruptured at the double linking of the allyl radicle and a tertiary hydroxy-acid,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , formed.

Thus, 3:4-xylylmethylallylcarbinol gives: (1)  $\beta$ -3:4-xylylpentane- $\beta\delta\epsilon$ -triol,  $\text{C}_{13}\text{H}_{20}\text{O}_3$ , small, white crystals, m. p. about  $98-102^\circ$ , and (2) the syrupy pale yellow acid,  $\text{C}_{12}\text{H}_{16}\text{O}_3$ , the silver, sodium, potassium, calcium, and barium salts of this being prepared.

2:4-Xylylmethylallylcarbinol gives: (1) the pale yellow syrupy  $\beta$ -2:4-xylylpentane- $\beta\delta\epsilon$ -triol,  $\text{C}_{13}\text{H}_{20}\text{O}_3$ , and (2) the syrupy  $\beta$ -2:4-xylyl- $\beta$ -methylhydracrylic acid, the silver, potassium, and barium salts of which were prepared. When the acid is boiled with calcium carbonate, it loses water and gives calcium  $\beta$ -2:4-xylyl- $\beta$ -methylacrylate, and when dry distilled it yields  $\beta$ -2:4-xylylpropene,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CMe}\cdot\text{CH}_2$ , b. p.  $194-200^\circ$ .

2:5-Xylylmethylallylcarbinol yields: (1) the syrupy  $\beta$ -2:5-xylylpentane- $\beta\delta\epsilon$ -triol,  $\text{C}_{13}\text{H}_{20}\text{O}_3$ , and (2)  $\beta$ -2:5-xylyl- $\beta$ -methylhydracrylic acid,  $\text{C}_{12}\text{H}_{16}\text{O}_3$ , the silver salt of which was prepared.

The syrupy acids obtained in this way gradually deposited small proportions of crystalline substances, apparently formed as a result of further oxidation. In order to investigate these products, oxidations were carried out in presence of excess of free alkali. Under these conditions, 3:4-xylylallylmethylcarbinol gives 3:4-dimethylbenzoic acid, whilst 2:5-xylylallylmethylcarbinol yields 2:5-dimethylbenzoic acid, which loses carbon dioxide and forms *as*-2:5-xylylmethylethylene (l), b. p.  $205-210^\circ$ , on distillation.

The removal of the elements of water from the xylylmethylallylcarbinols was studied by preparing the corresponding chloro-derivatives,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CMeCl}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ , from which hydrogen chloride was subtracted by the action of pyridine. Owing, however, to their ready oxidisability, the pentadienes obtained were invariably admixed with oxygenated compounds.

$\beta$ -3:4-Xylyl- $\Delta^{86}$ -pentadiene was obtained as an impure tarry mass.  $\beta$ -2:4-Xylyl- $\Delta^{76}$ -pentadiene is a colourless liquid, b. p.  $120-121^\circ/21.5$  mm.,  $D_4^{21}$  0.9097,  $n_D^{21}$  1.53233, and has the normal molecular weight in boiling ether.  $\beta$ -2:5-Xylyl- $\Delta^{86}$ -pentadiene is a mobile, colourless liquid, b. p.  $117.5-118^\circ/20-21$  mm.,  $D_4^{21}$  0.9062,  $n_D^{21}$  1.53690, and exhibits normal ebullioscopic behaviour in ether.

Phenyl- $\alpha$ -naphthylallylcarbinol,  $\text{C}_{10}\text{H}_7\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ , prepared by the interaction of phenyl  $\alpha$ -naphthyl ketone, magnesium and allyl bromide in ethereal solution, forms a brittle, white, crystalline mass, m. p.  $65-67^\circ$ , and yields a resinous dibromide,  $\text{C}_{20}\text{H}_{18}\text{OBr}_2$ .

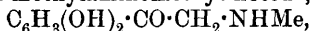


When oxidised with alkaline permanganate solution, it gives  $\alpha$ -naphthoic acid and a pale yellow trihydric alcohol. Replacement of the hydroxyl group by chlorine and treatment of the chloro-derivative with pyridine yields  $\alpha$ -phenyl- $\alpha$ -naphthyl- $\Delta^8$ -butadiene,  $C_{20}H_{16}$ , which could not be obtained pure owing to the readiness with which it oxidises to the compound,  $(C_{20}H_{16}O)_x$ .

Energetic oxidation of 1-allylcyclohexanol (compare Zaicev, A., 1912, i, 777) in presence of excess of alkali yields 1-cyclohexanol-1-acetic and adipic acids.

When oxidised by means of permanganate, 3:5-dimethyl-1-allyl- $\Delta^2$ -cyclohexenol yields (1) 3:5-dimethyl- $\Delta^2$ -cyclohexenol-propene- $\beta$ - $\gamma$ -diol,  $CH_2 \begin{smallmatrix} < CMe=CH \\ < CHMe \cdot CH_2 \end{smallmatrix} C(OH) \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$ , which crystallises in rectangular plates, m. p. 125–126°; (2) a viscous acid, which was not investigated. The chloro-compound corresponding with 3:5-dimethyl-1-allyl- $\Delta^2$ -cyclohexenol is unstable and readily undergoes decomposition and polymerisation. T. H. P.

**Preparation of an Aromatic Amino-alcohol.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (Swiss Patent 63012).— $\beta$ -3:4-Trihydroxy- $\beta$ -phenylethylmethylamine,  $C_6H_5(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NHMe$ , a colourless, crystalline substance, m. p. 207°, is prepared by reducing 3:4-dihydroxyphenyl methylaminomethyl ketone,

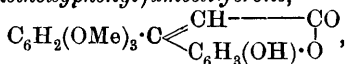


at 20–30° by means of hydrogen and a colloidal solution of a metal of the platinum group under  $1\frac{1}{2}$  atmospheres' pressure. J. C. C.

**Preparation and Properties of Certain Methoxylated Carbinols, Olefines, and Ketones, Derived from Trimethylgallic Acid.** MARSTON TAYLOR BOGERT and ROBERT MELVINE ISHAM (*J. Amer. Chem. Soc.*, 1914, 36, 514–530).—A study of the carbinols and olefines obtainable from methyl trimethylgallate [3:4:5-trimethoxybenzoate] has been carried out with the object of ascertaining the influence of the methoxyl group on the properties of such substances. The results confirm those of earlier workers, and also show that the presence of the methoxyl group in compounds of the type  $CPhR \cdot CH_2RCl$  increases the activity of the halogen.

Diphenyl-3:4:5-trimethoxyphenylcarbinol has been found to be more strongly basic than triphenylcarbinol, but less so than diphenyl-*p*-methoxyphenylcarbinol. The trimethoxyphenyldialkylcarbinols are generally unstable and readily lose water to form the olefine, whilst trimethoxyphenyldibenzylcarbinol is quite stable. None of the olefines described yields a stable dibromide.

4-(3':4':5'-Trimethoxyphenyl)umbelliferone,

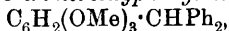


m. p. 253° (decomp.), obtained by the action of resorcinol on ethyl 3:4:5-trimethoxybenzoylacetate, forms colourless crystals.

3:4:5-Trimethoxycinnamic acid (methylsinapic acid) can be prepared by the action of active aluminium on ethyl trimethoxybenzoylacetate.

4-Hydroxy-3:5-dimethoxybenzoic acid (syringic acid) is produced when trimethylgallic acid is added gradually to 20% fuming sulphuric acid, the temperature being kept below 40°.

*Diphenyl-3:4:5-trimethoxyphenylcarbinol*,  $C_6H_2(OMe)_3 \cdot CPh_2 \cdot OH$ , m. p. 189°, obtained by the action of magnesium phenyl bromide on methyl trimethylgallate, forms colourless, hexagonal crystals and dissolves in concentrated sulphuric acid with production of a deep red solution; it is readily reduced by a solution of hydrogen chloride in alcohol to *diphenyl-3:4:5-trimethoxyphenylmethane*,



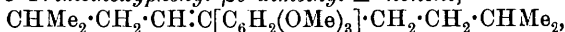
m. p. 133°, which crystallises in colourless needles. 3:4:5-*Diphenyl-trimethoxyphenylcarbinyl chloride* has m. p. 110°. *Diphenyl-3:4:5-trimethoxyphenylpyrrolmethane*,  $C_6H_2(OMe)_3 \cdot CPh_2 \cdot C_4H_4N$ , m. p. 155° (uncorr.), obtained by heating the carbinol with pyrrole in presence of glacial acetic acid, forms colourless, hexagonal crystals.

3:4:5-*Trimethoxy- $\alpha$ -methylstyrene*,  $C_6H_2(OMe)_3 \cdot CMe \cdot CH_2$ , b. p. 193°/40 mm., m. p. 37°, prepared by the action of magnesium methyl iodide on methyl trimethylgallate, crystallises in colourless needles. When ozone is passed into a solution of this compound in 70% acetic acid, 3:4:5-trimethoxyacetophenone, m. p. 78°, is produced; its *p*-nitrophenylhydrazone has m. p. 195—196° (uncorr.). By the condensation of 3:4:5-trimethoxyacetophenone with benzaldehyde, 3:4:5-trimethoxyphenyl styryl ketone,  $C_6H_2(OMe)_3 \cdot CO \cdot CH : CHPh$ , m. p. 78—78·5°, is obtained, which crystallises in yellow needles.

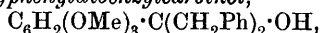
3:4:5-*Trimethoxyphenyldiethylcarbinol*,  $C_6H_2(OMe)_3 \cdot CEt_2 \cdot OH$ , m. p. 74°, prepared by the action of magnesium ethyl bromide on methyl trimethylgallate, forms colourless needles. The mother-liquor from this reaction yielded  $\gamma$ -3:4:5-trimethoxyphenyl- $\Delta^8$ -pentene,  $C_6H_2(OMe)_3 \cdot CEt \cdot CHMe$ , b. p. 210—220°/40 mm.,  $D_{20}^{20} 1.0462$ ,  $n_D^{20} 1.53600$ , which can also be obtained by saturating an ethereal solution of the carbinol with hydrogen chloride; the observed molecular refraction is 70·37, whereas that calculated from the Brühl-Conrady tables is only 67·9. By the action of ozone on a solution of the olefine in 70% acetic acid, 3:4:5-trimethoxypropiofenone,  $C_6H_2(OMe)_3 \cdot COEt$ , m. p. 53·5°, is produced, which forms lustrous, colourless needles; its *p*-nitrophenylhydrazone has m. p. 183—184°.

$\delta$ -3:4:5-*Trimethoxyphenyl- $\Delta^7$ -heptene*,  $C_6H_2(OMe)_3 \cdot CPr \cdot CHEt$ , b. p. 215—218°/40 mm.,  $D_{20}^{20} 1.0300$ ,  $n_D^{20} 1.52877$ , is obtained by the action of magnesium propyl iodide on methyl trimethylgallate; the observed molecular refraction is 79·12 as compared with 77·12 as the calculated value. 3:4:5-*Trimethoxybutyrophenone*,  $C_6H_2(OMe)_3 \cdot CO \cdot CH_2Et$ , b. p. 218—220°/40 mm., m. p. 51—52·5°, forms long, colourless needles; its *p*-nitrophenylhydrazone has m. p. 160°.

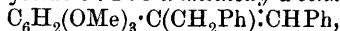
$\epsilon$ -3:4:5-*Trimethoxyphenyl- $\beta\theta$ -dimethyl- $\Delta^8$ -nonene*,



b. p. 235—237°/40 mm., from magnesium isoamyl iodide and methyl trimethylgallate, forms colourless, rhombohedral crystals, and has a molecular refraction 96·03 as compared with the calculated value 95·53. The mother-liquor yields a substance,  $C_{12}H_{14}O_6$  or  $C_{12}H_{16}O_6$ , m. p. 109—110°, b. p. 218°/40 mm., which forms colourless, rhombohedral crystals.

**3 : 4 : 5-Trimethoxyphenyldibenzylcarbinol,**

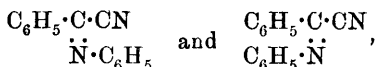
m. p. 116—117°, from magnesium benzyl chloride and methyl trimethylgallate, forms long prisms, and when treated with hydrogen chloride in ethereal solution yields 3 : 4 : 5-trimethoxy- $\alpha$ -benzylstilbene,



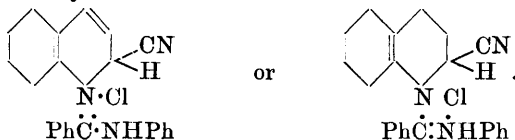
m. p. 93°. The latter compound is converted by ozone into 3 : 4 : 5-trimethoxydeoxybenzoin,  $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ , m. p. 99°, which furnishes a *p*-nitrophenylhydrazone, m. p. 194°. E. G.

**The Reaction of Acid Imino-chlorides with Hydrogen Cyanide.** OTTO MUMM, HANS VOLQUARTZ, and HUGO HESSE (*Ber.*, 1914, **47**, 751—758).—The authors have applied the discovery that the chlorine atom in imino-chlorides may be replaced by cyanogen by the action of aqueous potassium cyanide (A., 1910, i, 311) on a number of these compounds. Whereas those imino-nitriles in which an aromatic nucleus is attached to the imino-nitrogen atom are very stable,  $\alpha$ -methyliminophenylacetonitrile is very readily hydrolysed to benzoyl cyanide and methylamine, and decomposes in the dry state into benzonitrile and acetonitrile.

It was hoped that both the isomeric forms of  $\alpha$ -phenyliminophenylacetonitrile,



might have been obtained. This was not the case, and, therefore, experiments were carried out in absence of water, by treating the imino-chloride with hydrogen cyanide in presence of pyridine or quinoline. In these circumstances, however, compounds were obtained which contained the base in the molecule, and from which no nitrile could be isolated. From the analogy to the action of benzoyl chloride and hydrogen cyanide on quinoline (Reissert, A., 1905, i, 472) and from the reactions of the compound, the quinoline derivative may be represented by the alternative formulæ :



$\alpha$ -*o*-Tolyliminobenzyl chloride was obtained as a pale yellow oil, b. p. 203—205°/19 mm. (Just, A., 1886, 617, did not purify it), and converted into  $\alpha$ -*o*-tolyliminophenylacetonitrile (the 2-methylphenyl- $\mu$ -cyanazomethinphenyl of Sachs, A., 1901, i, 272).  $\alpha$ -*m*-Tolyliminobenzyl chloride, m. p. 49—50°, b. p. 215—220°/20 mm. (Just, *loc. cit.*), gave  $\alpha$ -*m*-tolyliminophenylacetonitrile,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N} : \text{CPh} \cdot \text{CN}$ , in yellow prisms, m. p. 37—38°, and the nitrile from  $\alpha$ -*p*-tolyliminobenzyl chloride (Just) was identical with Sachs' 4-methylphenyl- $\mu$ -cyanazomethinphenyl (*loc. cit.*).  $\alpha$ -*o*-Nitrophenyliminophenylacetonitrile, from the corresponding chloride (Ley, A., 1898, i, 252), formed long, yellow needles, m. p. 120°, and  $\alpha$ -*m*-nitrophenyliminobenzyl chloride (Pechmann, A., 1897, i, 515) yielded  $\alpha$ -*m*-nitrophenyliminophenylacetonitrile, m. p.

120—121°. *α*-Methyliminobenzyl chloride (Pechmann, A., 1896, i, 31) yielded *α*-methyliminophenylacetoneitrile,  $\text{NMe}:\text{CPh}:\text{CN}$ , in white leaflets, m. p. 37°.

An additive compound,  $\text{C}_{19}\text{H}_{16}\text{N}_3\text{Cl}$ , of pyridine, *α*-phenyliminobenzyl chloride and hydrogen cyanide was gradually deposited from a mixture of molecular quantities of the substances in dry ether. It formed pale yellow crystals, m. p. 253°, crystallised from water in large, yellow prisms with  $2\text{H}_2\text{O}$ , and yielded a dark red *picrate*, m. p. 180°. The corresponding quinoline compound,  $\text{C}_{23}\text{H}_{18}\text{N}_3\text{Cl}$ , also crystallised from water in large, yellow, hexagonal crystals with  $2\text{H}_2\text{O}$ . The free base could not be isolated, but the chloride was converted into a *picrate*, orange crystals, m. p. 180°, which combine with  $2\text{EtOH}$  to form dark red crystals, an almost insoluble *nitrate*, m. p. 210—213°, and a *hydrogen sulphate*, m. p. 223°. J. C. W.

### The Sensitiveness of Anthracene Derivatives towards Light.

I. The Anthracenecarboxylic Acids. FRITZ WEIGERT and LUDWIG KUMMERER (*Ber.*, 1914, 47, 898—908).—The anthracenecarboxylic acids in which the acid group is in the 9-, 2-, and 1-positions resemble anthracene and 2-methylanthracene in undergoing reversible chemical change under the influence of light.

The substances were exposed as solutions in Jena glass vessels of special shape, the usual source of light being a quartz-mercury lamp or a carbon arc.

Anthracene-9-carboxylic acid, m. p. 213—214° (decomp.), in aqueous solution as its sodium salt, when exposed to light and air undergoes oxidation to anthraquinone, the change being a genuine photochemical one. If air is excluded the sodium salt undergoes transformation with the production of the salt of a sparingly soluble, colourless acid which begins to go yellow near 180° and then melts gradually at 209—218° (decomp.). This photo-anthracene-9-carboxylic acid dissolves without fluorescence in ammonia, but on fusion is reconverted into the original acid. The new product is more easily obtained by illuminating solutions of the anthracene-9-carboxylic acid in organic solvents, when the sparingly soluble colourless photo-product separates in every case with solvent of crystallisation, for example, from alcohol in prisms or rhombohedral plates,  $\text{C}_{15}\text{H}_{10}\text{O}_2 \cdot \text{C}_2\text{H}_6\text{O}$ ; similar crystals were obtained with concurrent formation of anthraquinone and an odour of aldehyde when an alcoholic solution of the acid in a loosely closed vessel was exposed to sunlight for several days. Ebullioscopic experiments in alcoholic solution indicated a molecular weight between the single and the double value, so that the new acid is probably a dimeric form, a view which is somewhat confirmed by its separation from xylene and toluene solution with a half molecule of solvent of crystallisation if this is calculated on the single formula. The reversion of this acid to the simple anthracene-9-carboxylic acid also takes place rapidly in solution in boiling phenetole, a yellow solution being obtained which on cooling deposits yellow needles of the latter acid. At this temperature the equilibrium is preponderatingly in favour of the unimolecular acid, whilst in boiling xylene both the formation and reversion of the photo-product could be detected.

Anthracene-2-carboxylic acid, m. p. 271—277°, when illuminated in solution in acetic acid or toluene, is converted into a colourless, very sparingly soluble *photo-acid*, which separates from its dilute hot alcoholic solution in hexagonal leaflets; this begins to turn yellow at 200° and finally melts near 279° (decomp.). The substance, which gives non-fluorescent solutions in alkalis, can be reconverted into the original acid by fusion or by sublimation, and in boiling phenetole solution the direct change can be observed in the illumination of a carbon arc, whilst reversion occurs in the same solvent in diffused daylight.

Anthracene-1-carboxylic acid, m. p. 246°, when illuminated in alcoholic solution, undergoes concurrent oxidation to anthraquinone-1-carboxylic acid and conversion into a colourless new substance which is obtained more satisfactorily by the application of solutions in toluene or xylene. The new product is a *photo-acid* which dissolves in alkalis without fluorescence; it begins to turn yellow at 220°, and melts near 294° to a yellowish-brown liquid; this after solidifying gives a fluorescent solution in ammonium hydroxide, which is indicative of a reversion into the parent acid. The reversion is also induced by suspension of the colourless substance in boiling xylene, when a yellow solution of anthracene-1-carboxylic acid is gradually obtained. Judging from analogy to the first product described, this photo-product, as well as the preceding, probably has the bimolecular formula  $C_{30}H_{20}O_4$ .

Attention is drawn to the fact that the m. p.'s of these new substances are above the temperatures at which reversion sets in, so that the m. p.'s. lose in trustworthiness. The three examples of photo-chemical change now described resemble the cases of anthracene and 2-methylanthracene in that the products are not fluorescent and the shifting of the absorption towards the ultraviolet is easily recognised by the conversion of the three yellow acids into three colourless products.

D. F. T.

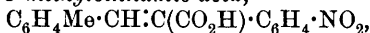
**Pschorr's Phenanthrene Synthesis.** FRITZ MAYER and GERHARD BALLE (*Annalen*, 1914, **403**, 167—203).—Pschorr's synthesis of phenanthrene derivatives (A., 1906, i, 848) from substituted benzaldehydes and nitrophenylacetic acids or from nitrobenzaldehydes and substituted phenylacetic acids leaves no doubt as to the constitution of the resulting phenanthrene derivative except when meta-substituted benzaldehydes or meta-substituted phenylacetic acids are employed; in such cases 2- and 4-phenanthrene derivatives are theoretically possible and are actually formed. The authors have prepared a number of phenanthrene derivatives by Pschorr's process. When the reaction results in the formation of two isomeric derivatives, guidance for the separation of the mixture has been obtained by adopting the plan of preparing, whenever possible, each of the isomerides by a reaction in which only that isomeride can be produced.

2-Nitro- $\alpha$ -phenyl-3-methylcinnamic acid,  $NO_2 \cdot C_6H_3Me \cdot CH \cdot CPh \cdot CO_2H$ , m. p. 221°, colourless prisms, obtained by heating equal molecular quantities of 2-nitro-*m*-tolualdehyde (m. p. 64°; compare Mayer, this vol., i, 291) and potassium phenylacetate with acetic anhydride and, a little zinc chloride at 110—120° in an atmosphere of carbon dioxide

is reduced by ferrous sulphate and aqueous ammonia to the corresponding *amino-acid*,  $C_{16}H_{15}O_2N$ , m. p.  $166^\circ$ , citron-yellow prisms. The latter yields 4-methylphenanthrene-9-carboxylic acid, m. p.  $211-212^\circ$ , almost colourless needles, by warming its diazotised solution in *N*-sulphuric acid on the water-bath. Starting with 4-nitro-*m*-tolualdehyde (m. p.  $44^\circ$ ; compare Mayer, *loc. cit.*) and by reactions similar to the preceding, 2-nitro- $\alpha$ -phenyl-5-methylcinnamic acid, m. p.  $203-204^\circ$ , colourless prisms, 2-amino- $\alpha$ -phenyl-5-methylcinnamic acid, m. p.  $211-212^\circ$ , citron-yellow needles, and 2-methylphenanthrene-9-carboxylic acid, m. p.  $252^\circ$ , have been prepared; the methyl ester of the last acid has m. p.  $104-105^\circ$ .

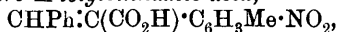
By distillation under diminished pressure or by heating with glacial acetic acid at  $220^\circ$ , 2-methylphenanthrene-9-carboxylic acid is converted into a substance,  $C_{17}H_{14}O_2$ , m. p.  $146-147^\circ$ , and 4-methylphenanthrene-9-carboxylic acid into a substance,  $C_{16}H_{14}O_2$ , m. p.  $188^\circ$ . Both substances are soluble in aqueous sodium hydroxide, and are reprecipitated by acids; they and also 2-methylphenanthrene-9-carboxylic acid do not yield by oxidation substances responding to Lauberheimer's reaction for phenanthraquinones.

*o*-Nitrophenyl-3-methylcinnamic acid,



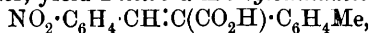
m. p.  $180-181^\circ$ , prepared by the condensation of *m*-tolualdehyde and sodium *o*-nitrophenylacetate, yields by reduction the corresponding *amino-acid*,  $C_{16}H_{15}O_2N$ , m. p.  $133^\circ$ , from which a mixture of the two preceding methylphenanthrenecarboxylic acids is obtained by shaking its diazotised solution with copper powder; the mixture is separated by means of glacial acetic acid, in which 2-methylphenanthrene-9-carboxylic acid is the less soluble.

The condensation of benzaldehyde and potassium 6-nitro-*m*-tolylacetate yields  $\alpha$ -6-nitro-*m*-tolylcinnamic acid,



m. p.  $202-203^\circ$ . The corresponding *amino-acid*,  $C_{16}H_{15}O_2N$ , exists in two modifications, m. p.  $153-154^\circ$ , colourless, rhombic plates, and  $189^\circ$ , yellow crystals, respectively; the former changes into the latter by warming. By heating its diazotised solution, the amino-acid yields 7-methylphenanthrene-9-carboxylic acid, m. p.  $227^\circ$ , prisms.

Potassium *m*-tolylacetate and *o*-nitrobenzaldehyde, by condensation in the usual manner, yield 2-nitro- $\alpha$ -*m*-tolylcinnamic acid,



m. p.  $141-142^\circ$  (methyl ester, m. p.  $70-71^\circ$ ), which is converted into the *amino-acid*,  $C_{16}H_{15}O_2N$ , m. p.  $152-153^\circ$ , citron-yellow crystals and also colourless crystals. The amino-acid is converted into 2-hydroxy-3-*m*-tolylquinoline,  $C_{16}H_{13}ON$ , m. p.  $213-214^\circ$ , by boiling with acetic anhydride and a little concentrated sulphuric acid, and by heating its diazotised solution yields a mixture of 2-hydroxy- $\alpha$ -*m*-tolylcinnamic acid,  $OH \cdot C_6H_4 \cdot CH : C(CO_2H) \cdot C_6H_4Me$ , m. p.  $210^\circ$ , 2-methylphenanthrene-10-carboxylic acid, and 5-methylphenanthrene-9-carboxylic acid, m. p.  $190^\circ$ ; attempts to eliminate carbon dioxide from the last acid or to oxidise it to a phenanthraquinone derivative have been unsuccessful.

3-Amino- $\alpha$ -phenylcinnamic acid,  $NH_2 \cdot C_6H_4 \cdot CH : CPh \cdot CO_2H$ , m. p.  $192^\circ$ , almost colourless needles, prepared by the reduction of the

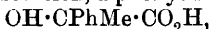
corresponding nitro-acid, yields 3-hydroxy- $\alpha$ -phenylcinnamic acid, not a phenanthrene derivative, by shaking its diazotised solution with copper powder. By similar treatment, diazotised  $\alpha$ -amino- $\alpha$ -phenylcinnamic acid also does not undergo ring closure. C. S.

**The Salicylonitriles.** COUSIN and VOLMAR (*Compt. rend.*, 1914, 158, 950—952).—The authors have determined the constitution of the two compounds described as salicylonitriles, one melting at 195° (compare Grimaux, *Bull. Soc. chim.*, 1870, 13, 26) and the other melting at 300° (compare Limpricht, *Annalen*, 1856, 98, 261, and Grimaux, *loc. cit.*).

The compound, m. p. 195°, obtained by dehydrating salicylamide by means of phosphoric oxide is better prepared by using ammonium salicylate instead of the amide, and is shown to be, in reality, disalicylamide,  $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO})_2\text{NH}$ .

The compound, m. p. 300°, obtained by heating salicylamide at 260—270° for one hour or the true salicylonitrile, m. p. 98°, at 160° for some time, is shown to be trihydroxytriphenyltriazine, as suggested without proof by Einhorn and Schmiedlin (*A.*, 1903, i, 31). By the action of nascent hydrogen generated by zinc in a solution of the compound in dilute aqueous potassium hydroxide, ammonia is evolved, and *trihydroxytriphenylglyoxaline hydrochloride* is finally obtained as a white, amorphous powder containing  $1\text{H}_2\text{O}$ . By precipitation from its alcoholic solution with ether, it is obtained anhydrous and crystalline in small, colourless prisms,  $\text{C}_{21}\text{H}_{16}\text{O}_3\text{N}_2\cdot\text{HCl}$ . The free *base* was obtained as a yellow powder, m. p. 207—208° (decomp.), and yielded a *platinichloride*, m. p. 226—227°. W. G.

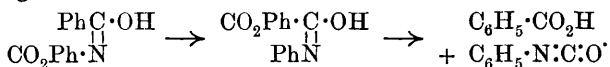
**The Nature of Racemisation.** OTTO ROTHE (*Ber.*, 1914, 47, 843—847).—The author supports the theory that racemisation is due to a mobile hydrogen atom, so that tautomerism and racemisation are regarded as analogous processes. In confirmation of this view he recalls the racemisation of the optically active  $\alpha$ -hydroxy-acids under the influence of alkali, and produces experimental evidence that although mandelic acid, which is capable of passing by enolisation from the structure  $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  to  $\text{OH}\cdot\text{CPh}\cdot\text{C}(\text{OH})_2$ , readily racemises in hot alkaline solution,  $\alpha$ -phenyl-lactic acid,



which is unable to isomerise in this manner, is stable under similar conditions. D. F. T.

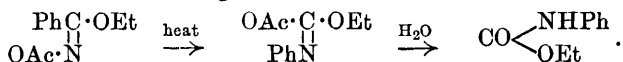
**The Beckmann Rearrangement.** III. MITSURU KUHARA and TEPPEI OKADA (*Mem. Coll. Sci. Eng. Kyōtō*, 1913, 6, 1—11. Compare *A.*, 1911, i, 213).—The decomposition of dihydroxamic acids is discussed, and it is shown that the facts support the authors' views concerning the Beckmann transformation. For example, the decomposition of dibenzhydroxamic acid or its potassium salt by water is explained by assuming an interchange of positions between the phenyl group and the benzoic acid residue, followed by disruption of the

intermediate compound into benzoic acid and phenylcarbimide, according to the scheme :



The carbimide would react with the water to form diphenylcarbamide or even aniline. Thus, on distilling an aqueous solution of the neutral potassium salt, aniline was obtained (compare Lossen, A., 1872, 415, and Rotermund, A., 1875, 768). Aniline could not be obtained in this way from potassium benzhydroxamate or the corresponding ethyl ester, the necessary acid residue attached to nitrogen being lacking. The formation of diphenylcarbamide by warming the potassium carbonate solution of acetylbenzhydroxamic acid (Hantzsch, A., 1894, i, 364) is also explained by assuming the Beckmann rearrangement. The decomposition of benzhydroxamic acid and its barium salt by dry distillation into aniline and carbon dioxide (Lossen, A., 1875, 769), on the contrary, is explained by assuming the intermediate formation of an anhydride (compare Hantzsch, *loc. cit.*).

The *syn*- and *anti*-acetyl derivatives of ethylbenzhydroxamic acid (Werner, A., 1892, i, 463) have also been examined. They were heated for some time above their melting points, and then the products were distilled from alkaline solutions in a current of steam. The *syn*-derivative yielded aniline, from the decomposition of diphenylurethane formed according to the scheme :



The *anti*-derivative did not yield a trace of aniline. The compounds were also heated with chloroform saturated with hydrogen chloride for twelve hours at 100°. Again, the *anti*-ester did not react, but the rearrangement of the *syn*-compound was accelerated, phenylurethane and acetylphenylurethane being formed.

The rearrangement of benzenesulphonyl and other acyl derivatives of ketoximes is also discussed in some remarks preliminary to a detailed communication in the near future. J. C. W.

**Friedel and Crafts' Reaction: The Preparation of *o*-Benzoylbenzoic Acid and Benzophenone.** C. R. RUBIDGE and N. C. QUA (*J. Amer. Chem. Soc.*, 1914, 36, 732—737. Compare Heller and Schülke, A., 1908, i, 994).—When 9 grams of anhydrous aluminium chloride are gradually added to a solution of 5 grams of phthalic anhydride in 18—20 c.c. of benzene, and the mixture, after keeping at the ordinary temperature for an hour, is heated on a water-bath for two hours, a 97% yield of *o*-benzoylbenzoic acid is obtained and rather more than a molecular proportion of hydrogen chloride is evolved.

With less aluminium chloride, the yield of *o*-benzoylbenzoic acid is considerably reduced, and diphenylphthalide is also produced together with phthalic acid, the formation of the former being due to the action of phthalic anhydride on the intermediate product of the action. It is found that diphenylphthalide is also obtained if other anhydrides, such



as succinic or acetic, are added to a mixture of less than the optimum amount of aluminium chloride with phthalic anhydride and benzene which has already been heated for some time and is again heated after the addition.

In the preparation of benzophenone from benzoyl chloride, benzene and aluminium chloride, reduction of the proportion of the last reagent causes a diminution in the yield. If the mixture which is obtained as reaction product is subsequently re-heated with the addition of phthalyl chloride, the yield of benzophenone is not materially diminished, although a considerable quantity of diphenylphthalide is formed. Benzophenone can also be obtained from benzoic anhydride, benzene, and aluminium chloride, but the yield is not good. D. F. T.

### Semicyclic 1:5-Diketones and Bicyclic Ketone Alcohols.

HANS STOBBE (*J. pr. Chem.*, 1914, [ii], 89, 184—189).—In continuation of previous work (Stobbe and others, A., 1912, i, 779—786) on the formation of semicyclic 1:5-diketones and bicyclic ketone-alcohols by the direct union of cyclic ketones with  $\alpha\beta$ -unsaturated ketones in the presence of sodium ethoxide or secondary amines, the author, in conjunction with Schwyzer and Cruikshanks (following abstracts), has examined the behaviour of *cyclopentanone* and 3-methyl*cyclohexanone* towards the ethyl esters of  $\alpha$ -benzylidenebenzoylacetic and  $\alpha$ -benzylideneacetoacetic acids, and finds that whilst the esters readily combine in the normal manner with *cyclopentanone*, in the case of 3-methyl*cyclohexanone* no condensation could be effected by any of the usual reagents.

The product from *cyclopentanone* and ethyl  $\alpha$ -benzylidenebenzoylacetate behaves as true diketone of the following constitution:

(I.)  $\begin{array}{c} \text{CH}_2\text{--CO} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CHPh}\cdot\text{CH} < \begin{array}{c} \text{CO}_2\text{Et} \\ | \\ \text{CO Ph} \end{array}$  The condensation product from ethyl  $\alpha$ -benzylideneacetoacetate and *cyclopentanone*, on the other hand, reacts towards semicarbazide and diphenylhydrazine as a monoketone, and therefore may be represented as a bicyclic ketone-alcohol of the constitution shown in (III.) rather than as a 1:5-diketone (II.), although all attempts to obtain evidence of the presence of a hydroxyl group proved unsuccessful.

(II.)  $\begin{array}{c} \text{CH}_2\text{--CO} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CHPh}\cdot\text{CH} < \begin{array}{c} \text{CO}_2\text{Et} \\ | \\ \text{COMe} \end{array}$

(III.)  $\text{CH}_2 < \begin{array}{c} \text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO} \\ | \\ \text{CH}_2\cdot\text{CH}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \end{array}$

The alcoholic solution of the compound shows no reaction with ferric chloride, but after fusion and resolidification gives in alcoholic solution with ferric chloride a deep cherry-red coloration, which the author ascribes to transformation into the enolic form (IV. or V.).

(IV.)  $\begin{array}{c} \text{CH}_2\text{--CO} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CHPh}\cdot\text{C} < \begin{array}{c} \text{CO}_2\text{Et} \\ | \\ \text{CMe}\cdot\text{OH} \end{array}$

(V.)  $\text{CH}_2 < \begin{array}{c} \text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{C}(\text{OH}) \\ | \\ \text{CH}_2\cdot\text{CH}\cdot\text{CHPh}\cdot\text{C}\cdot\text{CO}_2\text{Et} \end{array}$

If the enolised ester is kept for some time in the superfused condition at the ordinary temperature it is reconverted into the ketonic ester.

F. B.

**Reaction Products from Ethyl Benzylideneacetoacetate and Cyclic Ketones in the Presence of Secondary Bases or Sodium Ethoxide.** ALEXANDER SCHWYZER and GEORGE S. CRUIKSHANKS (*J. pr. Chem.*, 1914, [ii], 89, 189—193).—*Ethyl α-acetyl-β-phenyl-β-2-cyclopentanonylpropionate* or *ethyl 4-hydroxy-8-phenyloctahydroindene-7-carboxylate* (formula II or III, preceding abstract), prepared by maintaining a benzene solution of ethyl α-benzylideneacetoacetate and cyclopentanone, containing a little piperidine or piperidine carbonate, for several weeks at the ordinary temperature, has m. p. 173—174°, and is converted by the action of alcoholic piperidine and strong sulphuric acid into *esters* of m. p. 124° and 100° respectively, the constitution of which has not yet been determined; the *monosemicarbazone*, m. p. 140—142°, the *monodiphenylhydrazone*, m. p. 192° (decomp.), the *monophenylbenzylhydrazone*, m. p. 146°, were prepared.

Attempts to condense ethyl α-benzylideneacetoacetate with 3-methylcyclohexanone resulted in the formation of ethyl benzylidenediacetate (Rabe, A., 1902, i, 709), the *semicarbazone* of which has m. p. 215—216°.

F. B.

**Reaction Products from Ethyl Benzylidenebenzoylacetate and Cyclic Ketones in the Presence of Secondary Bases or Sodium Ethoxide.** GEORGE S. CRUIKSHANKS (*J. pr. Chem.*, 1914, [ii], 89, 194—198).—Ethyl α-benzylidenebenzoylacetate (Ruhemann, T., 1903, 83, 720) is obtained in good yield by the addition of alcoholic ammonia to a mixture of ethyl benzoylacetate and benzaldehyde. It condenses with cyclopentanone in benzene solution in the presence of piperidine or diethylamine, yielding *ethyl α-benzoyl-β-phenyl-β-2-cyclopentanonylpropionate*,  $\begin{matrix} \text{CH}_2\text{--CO} \\ \text{CH}_2\text{·CH}_2 \end{matrix} > \text{CH·CHPh·CH} < \begin{matrix} \text{CO}_2\text{Et} \\ \text{COPh} \end{matrix}$ , which could

not be isolated in a crystalline condition and was therefore characterised by conversion into the *disemicarbazone*, m. p. 200° (decomp.). If sodium ethoxide in alcoholic solution is employed as a condensing agent, the product consists of the sodium salt of α-benzylidenebenzoylacetate. Attempts to effect the condensation of ethyl α-benzylidenebenzoylacetate with 3-methylcyclohexanone by means of piperidine resulted in the formation of ethyl benzylidenebisbenzoylacetate (Bertini, A., 1904, i, 167).

F. B.

**Diphenylaminedicarboxylic Acids.** ARTILIO PURGOTTI (*Gazzetta*, 1914, 44, i, 386—388. Compare Farbwerke vorm. Meister, Lucius & Brüning A., 1904, i, 50, 168, 317; Ullmann & Hoz, A., 1907, 1, 846).—The compounds previously obtained by the author and Lunini (A., 1904, i, 315) by the action of 2-chloro-3:5-dinitrobenzoic acid on the three aminobenzoic acids are dinitro-derivatives of the three isomeric diphenylaminedicarboxylic acids, which have now been prepared.

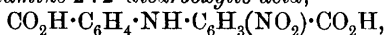
Diphenylamine-2:2'-dicarboxylic acid,  $\text{NH}(\text{C}_6\text{H}_4\text{·CO}_2\text{H})_2$ , prepared by boiling sodium o-chlorobenzoate (1 mol.), sodium anthranilate, (1 mol.), sodium carbonate (1 mol.), and a little powdered copper in

suspension in amyl alcohol, forms faintly yellow needles, m. p. 296—297° (decomp.).

Diphenylamine-2 : 3'-dicarboxylic acid,  $C_{14}H_{11}O_4N$ , similarly obtained from *o*-chlorobenzoic and *m*-aminobenzoic acids, forms minute, colourless crystals, m. p. 275°.

Diphenylamine-2 : 4'-dicarboxylic acid,  $C_{14}H_{11}O_4N$ , prepared from *o*-chlorobenzoic and *p*-aminobenzoic acids, crystallises in small, colourless plates, m. p. 253—254°.

4-Nitrodiphenylamine-2 : 2'-dicarboxylic acid,

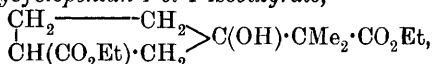


similarly prepared from *o*-aminobenzoic and 2-chloro-5-nitrobenzoic acids, forms a lemon-yellow, crystalline powder, m. p. about 300°.

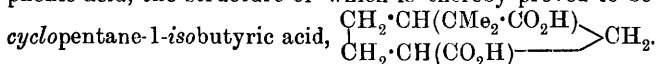
4-Nitrodiphenylamine-2 : 3'-dicarboxylic acid,  $C_{14}H_{10}O_6N_2$ , from *m*-aminobenzoic and 2-chloro-5-nitrobenzoic acids, has m. p. about 320°, and the isomeric 4-nitrodiphenylamine-2 : 4'-dicarboxylic acid, from *p*-aminobenzoic and 2-chloro-5-nitrobenzoic acids, m. p. about 314°.

T. H. P.

**Constitution and Synthesis of Camphenic Acid (Camphene-camphoric Acid).** PETER LIPP (*Ber.*, 1914, 47, 871—875).—Ethyl cyclopentan-1-one-3-carboxylate (Kay and Perkin, T., 1906, 89, 1643), ethyl  $\alpha$ -bromoisobutyrate and zinc turnings when heated together in boiling benzene undergo condensation to a grey gelatinous zinc compound which on treatment with ice and dilute sulphuric acid yields *ethyl 3-carbethoxycyclopentan-1-ol-1-isobutyrate*,



b. p. 164—170°/8—9 mm.; this was purified by redistillation under a pressure of approximately 1 mm., the yield being 43·5% of the theoretical. The hydroxy-ester loses the elements of water fairly readily, and when heated at 170—180° with potassium hydrogen sulphate for eight hours gives the *ethyl ester*, an oil, b. p. 112—115°/0·5 mm., of valerian-like odour, mixed with some of the *ethyl hydrogen ester*, and a viscous oil, b. p. 150—153°/1 mm., of  $\Delta^1$ - or  $\Delta^5$ -3-carboxycyclopentene-1-isobutyric acid, needles, m. p. 139—141° (corr.), which can be obtained by hydrolysis of either of the esters with alcoholic potassium hydroxide. If this acid is then submitted in ethereal solution to the action of hydrogen and platinum black, it is reduced to *dl-cis-camphenic acid*, the structure of which is thereby proved to be 3-carboxycyclopentane-1-isobutyric acid,



The structure suggested by Aschan (A., 1910, i, 709; 1911, i, 797) and supported by the author (A., 1913, i, 1077) is thus verified.

D. F. T.

**Tetrachlorofluorescein and Some of its Derivatives.** W. R. ORNDORFF and E. F. HITCH (*J. Amer. Chem. Soc.*, 1914, 36, 680—725).—Tetrachlorofluorescein was prepared by several modifications of Graebe's method (A., 1887, 832), and was purified by conversion into the colourless diacetate by means of acetic anhydride and sodium

acetate; the diacetate on hydrolysis with alcoholic potassium hydroxide yields the dipotassium salt of a yellow hydrate, which on heating passes into tetrachlorofluorescein itself.

When pure tetrachlorofluorescein in very dilute alkaline solution is poured into an excess of dilute mineral acid, tetrachlorofluorescein hydrate is obtained as a pale yellow solid; this readily undergoes dehydration, for example, slowly at  $110^{\circ}$  or even on boiling with water, with formation of the red tetrachlorofluorescein. It gives the same diacetate as is obtained from anhydrous tetrachlorofluorescein; it is completely soluble in ether, and separates from acetone in almost colourless crystals containing a molecular proportion of acetone which is easily yielded at  $160^{\circ}$ . By recrystallising in a moist condition from alcohol, it can be converted into the corresponding carbinol-carboxylic acid.

*Tetrachlorofluoresceincarbinolcarboxylic acid*, obtained also by hydrolysing tetrachlorofluorescein diacetate with alcoholic sodium hydroxide and pouring the diluted alkaline solution into an excess of dilute hydrochloric acid, is an almost colourless solid which separates with  $\frac{1}{2}\text{H}_2\text{O}$ ; at  $150^{\circ}$  or even when boiled with water it is converted into red tetrachlorofluorescein. It gives the same diacetate as is obtainable from tetrachlorofluorescein and its hydrate, and can be converted into the last-named substance by dissolving in alkali and acidifying the solution.

Tetrachlorofluorescein when heated with acetic anhydride and sodium acetate for three hours is converted into the *diacetate*, colourless crystals (with  $1\text{C}_6\text{H}_6$  from benzene), m. p.  $256^{\circ}$ . With benzoyl chloride and potassium hydroxide solution, tetrachlorofluorescein passes into a *monobenzoate*, colourless crystals, m. p.  $235^{\circ}$ , which on further treatment with boiling acetic anhydride is converted into a *benzoylacetyl* derivative. *Tetrachlorofluorescein dibenzoate* was obtained by heating tetrachlorofluorescein with excess of benzoyl chloride for a half hour, the product being quite colourless, m. p.  $247^{\circ}$ .

When some of the solvent is distilled under reduced pressure from a solution of tetrachlorofluorescein hydrate in ether, colourless crystals of an *etherate*,  $\text{C}_{20}\text{H}_8\text{O}_5\text{Cl}_4\cdot\text{Et}_2\text{O}$ , are obtainable; this slowly loses ether even at the ordinary temperature, giving tetrachlorofluorescein in a yellow *lactonoid* form (see below), but when heated with water gives the dark red quinonoid form. In a similar manner a crystalline *compound* of tetrachlorofluorescein with ethyl acetate can be prepared, and it is also possible that the crystals obtained from an acetone solution of tetrachlorofluorescein hydrate (see earlier) consist of a mixture of a diacetate of tetrachlorofluorescein with the colourless carbinol-carboxylic acid form of the substance.

Tetrachlorofluorescein when heated with an alcoholic solution of potassium acetate forms a pale red *monopotassium* salt, which crystallises with  $3\text{H}_2\text{O}$ , whilst the *dipotassium* salt is obtainable by hydrolysis of the diacetate with alcoholic potassium hydroxide; the latter forms dark red prisms with a green lustre and separates with  $5\text{H}_2\text{O}$ . Whether the yellow hydrate or the carbinol-carboxylic acid form of tetrachlorofluorescein will be formed on acidifying a solution of the dipotassium salt depends on the concentration and the excess of acid; very dilute solutions and

a very slight excess of acid favour the formation of the hydrate. The orange-yellow *monosodium* salt (with  $2\text{H}_2\text{O}$ ) and the *disodium* salt, dark red prisms with  $5\text{H}_2\text{O}$  were prepared similarly to the corresponding potassium salts.

The behaviour of the various forms of tetrachlorofluorescein towards dry ammonia was investigated. The red anhydrous tetrachlorofluorescein gave a *diammonium* salt which lost its ammonia at  $150^\circ$  in a current of hydrogen. The lactonoid form became bright red and gave a *triammonium* salt, all the ammonia being again yielded to a current of air or hydrogen at  $110^\circ$ . The carbinol-carboxylic acid and the yellow hydrate both became red, and also absorbed a termolecular proportion of ammonia, which they yielded again on heating, with simultaneous conversion into the red anhydrous form.

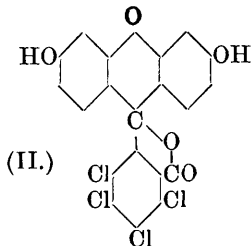
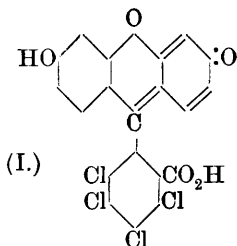
When heated for one hour at  $100^\circ$  with alcohol and sulphuric acid, anhydrous tetrachlorofluorescein is converted into a crystalline *monomethyl* ester, which gives fluorescent solutions in alkalis. In a current of hydrogen chloride the ester is converted into a *hydrochloride*,  $\text{C}_{20}\text{H}_7\text{O}_5\text{Cl}_4\text{Me}\cdot\text{HCl}$ , an orange-coloured solid. In a similar manner, red anhydrous fluorescein itself yielded a yellow *hydrochloride*,  $\text{C}_{20}\text{H}_{12}\text{O}_5\cdot\text{HCl}$ , but the red anhydrous tetrachlorofluorescein did not combine with hydrogen chloride in this manner.

*Tetrachloroeosin*,  $\text{C}_{20}\text{H}_4\text{O}_5\text{Cl}_4\text{Br}_4$ , was obtained by the direct bromination of anhydrous tetrachlorofluorescein suspended in acetic acid; it crystallised from acetic acid in colourless crystals containing a molecule of acetic acid which is lost at  $150^\circ$ . This substance becomes pink when heated at  $190\text{--}200^\circ$ , but without loss of water, and it appears to be the analogue of the lactonoid form of anhydrous tetrachlorofluorescein.

*Tetrachloroeosin hydrate*,  $\text{C}_{20}\text{H}_4\text{O}_5\text{Cl}_4\text{Br}_4\cdot\text{H}_2\text{O}$ , prepared analogously to tetrachlorofluorescein hydrate, is a pink solid, whilst *tetrachloroeosin diacetate*,  $\text{C}_{20}\text{H}_2\text{O}_5\text{Cl}_4\text{Br}_4\text{Ac}_2$ , is a colourless substance, m. p.  $298\text{--}300^\circ$ , which crystallises from ethyl acetate with  $1\text{CH}_3\cdot\text{CO}_2\text{Et}$ . Tetrachloroeosin gives a *dipotassium* derivative, deep red crystals, whilst dry ammonia is absorbed, both by the pink and colourless forms, to the extent of  $5\text{NH}_3$ , with the formation of a red *ammonium* salt.

An examination of the absorption spectra of fluorescein, eosin, and their tetrachloro-derivatives shows that the absorption is least marked with fluorescein; tetrachlorofluorescein and eosin have comparable absorption, whilst the effect is most marked with tetrachloroeosin. The fluorescence ranges from greenish-yellow with fluorescein to brick-red with tetrachloroeosin.

To the coloured and more stable form of tetrafluorescein is ascribed the quinonoid formula (I), whilst the colourless form is represented by the lactonoid formula II. The yellow hydrate is probably derived from formula I by the conversion of the  $-\text{CO}_2\text{H}$  group into  $-\text{C}(\text{OH})_3$ , instead of having the lactonoid structure assigned to it by Graebe (*loc. cit.*), whilst the colourless carbinol-carboxylic acid may be of the constitution  $\text{O} < \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix} > \text{C}(\text{OH})\cdot\text{C}_6\text{Cl}_4\cdot\text{CO}_2\text{H}$ . Constitutional formulæ are also suggested for the various acetates and benzoates, the



salts with the alkali metals and with ammonia, the compounds with hydrogen chloride, and also for the compounds separating from solution with solvent "of crystallisation."

The case of tetrachloroeosin is regarded as largely analogous to that of tetrachlorofluorescein.

D. F. T.

### Synthesis of Depsides from Pyrogallolcarboxylic Acid.

F. MAUTHNER (*J. pr. Chem.*, 1914, [ii], **89**, 302—309. Compare A., 1913, i, 50, 629).—The following compounds, all of which crystallise in colourless needles, have been prepared by the gradual addition of 2:3:4-trimethoxybenzoyl chloride dissolved in acetone to a well-cooled solution of the requisite hydroxy-acid or its ester in aqueous acetone, containing sodium hydroxide.

p-2:3:4-Trimethoxybenzoyloxybenzoic acid, m. p. 181—182°, from p-hydroxybenzoic acid; the methyl ester has m. p. 129—130°. m-2:3:4-Trimethoxybenzoyloxybenzoic acid, m. p. 145—146°; the methyl ester, m. p. 80—81°.

p-2:3:4-Trimethoxybenzoyloxy-3-methoxybenzoic acid, from vanillic acid, has m. p. 188—189°; the methyl ester, m. p. 97—98°.

2(2:3:4)-Trimethoxybenzoyloxy-3-naphthoic acid, from 2-hydroxy-3-naphthoic acid, has m. p. 167—168°.

2:3:4-Trimethoxybenzanilide forms colourless needles, m. p. 103—104°.

F. B.

### Constitutions of Certain Trimethoxyphthalic Acids. II.

G. BARGELLINI (*Gazzetta*, 1914, **44**, i, 182—192).—In continuation of earlier work (A., 1912, i, 773), the author has prepared 3:4:6-trimethoxyphthalic acid from Thiele and Günther's 2:3-dicyano-6-hydroxyquinol triacetate (A., 1906, i, 743). This acid is found to melt at a rather higher temperature than that obtained by Feist (A., 1908, i, 100) from the alkaloids of calumba root, but the author regards the two acids as identical, so that the three methoxyl or hydroxyl groups of these alkaloids would seem to be arranged asymmetrically in a single nucleus.

3:4:6-Trimethoxyphthalonitrile,  $C_6H(OMe)_3(CN)_2$ , obtained by the simultaneous action of potassium hydroxide and methyl sulphate on 2:3-dicyano-6-hydroxyquinol triacetate, forms white needles, m. p. 195—198°, and dissolves in concentrated sulphuric acid, giving a yellow solution, which exhibits green fluorescence.

3:4:6-Trimethoxyphthalic acid,  $C_6H(OMe)_3(CO_2H)_2$ , prepared by hydrolysis of the preceding compound, forms colourless, rhomboidal

crystals (+  $\text{H}_2\text{O}$ ). When slowly heated, it gradually turns yellow and melts at  $212\text{--}213^\circ$ , which is the melting point of the anhydride, but if the anhydrous acid is introduced into a bath at  $180^\circ$ , it first melts and loses water at about  $185^\circ$ . Both the acid and its derivatives dissolve in the cold in concentrated sulphuric acid, giving yellow solutions, which become reddish-brown when heated. The *anhydride*,  $\text{C}_{11}\text{H}_{10}\text{O}_6$ , forms pale greenish-yellow, microscopic needles, m. p.  $207\text{--}209^\circ$ , and with a number of organic solvents gives solutions showing blue fluorescence. The *imide*,  $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}$ , obtained by heating the ammonium salt of the acid, forms slender, white needles, m. p.  $244\text{--}246^\circ$ , its alcoholic solution exhibiting blue fluorescence; it could not be prepared by the action of concentrated sulphuric acid on 3:4:6-trimethoxyphthalonitrile (compare Thiele and Günther, *loc. cit.*), which yields a compound infusible at  $260^\circ$ . The *anilide*,  $\text{C}_{17}\text{H}_{15}\text{O}_5\text{N}$ , forms yellow needles, m. p.  $201^\circ$ , and 3:4:6-trimethoxyphthalanilic acid,  $\text{C}_{17}\text{H}_{17}\text{O}_6\text{N}$  ( $\text{CO}_2\text{H}:\text{CO}\cdot\text{NHPh}=1:2$  or  $2:1$ ), microscopic, white needles, m. p.  $158\text{--}159^\circ$ . T. H. P.

**Benzylthiolacetal and  $\beta$ -Phenylthiolpropaldehyde.** C. G. HUTCHISON and S. SMILES (*Ber.*, 1914, 47, 805—807).—*Benzylthiolacetal*,  $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , was prepared by the interaction of the sodium derivative of benzylmescaptan and chloroacetal for three hours in boiling alcoholic solution; it is a pungent, colourless oil, b. p.  $192\text{--}195^\circ/30$  mm.

*$\beta$ -Phenylthiolpropaldehyde*,  $\text{SPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$ , was obtained from  *$\alpha\beta$ -dihydroxy- $\gamma$ -phenylthiolpropane*,  $\text{SPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , by intramolecular rearrangement induced by dilute sulphuric acid. The latter substance, colourless leaflets, m. p.  $65\text{--}67^\circ$ , was obtained by treating sodium phenylmercaptide with an equivalent quantity of glycerol  $\alpha$ -chlorohydrin in concentrated solution; it is considerably associated in solution in alcohol and benzene. When the above glycol is heated with 50% sulphuric acid for three to four hours, a mixture of crystals and oil can be obtained; the former, leaflets, m. p.  $163^\circ$ , is a termolecular form of  $\beta$ -phenylthiolpropaldehyde, and does not give the usual aldehyde reactions, although it can be partly resolved into the unimolecular form by treatment with mineral acids or distillation. The oil, from which the crystals have been separated, gradually sets to a solid, which after purification by recrystallisation from alcohol forms needles, m. p.  $110^\circ$ ; this is likewise a termolecular modification of  $\beta$ -phenylthiolpropaldehyde.

It was not found possible to effect an intramolecular condensation of either of the above products to a cyclic structure (compare Autenrieth, A., 1891, 540). D. F. T.

**Formation of Cyclic Compounds from  $\alpha\delta$ -Diketones.** E. E. BLAISE (*Compt. rend.*, 1914, 158, 708—711).—*s*-Dipropionylethane on warming with a 10% solution of potassium hydroxide in methyl alcohol for twenty minutes is readily converted into 2-methyl-3-ethyl- $\Delta^2$ -cyclopenten-1-one, b. p.  $90\cdot5^\circ/15$  mm., giving a *semicarbazone*, m. p.  $267^\circ$ , and a *phenylhydrazone*, m. p.  $204^\circ$ . On oxidation with potassium permanganate this cyclic ketone gives acetic acid and  $\beta$ -propionyl-

propionic acid, thus proving its constitution. Neither acetonylacetone nor acetonylacetophenone, however, undergoes this conversion into cyclic ketones under similar conditions, the reaction being apparently not applicable to methylated  $\alpha\delta$ -diketones.

W. G.

**The Use of Manganous Oxide for the Catalysis of Acids: Preparation of Aliphatic and Aromatic Ketones.** PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1914, 158, 830—835).—Manganous oxide is an excellent catalyst for the preparation of simple or mixed aliphatic and aromatic ketones from the corresponding acids. The manganous oxide is readily prepared in situ by heating precipitated manganous carbonate in a current of methyl alcohol vapour at  $400^\circ$ . The vapours of the acid or mixture of acids are passed over the oxide at  $400$ — $450^\circ$ , a layer 60 cm. long being used. The yield is in most cases well over 70%.

The method has been applied to the preparation of a large number of ketones, of which the following have not yet been described. A mixture of pelargonic and benzoic acids yielded *phenyl octyl ketone*,  $\text{COPh}\cdot\text{C}_8\text{H}_{17}$ , m. p.  $46^\circ$ , b. p.  $298$ — $300^\circ$ , giving a *semicarbazone*, m. p.  $115^\circ$ , and on hydrogenation over reduced nickel at  $300^\circ$ , *nonylbenzene*,  $\text{C}_9\text{H}_{19}\text{Ph}$ , a colourless liquid, b. p.  $275^\circ$ .

From a mixture of myristic and benzoic acids, *phenyl tridecyl ketone*,  $\text{COPh}\cdot\text{C}_{13}\text{H}_{27}$ , m. p.  $55.5^\circ$ , was obtained, giving a *semicarbazone*, m. p.  $75^\circ$ .

W. G.

**The Use of Manganous Oxide for the Catalysis of Acids: Preparation of Aldehydes and cyclopentyl Ketones. Formation of cyclopentylamines.** PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1914, 158, 985—991. Compare preceding abstract).—Manganous oxide can with advantage be used in place of titanous oxide (compare A., 1912, i, 238) for the preparation of aldehydes from the mixed vapours of formic acid with aliphatic or arylacetic acids. The new catalyst retains its power much longer, is easier to prepare, and gives a better yield. The following aldehydes have been prepared by means of it: *isovaleraldehyde*, *hexaldehyde*, *heptaldehyde*, *octaldehyde*, *nonaldehyde*, and *phenylacetaldehyde*.

When adipic and  $\beta$ -methyladipic acids are passed separately over manganous oxide at  $350^\circ$ , they give a nearly theoretical yield of *cyclopentanone* and  $\beta$ -methylcyclopentanone respectively without any noticeable production of decomposition products. When the oximes of these ketones are passed with an excess of hydrogen over finely divided nickel at  $180^\circ$  (compare A., 1905, i, 635) they undergo hydrogenation.

*cyclopentanoneoxime* gives a mixture of *cyclopentylamine*, b. p.  $106^\circ$ , *dicyclopentylamine*,  $(\text{C}_5\text{H}_9)_2\text{NH}$ , a colourless liquid, b. p.  $205$ — $210^\circ$ , giving a *phenylurethane*, m. p.  $128^\circ$ , and *tricyclopentylamine*,  $(\text{C}_5\text{H}_9)_3\text{N}$ , a strongly alkaline liquid, b. p.  $320^\circ$ , which rapidly oxidises on exposure to air. The secondary amine constitutes the greater portion of the yield.

$\beta$ -Methylcyclopentanoneoxime similarly yields  $\beta$ -methylcyclopentylamine, b. p.  $124$ — $125^\circ$ , *di- $\beta$ -methylcyclopentylamine*,  $(\text{C}_6\text{H}_{11})_2\text{NH}$ , a



strongly alkaline, colourless liquid, b. p. 220—225°, giving a *phenylurethane*, m. p. 73°, and *tri-β-methylcyclopentylamine*,  $(C_6H_{11})_3N$ , b. p. 340°, rapidly oxidising in the air. W. G.

**Catalytic Preparation of New Ketones.** A. MAILHE (*Bull. Soc. chim.*, 1914, [iv], 15, 324—326).—By passing the mixed vapours of several pairs of acids over a layer of ferric oxide at 470—480°, the author has prepared a number of new ketones.

Benzoic and phenylacetic acids yield *phenyl benzyl ketone*,  $CH_2Ph \cdot CPh$ , m. p. 60°.

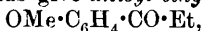
Benzoic and phenylpropionic acids yield *benzyl phenylethyl ketone*,  $CH_2Ph \cdot CH_2 \cdot CPh$ , m. p. 72°, b. p. 360°.

The three toluic acids with phenylacetic acid furnish the three *tolyl benzyl ketones*,  $C_6H_4Me \cdot CO \cdot CH_2Ph$ , of which the *ortho*-isomeride is a liquid, b. p. 318—326°; the *meta* has m. p. 42°, and gives a *semi-carbazone*, m. p. 168°; the *para* has m. p. 110°, and gives an oxime, m. p. 130—131°.

The three toluic acids react similarly with phenylpropionic acid, giving *o-tolyl phenylethyl ketone*,  $C_6H_4Me \cdot CO \cdot CH_2 \cdot CH_2Ph$ , b. p. 330—340°, yielding an *oxime*, m. p. 85°; *m-tolyl phenylethyl ketone*, b. p. 345—347°; *p-tolyl phenylethyl ketone*, m. p. 69°.

A mixture of acetic and anisic acids yields *anisyl methyl ketone*, m. p. 33°, which combines with sodium hydrogen sulphite.

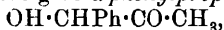
Propionic and anisic acids give *anisyl ethyl ketone*,



m. p. 29°, and butyric and anisic acids yield *anisyl propyl ketone*,  $OMe \cdot C_6H_4 \cdot COPr$ , b. p. 275°.

*m*-Aminobenzoic acid with acetic acid yields *m*-aminoacetophenone,  $NH_2 \cdot C_6H_4 \cdot COMe$ , m. p. 90°.

Mandelic and acetic acids give *α-phenylpropane-α-ol-β-one*,



b. p. 205—207°, which when passed over finely divided copper at 350° gives the *diketone*,  $CPh \cdot COMe$ , b. p. 214—215°.

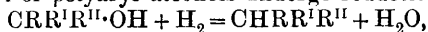
Mandelic and propionic acids similarly give *α-phenylbutane-α-ol-β-one*,  $OH \cdot CHPh \cdot COEt$ , b. p. 215°, which in the presence of divided copper gives the *diketone*,  $CPh \cdot COEt$ , b. p. 227—228°.

Finally, the mixed vapours of acetic and cinnamic acids yield methyl styryl ketone. W. G.

**Direct Hydrogenation by Catalysis of Diarylacetones and Aryl Alcohols. Preparation of Polyaryl Hydrocarbons.** PAUL SABATIER and M. MURAT (*Compt. rend.*, 1914, 158, 760—764. Compare Darzens, A., 1905, i, 66; and Sabatier and Mailhe, A., 1908, i, 36).—Diaryl ketones of the type of benzophenone and its homologues readily undergo hydrogenation in the presence of slightly active nickel at temperatures of 300—350°, giving the corresponding diaryl hydrocarbons. At lower temperatures with very active nickel the aromatic nucleus undergoes hydrogenation. The following reductions have been carried out, the yields being good in each case. Benzophenone at 300° gave diphenylmethane, and at 170° over very active nickel yielded *dicyclohexylmethane*. Phenyl benzyl ketone at 350° was

reduced to *s*-diphenylethane. *s*-Diphenylacetone at 40° yielded *s*-diphenylpropane with a small amount of toluene. Benzoylphenylethane,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , at 360° furnished *s*-diphenylpropane.

Similarly, aryl or polyaryl alcohols undergo reduction as follows :



where R is an aryl group and  $\text{R}^{\text{I}}$  and  $\text{R}^{\text{II}}$  are either an alkyl or an aryl group or a hydrogen atom. Thus benzyl alcohol yields toluene; phenylethyl alcohol gives ethylbenzene; phenylmethylcarbinol yields ethylbenzene; diphenylcarbinol furnishes diphenylmethane; phenyl-*p*-tolylcarbinol is reduced to phenyl-*p*-tolylmethane; benzylphenylcarbinol gives *s*-diphenylethane, and triphenylcarbinol yields triphenylmethane.

W. G.

**Synthesis by means of Sodamide.** Preparation of Allylated Ketones Derived from Alkylacetophenones and Pinacolone. A. HALLER and ED. BAUER (*Compt. rend.*, 1914, 158, 825—830. Compare A., 1909, i, 109).—The authors have prepared a number of trialkylacetophenones, in which one or more of the alkyl groups is an allyl group, and two allyl derivatives of pinacolone by the action of sodamide followed by allyl iodide on mono- and di-alkylacetophenones and pinacolone. The following compounds are described.

*aa*-Dimethyl-*a*-allylacetophenone,  $\text{COPh}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}::\text{CH}_2$ , b. p. 134—136°/16 mm. (compare *loc. cit.*), which on reduction with sodium in alcohol yields  $\epsilon$ -phenyl- $\delta\delta$ -dimethyl- $\Delta^5$ -pentene- $\epsilon$ -ol, a viscous, colourless oil, b. p. 133—134°/13 mm., giving a phenylurethane, m. p. 105—106°. To prove that this reduction has not saturated the ethenoid linking the authors reduced dimethylpropylacetophenone, obtaining :

*a*-Phenyl- $\beta\beta$ -dimethylpentan-*a*-ol, b. p. 141—142°/16 mm., giving a phenylurethane, m. p. 86°.

*a*-Methyl-*a*-ethyl-*a*-allylacetophenone,  $\text{COPh}\cdot\text{CMeEt}\cdot\text{C}_3\text{H}_5$ , a mobile liquid, b. p. 140—142°/16 mm.

*aa*-Diethyl-*a*-allylacetophenone,  $\text{COPh}\cdot\text{CEt}_2\cdot\text{C}_3\text{H}_5$ , b. p. 155—157°/14 mm.

*a*-Methyl-*a*-allylacetophenone,  $\text{COPh}\cdot\text{CHMe}\cdot\text{C}_6\text{H}_5$ , b. p. 130—132°/16 mm., and *a*-methyl-*aa*-diallylacetophenone,  $\text{COPh}\cdot\text{CMe}(\text{C}_3\text{H}_5)_2$ , b. p. 155—156°/14 mm.

*a*-Ethyl-*a*-allylacetophenone,  $\text{COPh}\cdot\text{CHEt}\cdot\text{C}_3\text{H}_5$ , b. p. 138—140°/15 mm., giving an oxime, b. p. 198°/15 mm.; and *a*-ethyl-*aa*-diallylacetophenone, a colourless oil, b. p. 160—162°/14 mm.

Owing to the impossibility of preparing allylacetophenone directly from acetophenone the authors have acted on ethyl ethylallylbenzoylacetate (compare Perkin, T., 1884, 45, 186; 1885, 47, 241) with sodamide followed by allyl iodide, and have obtained *aa*-diallylacetophenone, b. p. 144—146°/18 mm., together with some *aaa*-triallylacetophenone, b. p. 168—170°/18 mm. *a*-Benzyl-*a*-methyl-*a*-allylacetophenone,  $\text{COPh}\cdot\text{CMe}(\text{CH}_2\text{Ph})\cdot\text{C}_3\text{H}_5$ , b. p. 205—208°/17 mm.

*a*-Benzyl-*a*-ethyl-*a*-allylacetophenone, b. p. 212—214°/20 mm., is obtained by allylating *a*-benzyl-*a*-ethylacetophenone, b. p. 191—192°/17 mm., which is prepared together with some *aa*-dibenzyl-*a*-ethylacetophenone, b. p. 258—259°/13 mm., m. p. 67—68°, by benzylating the sodium derivative of butyrophenone.

Pinacolone readily undergoes allylation by the above method, giving a mixture of *allylpinacolone*,  $\text{CMe}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_3\text{H}_5$ , b. p. 60—65°/14—15 mm., and *diallylpinacolone*,  $\text{CMe}_3 \cdot \text{CO} \cdot \text{CH}(\text{C}_3\text{H}_5)_2$ , b. p. 83—86°/14—15 mm., together with a few drops of a *liquid*, b. p. 86°/14—15 mm., which is probably triallylacetophenone.

All these allyl ketones readily combine with bromine and decolorise solutions of potassium permanganate. W. G.

**Colour of Di-*p*-methoxystyryl Ketone and of Distyryl Ketone.** HANS STOBBE (*Annalen*, 1914, 404, 46—49).—The comparison of the absorption spectra of these two ketones in alcohol, in ether, and in chloroform indicates that di-*p*-methoxystyryl ketone is darker than distyryl ketone, and that the methoxy-groups in the para-position exert a bathochromic action. C. S.

**Oximes of Phenyl  $\alpha$ -Naphthyl Ketone.** MARIO BETTI and PASQUALE POCCIANI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 340—346).—The authors have obtained the two stereoisomeric oximes of this substance. When phenyl  $\alpha$ -naphthyl ketone is heated with hydroxylamine hydrochloride in alcoholic solution in an autoclave for eight hours, both oximes are produced, and by recrystallisation from alcohol either one or the other is obtainable in the pure state from a given product. The production of the *oxime*,  $\text{C}_{17}\text{H}_{13}\text{ON}$ , m. p. 127° (which crystallises in spherical aggregates of colourless crystals), is favoured by the addition of sodium hydroxide to the reaction mixture before heating, whilst the oxime,  $\text{C}_{17}\text{H}_{13}\text{ON}$ , m. p. 161° (which forms compact colourless crystals), is chiefly formed when this is not done. Both oximes have the normal molecular weight in boiling chloroform. The compound of m. p. 127° becomes converted into that of m. p. 161° spontaneously, or on boiling for nine hours with alcoholic hydrochloric acid. Working in the conditions given by Caille (A., 1908, i, 800), the authors could only obtain the original ketone (also of m. p. 73°), whilst when these conditions were somewhat modified, mixtures of the two oximes here described were obtained.

Both oximes yield the same *benzoyl* derivative,  $\text{C}_{24}\text{H}_{17}\text{O}_3\text{N}$ , which crystallises in small, rhombohedral prisms, m. p. 118°. Both oximes also yield the same benzyl- $\alpha$ -naphthylamine hydrochloride, m. p. 275—278°, when reduced with tin and hydrochloric acid, and this supports the view that they are stereoisomerides.

Benzyl- $\alpha$ -naphthylamine (compare Busch and Leefhelm, A., 1908, i, 152) yields a *benzoyl* derivative,  $\text{C}_{24}\text{H}_{19}\text{ON}$ , which forms long, silky needles, m. p. 178°. R. V. S.

**Action of Sodium Hydroxide on Iodoanil.** C. LORING JACKSON and E. K. BOLTON (*J. Amer. Chem. Soc.*, 1914, 36, 551—568).—When bromanil is treated with alkali hydroxide, bromanilic acid is invariably produced, but Torrey and Hunter (A., 1912, i, 475) have observed that iodoanil frequently yields a product other than iodoanilic acid.

It has now been found that the substances obtained by the action of sodium hydroxide on iodoanil differ according to the amount of

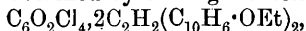
alcohol present and other conditions of the reaction. When 10 grams of iodoanil, suspended in a mixture of 15 c.c. of alcohol and 30 c.c. of water, are treated with 15 c.c. of 50% aqueous solution of sodium hydroxide, a reaction takes place with development of heat and formation of a deep brownish-red solution emitting a disagreeable odour. On addition of dilute sulphuric acid, the hemi-ether of iodoanilic acid is precipitated. If the mixture of iodoanil and sodium hydroxide is boiled for a minute, sodium iodoanilate is produced. When 10 grams of iodoanil are suspended in 50 c.c. of alcohol and 10 c.c. of 50% sodium hydroxide solution are added, heat is developed and the liquid becomes greenish-black and gives off an odour resembling that evolved in the preparation of the hemi-ether; on diluting the mixture with three or four times its volume of water and acidifying with dilute sulphuric acid, di-iodohydroxyethoxy-*p*-benzoquinone is precipitated.

Iodoanilic acid *hemi-ether*,  $(\text{OH} \cdot \text{C}_6\text{I}_2\text{O}_2)_2\text{O}$ , crystallises from toluene in red needles; it begins to decompose at  $215^\circ$  (uncorr.), and when heated with water is converted into iodoanilic acid. The *sodium* salt,  $[\text{ONa} \cdot \text{C}_6\text{I}_2(\text{OH})(\text{ONaO})]_2\text{O} \cdot 5\text{H}_2\text{O}$ , crystallises in purple prisms; the anhydrous form is dark brownish-purple. When the hemi-ether is warmed with aniline, dianilino-*p*-benzoquinone is produced. *Di-iodo-di-acetoxy-p-benzoquinone*,  $\text{C}_6\text{I}_2(\text{OAc})_2\text{O}_2$ , m. p.  $270^\circ$  (uncorr.), obtained by the action of acetic anhydride on the hemi-ether, crystallises in square, yellow plates.

*Di-iodohydroxyethoxy-p-benzoquinone*,  $\text{C}_6\text{I}_2(\text{OH})(\text{OEt})\text{O}_2$ , m. p.  $180^\circ$  (decomp.), forms long, red needles; its *potassium* salt crystallises in bluish-black needles; the *silver* and *barium* salts were also prepared, but the *sodium* salt could only be obtained in solution. When di-iodohydroxyethoxy-*p*-benzoquinone is treated with solution of sodium ethoxide, its *ethylhemi-acetal* is produced; this compound is unstable, and when it is warmed with dilute acid, di-iodohydroxyethoxy-*p*-benzoquinone is regenerated. The *aniline* salt of the quinone forms brownish-purple needles, and when treated with dilute sulphuric acid is converted into *di-iodohydroxyanilino-p-benzoquinone*,  $\text{C}_6\text{I}_2(\text{OH})(\text{NHPh})\text{O}_2$ , which decomposes at about  $190^\circ$ . *Di-iodo-acetoxyethoxy-p-benzoquinone*,  $\text{C}_6\text{I}_2(\text{OAc})(\text{OEt})\text{O}_2$ , m. p.  $166^\circ$  (uncorr.), crystallises in brilliant orange-red prisms; it reacts with aniline with production of *di-iodoethoxy-anilino-p-benzoquinone*, m. p.  $182^\circ$  (decomp.), which forms long, black, lustrous needles; and *di-iododianilino-p-benzoquinone*, which crystallises in dark brown needles and decomposes at about  $220^\circ$ . E. G.

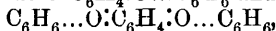
**Constitution of Quinhydrone.** P. PFEIFFER (*Annalen*, 1914, **404**, 1—20).—In consequence of recent work of Urban, Willstätter, Piccard, K. Meyer, and Schlenk, the view that quinhydrone is a typical molecular compound is becoming more and more widely accepted. The formula advocated by Willstätter and by Piccard, which represents the hydroxyl group of the benzenoid component of the quinhydrone as being linked co-ordinatively to the carbonyl oxygen of the quinonoid component, has been slightly modified by the author. In the first place the benzenoid and the quinonoid components of a quinhydrone cannot be united co-ordinatively by the oxygen or the hydrogen atom of the hydroxyl group because intensely coloured

molecular compounds have been prepared from quinones and phenolic ethers and from quinones and hydrocarbons. A solution of chloranil in anisole is reddish-orange, and a fused mixture of chloranil and *pp'*-dimethoxystilbene is deep blue; in neither case, however, can the solid coloured compound be isolated. From a hot solution of equal molecular quantities of chloranil and 4:4'-diethoxydinaphthastilbene in benzene is obtained by cooling a *substance*,



black crystals with a blue lustre, which forms a blue fluorescent solution in benzene and an almost colourless solution in boiling glacial acetic acid; evidence of the formation of a *substance*, dark green needles, probably  $\text{C}_6\text{O}_2\text{Cl}_4, 2\text{C}_2\text{H}_2(\text{C}_{10}\text{H}_6\cdot\text{OEt})_2$ , has also been obtained. A quite similar *substance*,  $\text{C}_6\text{O}_2\text{Br}_4, 2\text{C}_2\text{H}_2(\text{C}_{10}\text{H}_6\cdot\text{OEt})_2$ , black crystals with a blue lustre, has been obtained from bromanil and 4:4'-diethoxydinaphthastilbene. The solution of *p*-benzoquinone in fused stilbene, fluorene, naphthalene, or anthracene is orange-yellow, and in fused phenanthrene orange; the solution of chloranil in fused naphthalene is orange-red, in fused stilbene, red, and in fused anthracene, blue. In none of these cases, however, can a coloured substance be isolated in the solid state. Chloranil and durene in glacial acetic acid yield a *substance*,  $\text{C}_6\text{O}_2\text{Cl}_4, 2\text{C}_6\text{H}_2\text{Me}_4$ , red plates, whilst bromanil under the same conditions yields a *substance*,  $\text{C}_6\text{O}_2\text{Br}_4, \text{C}_6\text{H}_2\text{Me}_4$ , red needles. Both of these substances decompose, gradually at the ordinary temperature, rapidly at 80–90°, readily in the presence of a solvent.

The author is of opinion that quinhydrones are derivatives of parent substances such as  $\text{O}:\text{C}_6\text{H}_4:\text{O}\dots\text{C}_6\text{H}_6$  and

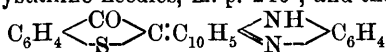


which function as chromogens; by the replacement of hydrogen atoms by auxochromic hydroxyl, amino-, or equivalent groups, the intensely coloured quinhydrones and allied molecular compounds are produced. A great advantage of this theory is that it emphasises the near relation of the quinhydrones to the coloured metallic salt- and acid-compounds of ketones ( $\text{R}_2\text{C}:\text{O}\dots\text{SnCl}_4$ ,  $\text{R}_2\text{C}:\text{O}\dots\text{HCl}$ ), to the coloured molecular compounds of nitro-compounds ( $\text{R}_2\text{C}:\text{O}\dots\text{C}_6\text{H}_6$ ), and possibly also to Schlenk's coloured metal ketyls ( $\text{R}_2\text{C}:\text{O}\dots\text{K}\dots\text{O}:\text{CR}_2$ ).

C. S.

#### Condensations with 1:2-Naphthaquinone-4-sulphonic Acid.

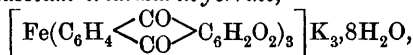
IV. Oxythionaphthen and Fluorene. FRANZ SACHS and L. ÖHOLM (*Ber.*, 1914, **47**, 955–961).—1:2-Naphthaquinone-4-sulphonic acid and 3-oxythionaphthen interact to form “2-oxy-1:4-naphthalene-2-thionaphthen-indigo” [2-hydroxy-1-keto-4-oxythionaphthenylidenenaphthalene],  $\text{O}:\text{C}_{10}\text{H}_5(\text{OH})\text{C}\begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix}\text{C}_6\text{H}_4$ , brownish-violet needles, which sublime at 170° and have m. p. 224° in a closed tube. This substance dyes mordanted cotton, and is also a vat dye producing deep blue shades, which are, however, not fast to acids. The *methyl ether* forms reddish-brown, crystalline needles, m. p. 240°, and the *azine*,



or  $C_6H_4 \langle \text{C}(\text{OH}) \rangle \text{S} \cdot C_{10}H_5 \langle \text{N} \rangle \text{N} \rangle C_6H_4$ , needles, m. p.  $264^\circ$ . On reduction the dye yields 1 : 2-dihydroxy-4-oxythionaphthénylnaphthalene,  $C_{10}H_5(\text{OH})_2 \cdot \text{CH} \langle \text{CO} \rangle \text{S} \cdot C_6H_4$ , almost colourless needles, m. p.  $196^\circ$ .

Fluorene condenses with 1 : 2-naphthaquinone-4-sulphonic acid in alcoholic-alkaline solution to form 2-hydroxy-1-keto-4-fluorenylidene-naphthalene,  $O \cdot C_{10}H_5(\text{OH}) : \text{C} \langle \text{C}_6H_4 \rangle \text{C}_6H_4$ , brownish-violet needles, m. p.  $240^\circ$ , which dyes mordanted cotton. The *leuco*-compound has m. p.  $175^\circ$ , and the *methyl ether* forms red needles, m. p.  $201^\circ$ . J. C. C.

**Iron Compounds of Phenols. VI. Salts of an Alizarin-ferric Acid.** R. F. WEINLAND and KARL BINDER (*Ber.*, 1914, 47, 977—985).—*Potassium trializarin-ferrate*,



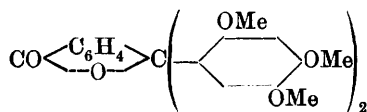
a dark reddish-brown, crystalline powder, is obtained by adding alcoholic potassium hydroxide to a mixture of alcoholic solutions of alizarin and ferric acetate. The corresponding *sodium* salt ( $12H_2O$ ), reddish-brown powder, *ammonium* salt ( $4H_2O$ ), bronze powder, and calcium salt ( $6H_2O$ ) (compare Möhlau and Maetzel, A., 1912, i, 407) are also described.

By adding alcoholic potassium acetate to an alcoholic solution of alizarin, a salt of the composition  $C_{14}H_6O_2(\text{OK}) \cdot \text{OH} \cdot C_{14}H_8O_4$  is formed and, with different proportions of the reagents, the known monopotassium salt (Perkin, T., 1899, 75, 434). *Tripotassium dializarate*,  $C_{14}H_6O_2(\text{OK})_2 \cdot C_{14}H_6O_2(\text{OK}) \cdot \text{OH} \cdot 4H_2O$ , is obtained by the use of potassium hydroxide instead of the acetate. J. C. C.

**Some Derivatives of Hydroxyquinol. X. G. BARGELLINI** (*Gazzetta*, 1914, 44, i, 193—200 Compare A., 1913, i, 460).—Purpurin has been repeatedly synthesised from alizarin or other anthraquinone derivatives, but in no case from a compound containing three phenolic groups in the 1 : 2 : 4-positions, so that no proof exists that purpurin may be regarded as a derivative of hydroxyquinol. From the trimethyl ether of the latter, the author has succeeded in preparing a monomethyl ether of purpurin.

The interaction of hydroxyquinol trimethyl ether and phthalic anhydride in presence of sublimed aluminium chloride (compare Limpricht, A., 1898, i, 322) yields :

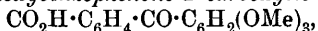
(1) *Hexamethoxydiphenylphthalide* (annexed formula), which is isomeric with the compound, m. p.  $79^\circ$ , obtained from phthalyl chloride and pyrogallol trimethyl ether in presence of aluminium chloride (compare Perkin and Weizmann, T., 1906, 89, 1657), and forms minute, white needles, m. p.  $177$ — $178^\circ$ . It dissolves in cold



concentrated sulphuric acid, giving a green coloration changing to red on heating, probably owing to the formation of an anthraquinone

derivative, which is usually obtained from a triphenylmethane compound, and especially from a phthalein under these conditions; the expected purpurin methyl ether could not, however, be isolated from the solution.

(2) 2:4:5-Trimethoxybenzophenone-2'-carboxylic acid,



which forms white needles, m. p. 191—192°, and gives a green solution in cold concentrated sulphuric acid; its *methyl* ester,  $\text{C}_{18}\text{H}_{18}\text{O}_6$ , forms white crystals, m. p. 102—103°.

When heated with concentrated sulphuric acid, the preceding acid loses a molecule of water, yielding purpurin trimethyl ether, which at the same time undergoes partial demethylation to purpurin monomethyl ether [ $\text{OH}:\text{OH}:\text{OMe} = 1:4:2$ ], m. p. 240°, for which Perkin (T., 1899, 446) gave m. p. 228—230°, and Graebe and Bernhard (A., 1906, i, 865), m. p. 240°.

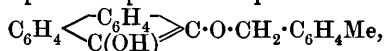
Unsuccessful attempts were made to obtain the purpurin trimethyl ether by treating the 2:4:5-trimethoxybenzophenone-2'-carboxylic acid with concentrated sulphuric acid in the cold or with phosphoric oxide in xylene solution. T. H. P.

**Galloflavin and Purpurogallin.** J. HERZIG (*Ber.*, 1914, 47, 953—955).—In view of Dean and Nierenstein's statement (this vol., i, 60) that dihydroxyhemimellitic acid is obtained by oxidising purpurogallin with dilute nitric acid, the author has submitted galloflavin and isogalloflavin to the same process. The acid obtained had m. p. 101—103°, and its methyl ether, 54—56°, whilst Dean and Nierenstein give m. p. 106—107° for their acid and 56—57° for its methyl ether. Other slight differences between the two acids are noted, but that obtained by the author proved to be oxalic acid. The author does not deny the possibility of the existence of Dean and Nierenstein's acid, although attempts to prepare dihydroxyhemimellitic acid by these authors' methods from purpurogallin (prepared according to Nietzki and Steinmann) were unsuccessful, oxalic acid only being produced.

J. C. C.

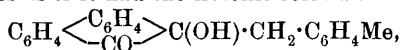
**Action of Benzene Hydrocarbons on Phenanthraquinone in Sunlight.** ALFRED BENRATH and ALEXANDER VON MEYER (*J. pr. Chem.*, 1914, [ii], 89, 258—270).—When exposed to sunlight in the presence of *m*-xylene, mesitylene, *p*-cymene, toluene or ethylbenzene, phenanthraquinone is reduced to phenanthraquinhydrone,  $2\text{C}_{14}\text{H}_8\text{O}_2 + 2\text{C}_6\text{H}_4\text{Me}_2 = \text{C}_{28}\text{H}_{18}\text{O}_4 + \text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$ . With *o*- and *p*-xylene,  $\psi$ -cumene, and quinaldine it yields additive compounds of the general formula  $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\rangle\text{C}_6\text{H}_4\text{OR}$ .

The *additive* compound of phenanthraquinone and *o*-xylene,



obtained by exposing a mixture of the quinone and hydrocarbon to sunlight for four months, forms light yellow crystals, m. p. 148—149°. It is stable towards acetyl chloride and benzoyl chloride at the

ordinary temperature, but when fused with benzoic anhydride yields the dibenzoyl derivative of phenanthraquinol. When heated with hydrogen bromide in glacial acetic acid solution it is converted into phenanthraquinol and xylol bromide. Towards phenylhydrazine the compound behaves as if it had the ketonic formula

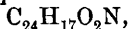


and yields a red, crystalline *phenylhydrazone*, m. p. 203—204°.

The *additive* compounds of phenanthraquinone with *p*-xylene and  $\psi$ -cumene crystallise in yellow needles, m. p. 129—130° and 148° respectively.

In addition to phenanthraquinhydrone, the product formed by exposing a mixture of mesitylene and phenanthraquinone to sunlight for five months yielded a small amount of a *substance*, which crystallises in microscopic plates, m. p. 126—128°, and probably consists of an additive compound of the quinone and hydrocarbon.

The *additive* compound of quinaldine and phenanthraquinone,



crystallises in slender, felted needles, m. p. 165°, and is simultaneously resolved into its components. It forms a *hydrochloride*, *sulphate*, *nitrate*, *chromate*, and *dichromate*; the *platinichloride* crystallises in small, yellowish-red needles, m. p. 188—189° (decomp.). When heated with an excess of benzoyl chloride, it yields a yellow, crystalline *compound*,  $\text{C}_{14}\text{H}_8\text{O}_2, 3\text{C}_{10}\text{H}_9\text{N}, 3\text{C}_6\text{H}_5 \cdot \text{COCl}$ ; a similar *compound*, crystallising in long needles, is formed from acetyl chloride. The action of phenylhydrazine in acetic acid solution results in the removal of the quinaldine residue and the formation of phenanthraquinonemono-phenylhydrazone.

F. B.

**Syntheses by means of Sodamide.** Preparation of Some Higher Homologues of Mono- and Di-methylcamphor as well as the Corresponding Borneols. A. HALLER and JEAN LOUVRIER (*Compt. rend.*, 1914, 158, 754—760. Compare Haller and Buer, A., 1909, i, 594, 595).—By the method already applied to the preparation of mono- and di-methylcamphors (compare *loc. cit.*), the authors have prepared a number of their homologues, which on reduction have yielded the corresponding borneols.

Ethylcamphor,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CHEt} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ , a colourless liquid, b. p. 108°/14 mm.,  $D_0^{20} 0.927$ ,  $[\alpha]_D^{20} +44.40'$  to  $45.29'$  in alcohol (compare Brühl, A., 1892, 200), which on reduction gives *ethylborneol*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CHEt} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{OH} \end{array}$ , an oily liquid with an odour of borneol, b. p. 110°/14 mm.,  $[\alpha]_D^{18} +36.59'$  to  $37.4'$  in alcohol, yielding a *phenylurethane*, microscopic, white crystals, m. p. 47°.

Diethylcamphor,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CEt}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ , b. p. 132—133°/14 mm.,  $D_0^{20} 0.969$ ,  $[\alpha]_D^{15} +90.31'$  to  $91.21'$  in alcoholic solution; *diethylborneol*,  $\text{C}_{10}\text{H}_{16}\text{Et}_2 \cdot \text{OH}$ , a very viscous, colourless liquid, b. p. 134°/12 mm.,  $[\alpha]_D^{18} +50.41$  to



51°37', giving a *phenylurethane*, microscopic, white needles, m. p. 106°,  $[\alpha]_D^{17} + 43^\circ 35'$  to 42°3'.

*Methylethylcamphor*,  $C_{10}H_{14}OMeEt$ , a colourless liquid, b. p. 112—114°/11 mm.,  $[\alpha]_D^{14} + 98^\circ 59'$  to 99°54'; *methylethylborneol*,  $C_{10}H_{16}MeEt \cdot OH$ , a viscid, colourless liquid, b. p. 120°/130 mm.,  $[\alpha]_D^{14} + 38^\circ 19'$  to 39°1'. *Propylcamphor*,  $C_{10}H_{15}OPr$ , a colourless liquid, b. p. 116°/11 mm.,  $D_4^{20}$  0.942,  $[\alpha]_D^{15} + 60^\circ 24'$  to 60°57' (compare Haller and Minguin, A., 1906, i, 594), yielding on reduction propylborneol, m. p. 59°, b. p. 110°/11 mm.

*Dipropylcamphor*,  $C_{10}H_{14}OPr_2$ , b. p. 157°/14 mm.,  $[\alpha]_D^{17} + 53^\circ 13'$  to 54°21'.

*Benzylcamphor*, m. p. 51°,  $[\alpha]_D^{14} + 146^\circ 25'$  to 149°6'.

*Dibenzylcamphor*,  $C_{10}H_{14}O(CH_2Ph)_2$ , m. p. 103°, b. p. 255°/12 mm.,  $[\alpha]_D^{20} + 102^\circ 57'$  to 103°24'; *dibenzylborneol*, m. p. 84°,  $[\alpha]_D^{19} - 14^\circ 19'$  to -15°43', giving a *phenylurethane*, m. p. 82°.

*Benzylethylcamphor*, a pale yellow, viscous liquid, b. p. 193°/11 mm.,  $[\alpha]_D^{19} + 90^\circ 37'$  to 91°30'.

The following oximes were prepared.

*Ethylcamphoroxime*,  $C_{10}H_{15}Et \cdot NOH$ , b. p. 145°/11 mm., m. p. 93°,  $[\alpha]_D^{13} + 45^\circ 54'$  to 46°10', giving a *phenylurethane*,  $C_{10}H_{15}Et \cdot NO \cdot CO \cdot NHPh$ , fine needles, m. p. 146°.

*Propylcamphoroxime*,  $C_{10}H_{15}Pr \cdot NOH$ , long, white crystals, m. p. 79°,  $[\alpha]_D^{15} + 53^\circ 59'$  to 54°8'.

The ease with which the alkyl group can be introduced into camphor by this method diminishes on ascending the series. Only the monoalkylcamphors yield oximes. The rotatory power of the monoalkylcamphors increases with the molecular weight, whilst the rotatory powers of the dialkyl derivatives oscillate between 90° and 100°, the exception being dipropylcamphor.

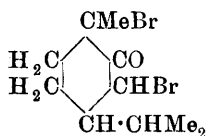
W. G.

**Dibromotetrahydrocarvone and Its Conversion into Buchu-camphor.** G. CUSMANO and P. POCCIANI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 347—353. Compare Cusmano, this vol., i., 303).—This paper deals with the preparation of a dibromotetrahydrocarvone, which is shown to have the annexed formula. It is obtained by acting on tetrahydrocarvone in chloroform solution with bromine, and forms colourless needles, m. p. 81°,  $[\alpha]_D^{12} - 147.5^\circ$ . It yields a *piperidide*,  $C_{15}H_{26}ONBr$ , which crystallises in colourless needles, m. p. 117°.

When this dibromotetrahydrocarvone is treated with potassium hydroxide (2.5% aqueous solution) at 40—50°, it is converted into buchu-camphor.

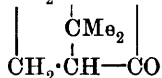
R. V. S.

**Complete Synthesis of Fenchocamphorone and Its Oxidation with Caro's Acid.** GUST. KOMPPA (*Ber.*, 1914, 47, 933—936).—In a previous paper (A., 1911, i, 642) the author stated that homoapocamphoric acid yielded a small amount of the corresponding cyclic ketone, but he was not able to say whether this was identical with fenchocamphorone (*apocamphor*) or not. It is now found that by



distilling lead homoapocamphorate in a stream of carbon dioxide a fairly good yield of the ketone is obtained, the semicarbazone of which (m. p.  $220^{\circ}$ ; previously given as  $209-211^{\circ}$ ) is identical with the semicarbazone of *r*-fenchocamphorone prepared from *r*-fenchyl alcohol.

As *r*-fenchocamphorone corresponds with Wallach's  $\text{CH}_2\cdot\text{CH}-\text{CH}_2$  *D-d*-fenchocamphorone, the annexed formula for the latter is thus confirmed.



[With S. V. HINTIKKA.]—The above constitution

was confirmed by the conversion of *D-d*-fenchocamphorone by oxidation with Caro's acid into apo-

campholide,  $\text{C}_7\text{H}_{12}\langle\text{CH}_2\text{CO}\rangle\text{O}$ , which was obtained in the pure state by conversion into bromoapocampholic acid and treating this with sodium carbonate solution. J. C. C.

**Ozonisation of the Different Fenchenes.** GUST. KOMPPA and S. V. HINTIKKA (*Ber.*, 1914, 47, 936–938).—*D-l*-Fenchene, prepared

from fenchylamine and also from *l*-fenchyl alcohol, and *D-d*-fenchene furnish *D-d*-fenchocamphorone (preceding abstract) on treatment with ozone, a result which confirms Wallach's formula (annexed) for *D-d*-fenchene. In the ozonisation of *D-l*-fenchene a monocarboxylic acid, m. p.  $70-71^{\circ}$ , is also produced, which is being further investigated. J. C. C.

**Transformation of Limonene into Carvomenthene and Menthane.** G. VAVON (*Bull. Soc. chim.*, 1914, [iv], 15, 282–287).

—The hydrogenation of limonene by means of platinum black has been followed quantitatively in conjunction with the rotation. It is shown that the reduction proceeds in two stages, carvomenthene being the intermediate product. The rotation falls off slowly until two atoms of hydrogen have been absorbed, and then quickly drops to zero with the further reduction to inactive menthane.

Carvomenthene has been prepared by many methods, but the highest rotation was recorded by Bacon (A., 1908, i, 814), who decomposed the magnesium derivative of limonene hydrochloride with water. It is now shown that in the production of this hydrochloride there is a peculiar susceptibility to racemisation, for widely differing values for the rotation were obtained by altering the speed of the current of hydrogen chloride which was passed into the ethereal solution of limonene. Carvomenthene prepared by hydrogenation has b. p.  $175-177^{\circ}$ ,  $n_D^{18}$  1.4563,  $D_4^{18}$  0.8246,  $[\alpha]_{578}^{18} + 118^{\circ}$ ,  $[\alpha]_{436}^{18} + 234^{\circ}$ , and gives an inactive additive compound,  $\text{C}_{10}\text{H}_{19}\text{Cl}$ , with hydrogen chloride, b. p.  $85-86^{\circ}/13$  mm.,  $180-185^{\circ}/\text{atm.}$ ,  $n_D^{21}$  1.460,  $D_4^{21}$  0.934, and a dibromide,  $\text{C}_{10}\text{H}_{18}\text{Br}_2$ , b. p.  $136-140^{\circ}/16$  mm.,  $n_D^{21}$  1.5236,  $D_4^{21}$  1.459. The nitroso-chloride prepared from this specimen of carvomenthene has m. p.  $95^{\circ}$ ,  $[\alpha]_{578}^{18} + 344^{\circ}$ ,  $[\alpha]_{436}^{18} + 724^{\circ}$ . Wallach only obtained an inactive product (A., 1911, i, 469). J. C. W.

**The Constituents of Essential Oils.** The Sesquiterpene,  $\beta$ -Gurjunene. F. W. SEMMLER and K. E. SPORNITZ (*Ber.*, 1914, 47, 1029–1030).—Gurjun balsam oil has been shown by Deussen and

Philipp (A., 910 i, 575) to contain two sesquiterpenes,  $\alpha$ - and  $\beta$ -gurjunene. The latter is described as a slightly dextrorotatory oil, b. p. about  $122.5\text{--}123.5^{\circ}/12\text{ mm.}$ , and is considered to be a tricyclic compound.

By taking advantage of the fact that  $\alpha$ -gurjunene is readily oxidised by permanganate in aqueous acetone solution, whereas the  $\beta$ -isomeride is attacked with difficulty, the authors have succeeded in isolating the latter and give the constants: b. p.  $113.5\text{--}114^{\circ}/7\text{ mm.}$ ,  $D^{20}_{20} 0.9329$ ,  $n_D 1.50526$ ,  $\alpha_D + 19^{\circ}$  (the latter value has been subsequently found to be too low). When reduced by spongy platinum in glacial acetic acid solution, it yields *dihydro- $\beta$ -gurjunene*,  $C_{15}H_{26}$ , b. p.  $115\text{--}117^{\circ}/7\text{ mm.}$ ,  $D^{20} 0.9239$ ,  $n_D 1.49490$ ,  $\alpha_D - 37^{\circ}$ .

In its physical constants,  $\beta$ -gurjunene shows considerable similarity to the tricyclic cedrene (A., 1912, i, 573). To compare the hydrogenated products, therefore, cedrene has been reduced to *dihydrocedrene* b. p.  $119\text{--}120^{\circ}/8\text{ mm.}$ ,  $D^{20} 0.9247$ ,  $n_D 1.49204$ ,  $\alpha_D - 6^{\circ}$ .

The action of ozone on cedrene and  $\beta$ -gurjunene shows that the idea of a chemical similarity of the two hydrocarbons is untenable; whereas the former yields a characteristic ketonic acid (A., 1912, i, 367, 573), a definite product of decomposition of the ozonide of the latter could not be obtained.

H. W.

**Oil of Amber.** ALEXANDER KÁROLY (*Ber.*, 1914, 47, 1016—1023).—The starting material was a specimen of rectified oil of amber which had been previously freed from constituents of high boiling point and did not contain aldehyde or ketonic substances (compare Jolles, D. 1893, 22, 288). Attempts to separate well defined constituents by cooling or by chemical methods were unsuccessful.

After removal of higher fatty acids by agitation with dilute alkali hydroxide, the oil was submitted to fractionation. The majority of the fractions contained small quantities of oxygen, which was removed by distillation over sodium at the ordinary pressure, whereby two portions, b. p.  $154\text{--}177^{\circ}$  (terpenes,  $C_{10}H_{16}$ ) and  $240\text{--}260^{\circ}$  (sesquiterpenes,  $C_{15}H_{24}$ ) respectively, were obtained.

The physical constants of the different fractions of lower b. p. indicate the presence of mono- and di-cyclic terpenes, and this is confirmed by the properties of the additive compounds formed by halogens and halogen acids. Addition of the latter occurs readily, but, in general, only oily products are obtained, and a similar result is obtained in attempts to prepare nitroso-compounds, nitrites or nitrosates. By the action of bromine vapour, however, a crystalline substance, needles, m. p.  $242^{\circ}$ , can be obtained, which is probably identical with tribromohemimellitene (Jacobsen, A., 1887, 36; Lapworth and Chapman, T., 1900, 77, 317), and from the formation of which the conclusion is drawn that dihydrohemimellitene,  $C_9H_{14}$ , is present in the fraction b. p.  $170\text{--}180^{\circ}$ . The substance is very stable. Bromine is not eliminated by heating with silver acetate and glacial acetic acid at  $200^{\circ}$  for ten hours, by distillation with quinoline, by protracted boiling with alcoholic potassium hydroxide, by zinc and acetic acid or by sodium alkylxide. It is not attacked by warm nitric acid (D 1.4), although completely decomposed by protracted heating with this substance; chromic acid and potassium permanganate

behave similarly. By similar treatment of the fraction b. p. 245—255° with bromine, a similar substance, m. p. 254—256°, is obtained.

Hydration of the fraction b. p. 150—170° by the method of Bertram and Walbaum (A., 1894, i, 204) yields a bicyclic saturated alcohol,  $C_{10}H_{18}O$ , six-sided plates, m. p. 186—188° (identical with the substance obtained by Berthelot and Buignet, *Compt. rend.*, 1860, 50, 606; *Annalen*, 1860, 115, 244, by the distillation of powdered amber with alkali hydroxide and water), together with about 80% of unchanged hydrocarbons, from which further quantities of the alcohol could not be obtained. The alcohol has been regarded by Aweng (A., 1895, i, 384) as identical with borneol. The phenylurethanes of the alcohol and of borneol have therefore been examined, and have m. p. 137—138° and 138—139° respectively, mixed m. p. 137—138°. The phthalic acid ester of the alcohol, however, has m. p. 118—119°, whereas the corresponding ester from commercial borneol melts at 164—165°. Saponification of each ester yields the corresponding alcohol, but a rise in the m. p. of the latter could not thus be effected. Oxidation with chromic acid transforms the alcohol into a ketone,  $C_{10}H_{16}O$ , the semicarbazone of which, needles, has m. p. 232°. The semicarbazone from commercial camphor has m. p. 238°, and a mixture of the two shows no great depression in m. p., although an apparent difference exists in their solubilities in methyl alcohol. Both ketone and semicarbazone are optically inactive. Nitric acid and potassium hydrogen sulphate effect elimination of water from the alcohol with formation of camphene, b. p. 158—161°, m. p. 49°.

On oxidation with 1% potassium permanganate solution, the greater part of the oil is recovered unchanged; a certain amount of a fatty acid, presumably heptic acid, is obtained, the silver salt of which,  $C_7H_{13}O_2Ag$ , was analysed. A similar result is obtained by the use of 0.5% potassium permanganate.

Oxidation with nitric acid is effected by gradual addition of the oil to warm nitric acid (D 1.30) and subsequent warming on the water-bath. A mixture of acids is obtained which can be separated by means of boiling alcohol. Thereby, terephthalic acid (also identified in the form of its methyl ester, m. p. 140°) and an acid,  $C_{10}H_{10}O_4$ , m. p. 290—293°, are obtained. The latter is in all probability identical with 1:3-dimethylterephthalic acid obtained by Jannasch and Weiler by the oxidation of isodurene with dilute nitric acid. The lead salt,  $C_{10}H_8O_4Pb$ , and silver salt,  $C_{10}H_8O_4Ag_2$ , were analysed. The formation of this acid from a terpene hydrocarbon cannot be explained, and the conclusion is therefore drawn that oil of amber contains hydroaromatic hydrocarbons in addition to terpenes, and that the acid is derived from the unknown 1:2:3:5-tetramethylcyclohexene.

By slow evaporation of the nitric acid mother liquors, a third acid,  $C_8H_7O_4N$ , large prisms, m. p. 189—190°, is obtained. It is probably identical with 2-nitro-*p*-toluic acid prepared by Noad (*Annalen*, 1847, 63, 297) and Fittica (A., 1873, 1227).

H. W.

The Essential Oil of *Lophantus rugosus*. PH. DE VILMORIN and F. LEVALLOIS (*Bull. Soc. chim.*, 1914, [iv], 15, 342—345).—A study of the composition of the essential oil of *Lophantus rugosus*

found in Asia, a detailed, botanical description of the plant being given. The oil is an amber-coloured liquid, which thickens without crystallising on cooling to  $-15^{\circ}$ . It has  $D_4^{15}$   $0.962-0.967$  and  $[\alpha]_D + 4.89^{\circ}$  to  $6.19^{\circ}$  varying with the specimen. It is neutral to phenolphthalein and contains no free acids or phenols. Its saponification index is  $3.7$ , and after acetylation  $7.4$ . On fractionation four fractions were obtained: (1) b. p.  $60-63^{\circ}/10$  mm.; (2) b. p.  $63-90^{\circ}/10$  mm.; (3)  $90-94^{\circ}/10$  mm.; (4) residue boiling above  $100^{\circ}/10$  mm. and partly decomposing. The most important fraction is (3) b. p.  $90-92^{\circ}/9-10$  mm. It has no appreciable rotating power, unites with bromine, and has an odour characteristic of estragon. It seems to be methylchavicol and on boiling with alcoholic potassium hydroxide for twenty hours is converted into anethole. Fraction (2) consists of estragole and a portion b. p.  $170-174^{\circ}/760$  mm.,  $D_4^{15}$   $0.8494$ ,  $[\alpha]_D + 106.8^{\circ}$ , and from its physical and chemical properties would seem to be limonene, the  $\alpha$ - and  $\beta$ -limonene nitroschlorides having been obtained from it. W. G.

**Synthetic Resins.** L. V. REDMAN, A. J. WEITH, and F. P. BROCK (*J. Ind. Eng. Chem.*, 1914, **6**, 263-265).—A reply to Baekeland (this vol., i, 423). T. S. P.

**Caoutchouc.** A. HOLT (*Zeitsch. angew. Chem.*, 1914, **27**, 153-158).—A lecture delivered before the Heidelberger Chem. Ges. J. C. W.

**Synthetic Caoutchouc from Isoprene.** G. STEIMMIG (*Ber.*, 1914, **47**, 852-853. Compare this vol., i, 307).—A reply to Harries (this vol., i, 422). D. F. T.

**Biochemical Synthesis of  $\beta$ -o-Methoxybenzylglucoside and of  $\beta$ -m-Nitrobenzylglucoside.** EM. BOURQUELOT and ALEXANDRU LUDWIG (*Compt. rend.*, 1914, **158**, 1037-1040\*).—These two glucosides have been obtained by the action of emulsin on solutions of dextrose and the corresponding alcohols in 80% aqueous acetone.  **$\beta$ -o-Methoxybenzylglucoside**,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5$ , crystallises in long, colourless, radiating needles, m. p.  $127-128^{\circ}$ ,  $[\alpha]_D - 52.24^{\circ}$ , and is very soluble in alcohol, sparingly in water. It does not reduce Fehling's solution and is rapidly hydrolysed by boiling with dilute sulphuric acid, or by the action of emulsin on an aqueous solution.

**$\beta$ -m-Nitrobenzylglucoside**,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5$ , crystallises in pale yellow, massive prisms, having a bitter taste, m. p.  $157-158^{\circ}$ ,  $[\alpha]_D - 52.59^{\circ}$ . It is sparingly soluble in water and alcohol. It does not reduce Fehling's solution, and is but slightly hydrolysed on boiling with 3% sulphuric acid. It is, however, rapidly hydrolysed in aqueous solution by emulsin. W. G.

**Synthetic  $\beta$ -Glucosides of the Terpene Alcohols. IV.** J. HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1914, **61**, 1-5. Compare A., 1913, i, 497, 639, 989).—By the methods already described, the following substances were prepared: 1:2-methylcyclohexanol-tetracetyl-d-glucoside,

\* and *J. Pharm. Chim.*, 1914, [vii], **9**, 441-446.

$C_{21}H_{32}O_{10}$ , m. p.  $107.5^\circ$  (corr.) ; 1:2-methylcyclohexanol-d-glucoside,  $C_{13}H_{24}O_6$ , m. p.  $148^\circ$  (corr.),  $[\alpha]_D^{18} - 27.80^\circ$  ; 1:3-methylcyclohexanol-tetracetyl-d-glucoside,  $C_{21}H_{32}O_{10}$ , m. p.  $153^\circ$  (corr.) ; 1:3-methylcyclohexanol-d-glucoside,  $C_{13}H_{24}O_6$ , m. p.  $162.5^\circ$  (corr.),  $[\alpha]_D^{18} - 29.84^\circ$  ; 1:4-methylcyclohexanol-tetracetyl-d-glucoside,  $C_{21}H_{32}O_{10}$ , m. p.  $145.5^\circ$  (corr.) ; 1:4-methylcyclohexanol-d-glucoside,  $C_{13}H_{24}O_6$ , m. p.  $163.5^\circ$  (corr.),  $[\alpha]_D^{18} - 38.42^\circ$ .  
S. B. S.

**Anemonin.** YASUHIKO ASAHINA (*Ber.*, 1914, 47, 914—916. Compare Beckurts, A., 1892, 1241 ; H. Mayer, A., 1896, i, 623 ; 1899, i, 930).—The author describes the isolation of anemonin from the leaves of *Ranunculus Japonicus*. The substance melts at  $157$ — $158^\circ$  (uncorr.), and at a higher temperature appears to polymerise.

On hydrogenation in the presence of platinum black, anemonin gives tetrahydroanemonin,  $C_{10}H_{16}O_4$ , which forms tablets, m. p.  $155^\circ$ . The production of this compound is not in accord with H. Mayer's formula for anemonin, which shows only one double linking.

J. C. C.

**The Action of Light on Chlorophyll.** HAROLD WAGER (*Proc. Roy. Soc.*, 1914, [B], 87, 386—407).—An account is given of some of the effects produced by light on chlorophyll.

When chlorophyll is exposed to the light, at least two substances are formed, one of which is an aldehyde or mixture of aldehydes, and the other an active chemical agent, capable of bringing about the liberation of iodine from potassium iodide. These products of decomposition can be readily demonstrated by means of strips of paper tinged with chlorophyll. When bleached in the light and placed in Schiff's solution, a deep pink colour is developed ; but if placed in a 10% solution of potassium iodide, a reddish-blue coloration, which becomes blue on washing with water, is formed. The same products are obtained when films of chlorophyll on glass are bleached in the light. The bleaching of chlorophyll is less at the blue end of the spectrum than at the red end, with a corresponding variation both in the aldehyde and potassium iodide reactions. If, however, the exposure to the blue light is prolonged to about eight or ten times that of the red light, the reactions are just as pronounced. The bleaching and the corresponding products of decomposition are probably therefore proportional to the photo-synthetic activity of the chlorophyll in the different parts of the spectrum.

The presence of formaldehyde is not very clearly indicated. Rimini's test, as modified by Schryver (A., 1910, ii, 357), gives indications of a trace of formaldehyde when chlorophyll is exposed to light both in the presence and in the absence of carbon dioxide, but the reaction given is not so strong as is indicated by Schiff's solution. The test used by Harvey Gibson is also very sensitive to formaldehyde, but is untrustworthy, as it gives a pronounced reaction with solutions of sugar, starch, and other substances. All that can be said at present is that in the photo-decomposition of chlorophyll a considerable quantity of aldehyde is formed, with possibly a small amount of formaldehyde.

The oxidising substance does not appear to be hydrogen peroxide, since the usual more delicate reactions for this substance are not given

by bleached chlorophyll solutions, and, further, a film of chlorophyll is not completely bleached by ten days' treatment with 20% hydrogen peroxide solution in the dark; it is possibly an organic peroxide derivative of chlorophyll.

The bleaching of chlorophyll in situ in dead green leaves, algæ and other chlorophyll-containing organisms gives the same products as the chlorophyll extracts outside the plant.

If a fresh green leaf of *Oxalis acetosella* is exposed to an intense light concentrated upon it by a lens, as in Pringsheim's experiments, the bleached chlorophyll gives an aldehyde reaction when placed in Schiff's solution. If the leaf contains abundance of starch, it may, after the action of the intense sunlight, be placed in a solution of potassium iodide, when the oxidising agent set free from the chlorophyll will liberate the iodine and the starch grains will be coloured blue, but the experiment is somewhat difficult to perform. In a somewhat similar manner, fresh fronds of *Laminaria* are found to contain free iodine, which is absorbed by the secreted slime. It seems probable, therefore, though not quite certain, that the action of light on the chlorophyll of *Laminaria* brings about the production of an oxidising substance capable of effecting the decomposition of the iodine compounds which may be contained in the chlorophyll cells of the plant, and that the iodine thus set free may thus escape or be re-absorbed by the slime.

The decomposition of chlorophyll with the production of aldehyde and peroxide takes place just as readily in the absence of carbon dioxide as when the latter is present. Carbon dioxide is not used up in the process, even when present in considerable amount. It is not necessary therefore to the production of aldehyde.

The photo-decomposition of chlorophyll takes place only in the presence of oxygen, the latter being used up in the process. If sufficient chlorophyll is present, all the oxygen in the air in contact with the chlorophyll is absorbed, so that the latter may be used instead of potassium hydroxide and pyrogallol in the analysis of air.

Chlorophyll is slowly oxidised in the dark by a solution of hydrogen peroxide. In the light the action is more rapid, but not more so than when light acts on chlorophyll in the presence of oxygen. A rapid oxidation of the chlorophyll takes place in the dark in the presence of a dilute solution of potassium permanganate to which a few drops of sulphuric acid have been added. In both cases an aldehyde is produced which can be detected by means of Schiff's reagent.

If a strip of potassium iodide-starch paper is exposed to light under coloured filters, the paper turns reddish-blue under the blue filter, showing the liberation of iodine, but not under the red filter. If, however, the iodised starch paper is first of all tinged with chlorophyll and then exposed to light under the same filters, a strong reaction takes place under the red filter. A strip of bleached chlorophyll paper, placed in contact with a strip of damp iodised starch paper in the dark, is also capable of effecting the liberation of iodine, and the starch paper turns blue.

Finally, it is suggested that the production of sugars and starch in the green leaf may be initiated by the photo-oxidation of chlorophyll and

the subsequent polymerisation of the aldehyde thus formed, rather than by the direct photo-synthesis of carbon dioxide and water. H. W.

**Formaldehyde as an Oxidation Product of Chlorophyll Extracts.** CHARLES HORNE WARNER (*Proc. Roy. Soc.*, 1914, [B], 87, 378—385. Compare Usher and Priestley, A., 1906, ii, 881; Ewart, A., 1908, ii, 217; Schryver, A., 1910, ii, 334).—Grass was extracted with alcohol usually in the cold and in the presence of calcium carbonate. In some experiments, the alcoholic liquid was evaporated to dryness under diminished pressure and the residue extracted with ether; in others, a solution of chlorophyll in light petroleum was obtained by shaking the alcoholic solution with that liquid. The ether or petroleum extract was allowed to evaporate on glass plates and exposed to light under various conditions. Schryver's test was adopted for the detection of formaldehyde.

Similar films of chlorophyll were exposed to sunlight or electric light in air in the presence and absence of carbon dioxide. In all cases, the formation of formaldehyde was observed, the amount being apparently independent of the presence of carbon dioxide. Control films which had been kept in the dark showed no trace of formaldehyde. On the other hand, the presence of moisture appeared to favour the production of formaldehyde. The latter was not produced when the air was replaced by nitrogen or by carbon dioxide. The author is therefore led to the conclusion that there is thus at present no evidence for the photo-synthesis of the aldehyde from carbon dioxide by chlorophyll outside the plant.

Chlorophyll in air became bleached by light both in the presence and absence of carbon dioxide, and it was found that formaldehyde was produced whenever bleaching had occurred. The bleaching was not more marked in moist air containing carbon dioxide than in air placed over a solution of potassium hydroxide, but when the effect of air containing appreciable quantities of water vapour was compared with that of an atmosphere relatively dry, it was found that the degree of decolorisation (especially in the case of rather short exposures in comparatively dull light) was somewhat greater under the moist conditions. Bleaching could not be detected in the absence of oxygen. The evidence obtained by Usher and Priestley (A., 1911, ii, 817), taken in conjunction with the fact that the bleached films slowly liberate a small amount of iodine from a solution of potassium iodide, ferrous sulphate, and acetic acid, points to the fact that the bleaching of chlorophyll in oxygen is due partly, if not entirely, to the action of hydrogen peroxide.

When films of carotin are exposed to air, they become bleached both in the light and in the dark (compare Willstätter and Escher, A., 1910, i, 330), and formaldehyde is produced in both cases. In an atmosphere of carbon dioxide, bleaching is not observed, and there is no evidence of the production of formaldehyde. H. W.

**Synthesis of an isoCurcumin.** GUSTAV HELLER (*Ber.*, 1914, 47, 887—890).—An attempt to synthesise curcumin in the light of the structure,  $\text{CH}_2[\text{CO}\cdot\text{CH}:\text{CH}:\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OH}]_2$ , suggested by Milobendzki, Kostanecki, and Lampe (A., 1910, i, 628).



Vanillin slowly condenses with acetylacetone in an alcoholic solution of hydrogen chloride (compare Knoevenagel and Langensiepen, A., 1905, i, 64) at  $0^{\circ}$ , giving an oily product from which can be separated a small quantity of an isomeride or of a mixture of isomerides of curcumin; this product, to which the name *isocurcumin* is applied, is a reddish-yellow, semicrystalline solid, which begins to sinter near  $140^{\circ}$ , and melts near  $180^{\circ}$ . The isomerism with curcumin is believed to be of a steric nature. D. F. T.

**Pigments of Blossoms and Fruits.** RICHARD WILLSTÄTTER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 12, 402—411).—In a previous paper (A., 1913, i, 1371), Willstätter and Everest have described the isolation of the pigment cyanin from cornflowers, and have expressed the opinion that all anthocyanins are present in flowers as glucosides, and that their basic functions are due to the presence of a quadrivalent oxygen atom. These conclusions have been confirmed by the investigation of a number of other anthocyanins.

[With MALLISON].—Cyanidin chloride, to which the formula  $C_{15}H_{13}O_7Cl$  was previously ascribed (*loc. cit.*), is shown to have the composition  $C_{15}H_{11}O_6Cl$ , the previous error being due to the tenacity with which water is retained by the compound, so that prolonged desiccation at  $105^{\circ}$  in a vacuum is necessary to obtain the anhydrous substance. The pigment of the cranberry yields the same cyanidin, together with galactose, whilst [with NOLAN] that from *Rosa gallica* is a diglucoside of the cyanidin.

The instability of the anthocyanins renders their isolation a matter of difficulty; aqueous and alcoholic solutions of most of the pigments of this group become decolorised with greater or less rapidity in consequence of an isomerisation analogous to the conversion of the dyes of the triphenylmethane series into the corresponding carbinols. Decolorisation can be retarded by addition of certain salts, such as sodium chloride or nitrate, and prevented by the use of an excess of acid. Hence a practical method for their isolation has been worked out, which depends on obtaining sparingly soluble oxonium salts. In this connexion picric acid is frequently of service.

The anthocyanin of grapes, *oenin*, is obtained by extracting grape skins with glacial acetic acid and adding ether to the extract. A syrupy precipitate is obtained which, when treated with aqueous picric acid solution, yields *oenin picrate*, long, red prisms. Alcoholic hydrogen chloride transforms it into the corresponding *chloride*, prisms with green gl'ance.

[With ZOLLINGER].—*Myrtillin*, the anthocyanin of the bilberry, is isolated by extracting the skins of the bilberry with warm ethyl alcohol containing 1% hydrogen chloride and precipitation with ether. The precipitate is treated with water and concentrated hydrochloric acid added to the solution. On repetition of the process, the *chloride*, prisms, is obtained in the pure condition.

The following anthocyanins have also been obtained in the pure state: [with MIEG] *delphinin*, which on hydrolysis yields dextrose (2 mols.), *p*-hydroxybenzoic acid (2 mols.), and *delphinidin*,  $C_{15}H_{11}O_7Cl$  (1 mol.); [with BOLTON] *pelargonin*, giving on hydrolysis dextrose

(2 mols.) and *pelargonidin*,  $C_{15}H_{11}O_6Cl$  (1 mol.); [with ZOLLINGER] *oenin*, a monoglucoside of *oenidin*,  $C_{17}H_{15}O_7Cl$ .

[With MARTIN.]—Myrtillin is a glucoside of another anthocyanidin which is also present in the anthocyanin of *Althaea rosea*.

The above anthocyanins yield similar absorption spectra, giving, in acid solution, a broad band which becomes flatter towards the violet, and extends over a great portion of the blue and green regions. They can be more readily differentiated by determination of the specific rotation, for which high values (200—1400°) are observed.

The anthocyanidins also exhibit considerable similarity, but can be distinguished by colour, solubility, and ferric chloride reaction.

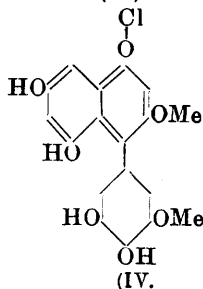
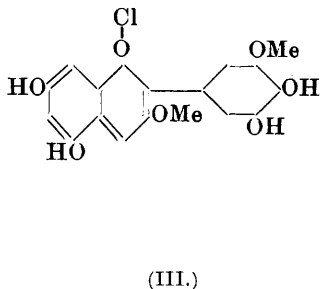
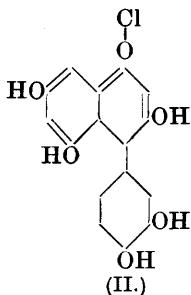
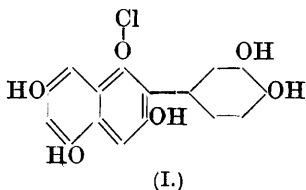
Whereas the anthocyanins, with exception of delphinin, are decolorised in cold aqueous solution, the corresponding anthocyanidins are practically stable in the cold, but are without exception decolorised on warming. The colour can only be restored by the action of warm mineral acid.

The anthocyanin of the scarlet pelargonium has been investigated by Grafe, who obtained it in the crystalline state and regarded it as a sugar-free substance which readily yielded protocatechuic acid and gave, when melted with alkali, catechol. On the other hand, the author finds that pelargonin is a glucoside, and that its sugar-free derivative shows no relationship to protocatechuic acid or catechol.

The anthocyanidins, according to empirical formula, are closely related to the flavone dyes, and this relationship is borne out by their behaviour towards alkalis at a high temperature. Thus, pelargonidin yields phloroglucinol and *p*-hydroxybenzoic acid, cyanidin gives phloroglucinol and protocatechuic acid, whilst delphinidin yields phloroglucinol and gallic acid.

The cyanidins are related to benzopyryonium (Decker and Fellenberg,

A., 1909, i, 116), but the point of attachment of the benzene nucleus cannot yet be definitely decided. For cyanidin chloride, one of the two formulæ I. and II. is proposed. For pelargonidin chloride there are two similar possibilities, the benzene nucleus containing, however, only one hydroxyl group in the position 4. In delphinidin chloride, the benzene nucleus has three hydroxyl groups in positions 3, 4 and



5, whilst for oenidin chloride the alternative formulæ (III. and IV.) are advanced, in which the positions of the methoxy-groups are uncertain. Confirmation of this formulation is found in the fact that the similarly constituted 3:5:7-trihydroxy-2-*m-p*-dihydroxyphenyl-4-ethyl-1:4-benzopyran anhydrohydriodide described by Watson and Sen (T. 1914, 105, 391) has properties analogous to those of cyanidin.

Analysis of the colourless *iso*-forms of the anthocyanidins shows that, for example, in the case of delphinidin, the transformation of the quinonoid into the non-quinonoid form is accompanied by the addition of a molecule of water:  $C_{15}H_{11}O_7Cl + H_2O = HCl + C_{15}H_{12}O_8$ ; the colourless compounds are therefore carbinols or pseudo-bases of the dye salts.

According to this conception, those anthocyanidins which contain the phenyl group in the  $\beta$ -position to the carbonyl of the benzopyryrium should be obtained by reduction of flavones and flavonols and transformation into an orthoquinonoid form with quadrivalent oxygen. This relationship has not yet, however, been conclusively proved.

[With MALLISON.]—The production of solutions of substances similar to the anthocyanins by the gentle reduction of morin, luteolin, quercetin and other flavones as well as of the pigment of *Ampelopsis hederacea* has been described by various observers. On repetition of these experiments, the authors find that the products are different from such anthocyanidins as have been yet investigated. They are very unstable. In aqueous solution, the colour is discharged in the cold, even in the presence of mineral acids, and cannot be restored by the help of an excess of, or by more, concentrated acid. H. W.

**Colloido-chemical Study of Tannin.** M. NAVASSART (*Koll. Chem. Beihefte*, 1914, 5, 299—374).—A detailed examination has been made of the physical and colloido-chemical properties of tannin solutions, including the density, optical rotatory power, viscosity, the behaviour when subjected to dialysis, and the ultra-microscopic appearance of the solutions.

In contradiction to previous statements, it is found that tannin is unlimitedly soluble in water, ethyl alcohol, acetone, acetic acid, and formol. It is practically insoluble in ethyl ether, chloroform, benzene, carbon disulphide, carbon tetrachloride, xylene, and light petroleum.

The density of aqueous and non-aqueous solutions is found to be a linear function of the percentage concentration up to 20—30%.

The specific rotatory power of aqueous solutions increases as the concentration falls, whereas the rotatory power of non-aqueous solutions is nearly independent of the concentration and much smaller than that of aqueous solutions.

Up to a concentration of about 10%, the viscosity of aqueous tannin solutions is not greatly different from that of water, but between 20 and 30% it increases very rapidly, so that the viscosity of a 30% solution is approximately ten times as large as the viscosity of water. Dilute non-aqueous solutions have a much higher viscosity than aqueous solutions of the same concentration, the viscosity increasing in the order water, acetone, ethyl alcohol, acetic acid. It would seem that

the viscosity increases as the molecular weight of the dissolved tannin diminishes, whereas the optical rotatory power increases with increasing molecular weight.

The behaviour of tannin solutions on dialysis is dependent on the nature of the dialytic membrane, and also on the solvent and the degree of dispersity of the tannin. The physical properties of the solutions of tannin which has passed through different dialysing membranes have been compared with those of the undialysed solutions. The former solutions are more highly disperse, and this is exhibited in the general behaviour as well as in the ultra-microscopic appearance. Some evidence of "ageing" has been found in the gradual change of the viscosity of the more highly disperse solutions. In general, the properties of the aqueous solutions are consistent with the view that they form an intermediate stage in the transition from true to colloidal solutions and from suspensoid to emulsoid systems.

H. M. D.

**The Constitution of Tannin. XI.** A. GEAKE and M. NIERENSTEIN (*Ber.*, 1914, **47**, 891—898. Compare A., 1912, i, 202, 468, 566; 1911, i, 642; etc.).—The presence of dextrose in the tannin molecule is accepted by the authors, and the conception of tannin as a poly-digalloyl-leucodigallic anhydride (Nierenstein, A., 1912, i, 468) is withdrawn, together with the criticism (Manning and Nierenstein, A., 1912, i, 566) of the structure suggested by Fischer and Freudenberg (A., 1912, i, 471).

Careful repetition of the work of Biddle and Kelley (A., 1912, i, 713) on the action of yeast on tannin leads to the conclusion that the optical activity of the tannin is unaffected by the yeast, and that any decrease which may be observed in the rotation is due to the growth of moulds. Contrary to the views of the last-named investigators, therefore, the dextrose molecule is regarded as a firmly attached part of the tannin molecule.

On treatment for four hours at 100° with ten times its weight of 5% sulphuric acid, tannin undergoes partial hydrolysis with formation of an amorphous substance (60—70%) containing sugar, and considerably resembling tannin, but of higher rotation, together with gallic acid (20—25%) and a crystalline, sugar-free substance (2·5—4%) which was not identified.

D. F. T.

**The Composition of Tannin. III.** LEO F. ILJIN (*Ber.*, 1914, **47**, 985—993).—The author has submitted commercial tannin to Trimble's method of purification ("The Tannins," 1892, vol. i, p. 85), which consists in the partial precipitation of a solution of tannin with lead acetate and extraction of the filtrate with ethyl acetate. This process was repeatedly carried out with a sample of tannin, and led finally to a specimen having  $[\alpha]_D + 117\cdot04^\circ$ , and giving gallic acid and dextrose on hydrolysis. The precipitate, after purification, gave a substance with  $[\alpha]_D + 28\cdot78^\circ$ , and the author is of the opinion that a tannin having  $[\alpha]_D + 75^\circ$  is a mixture of two substances, the one having the higher rotatory power being regarded by him as a pentadigalloylglucose.

By using zinc acetate instead of lead acetate in the above method of purification, one of the fractions obtained had  $[\alpha]_D + 5.16^\circ$  (lowest value observed), and another had  $[\alpha]_D + 137.85^\circ$  (highest value observed). Each of these two substances gave gallic acid and dextrose on hydrolysis. J. C. C.

**Nickel Tannates.** PURAN SINGH (*J. Soc. Chem. Ind.*, 1914, 33, 172—173).—The *nickel tannates* were obtained by precipitating a solution of nickel hydroxide in ammonium salts with tannic acid. According as the nickel hydroxide or the tannic acid were in excess, the salts,  $Ni_3(C_{14}H_7O_9)_2$  and  $Ni(C_{14}H_9O_9)_2$ , are said to be formed. T. S. P.

**Tanning of Hides with Insoluble Compounds and Observations on Analysis of Tannins.** E. SOMMERHOFF (*Anal. Chim. Applicata*, 1914, 1, 126—127).—The author finds that compounds as insoluble as freshly precipitated copper phosphate and chromium hydroxide exert a very marked tanning action, the proportions of these compounds absorbed by the hides diminishing with increase of the time elapsing since their precipitation. The closest analogy is shown between these heavy metal salts in the state of gel and insoluble tanning phlobaphens, and when the latter are separated in the cold from a tanning material, such as quebracho or gambier, the tanning bath should be heated and cooled rapidly immediately before the hides are introduced, and then kept as far as possible in the dark; any phlobaphen separating during tanning, being freshly precipitated, will be readily absorbed by the hides.

Erroneous results are obtained by the methods now in use for determining the tanning value, owing to the fact that these phlobaphens are not taken into account. T. H. P.

**Tanning with Fatty and Resin Acids.** F. GARELLI and C. APOSTOLO (*Ann. Chim. Applicata*, 1914, 1, 121—124).—In oil tanning, the action is due more especially to the fatty acids, the neutral glycerides only oiling the hide without tanning it. Such acids as palmitic, stearic, hexoic, octoic, etc., may be used, and solution of them in a solvent like alcohol or conversion of them into ammonia soaps is unnecessary, since aqueous suspensions of the insoluble acids themselves act equally well. Colophony and probably all similar resin acids behave similarly to the fatty acids, but give a less pliable leather. These results do not agree with the theory advanced by Fahrion, who attributes the tanning action only to the unsaturated fatty acids. T. H. P.

**$\omega$ -Chloromethyl- and Ethoxymethyl-furfuraldehyde.** EMIL FISCHER and HANS VON NEYMAN (*Ber.*, 1914, 47, 973—977, 1323).—The authors have devised a more convenient method than that described by Fenton and Gostling (*T.* 1899, 75, 423; 1901, 79, 361, 807) for the preparation of  $\omega$ -chloromethylfurfuraldehyde, which consists in dissolving sucrose (200 grams) in fuming hydrochloric acid (1400 c.c.) previously warmed to  $40^\circ$  and heating the solution rapidly to  $75$ — $80^\circ$ ;

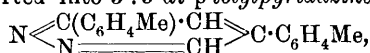
the operation should not last longer than fifteen minutes. After addition of ice and sodium carbonate the substance (35—40 grams) is extracted with ether.

On warming with alcohol in the presence of barium carbonate, the chloro-compound yields  $\omega$ -ethoxymethylfurfuraldehyde (Erdmann, A., 1910, i, 762; Cooper and Nuttall, T., 1911, **99**, 1193), b. p. 114—115°/8.5 mm., of which the *semicarbazone* has m. p. 169° (corr.), and the *ethylacetal*, b. p. 126°/8—9 mm.  $\omega$ -Ethoxymethylpyromucic acid has m. p. 62° (Cooper and Nuttall, *loc. cit.*, give 57.5—58.5°). J. C. C.

**Some New Oxidohydrofuran Derivatives.** G. KARL ALMSTRÖM (*Ber.*, 1914, **47**, 848—851).—An extension of the work of Widman and Almström (A., 1913, i, 1219) on the reaction between  $\omega$ -halogen-acetophenones and sodium ethoxide.

It was not found possible to convert bromoketones of the type C<sub>6</sub>H<sub>4</sub>·CHRBr (where R represents a hydrocarbon radicle) into furan derivatives, but ring substituted derivatives of the  $\omega$ -halogen substituted acetophenones proved capable of this change.

*p*-Tolyl chloromethyl ketone was treated in alcoholic solution at -10° with a solution of a semimolecular quantity of sodium ethoxide. On subsequently adding water a deposit was produced which could be separated by crystallisation from alcohol into *trans*-2-chloro-3:4-oxido-3:5-di-*p*-tolyltetrahydrofuran, 
$$\text{O} \begin{array}{c} \text{CH}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{CH} \\ \text{CHCl} \text{---} \text{C}(\text{C}_6\text{H}_4\text{Me}) \end{array} \text{O},$$
 long needles, m. p. 127—129°, and its *cis-isomeride*, thin, rectangular tablets, m. p. 100—104°. On boiling with hydrazine hydrate, both these substances are converted into 3:5-di-*p*-tolylpyridazine,



leaflets, m. p. 199—200°.

In a similar manner to the above, *p*-tolyl bromomethyl ketone gives rise to *trans*-2-bromo-3:4-oxido-3:5-di-*p*-tolyltetrahydrofuran, needles, m. p. 142°, and the *cis-isomeride*, leaflets, m. p. 93°. The *cis*-compound yielded the above-mentioned ditolylpyridazine on treatment with hydrazine hydrate, but the *trans*-compound gave only a resinous product.

1:3:4-Xylyl bromomethyl ketone, obtained by the bromination of 1:3:4-xylyl methyl ketone in chloroform solution in the presence of a little stannic chloride, forms colourless tablets, m. p. 42—43.5°, b. p. 164—170°/32 mm. Treatment with sodium ethoxide produced only an oil which contained bromine. D. F. T.

**Dicyclic Compounds and their Comparison with Naphthalene.** II. K. FRIES (*Annalen*, 1914, **404**, 50—52).—The author has applied a number of simple reactions to comparable benzene and naphthalene derivatives and thereby proved a fundamental difference in these two nuclei (A., 1912, i, 656). The same method has now been applied to dicyclic compounds containing one benzene nucleus in order to ascertain whether the C<sub>6</sub>-ring resembles the benzene or the naphthalene nucleus. 6- and 7-Hydroxy-4-methylcoumarins, which are com-

parable to  $\beta$ -naphthol according to their formulæ, do not resemble it in their behaviour except that during substitution the first substituent seeks the  $\alpha$ -position to the hydroxyl group. 6-Hydroxyindazole occupies an intermediate position; in some reactions it resembles  $\beta$ -naphthol, in others phenol. Benziminazole resembles the coumarins rather than the indazoles in that it shows very few points of similarity to naphthalene. C. S.

**Coumarins.** K. FRIES and H. LINDEMANN (*Annalen*, 1914, **404**, 53—80).—In order to appreciate the difference between the  $C_6$ -rings in coumarin and in naphthalene (preceding abstract), the following reactions of coumarin derivatives should be mentally contrasted with those of  $\beta$ -naphthol under the same conditions.

4-Bromoresorcinol,  $C_6H_5O_2Br, \frac{1}{2}H_2O$ , b. p.  $155^\circ/12$  mm., is easily obtained by brominating resorcinyl benzoate in glacial acetic acid on the water-bath and hydrolysing the resulting *bromoresorcinyl benzoate*, m. p.  $165^\circ$ . It condenses with ethyl acetoacetate in cold concentrated sulphuric acid to form *6-bromo-7-hydroxy-4-methylcoumarin*, m. p.  $284^\circ$ , small plates. The bromination of 7-hydroxy-4-methylcoumarin ( $\beta$ -methylumbelliferone) in boiling glacial acetic acid yields *8-bromo-7-hydroxy-4-methylcoumarin*, m. p.  $204^\circ$ , slender needles, the position of the halogen atom being assumed because the substance is different from 6-bromo-7-hydroxy-4-methylcoumarin. *8-Chloro-7-hydroxy-4-methylcoumarin*, needles, has m. p.  $195^\circ$ , and resembles the other halogenated  $\beta$ -methylumbelliferones here mentioned in forming yellow alkali salts. By further chlorination, 7-hydroxy-4-methylcoumarin yields *6:8-dichloro-7-hydroxy-4-methylcoumarin*, m. p.  $240^\circ$ , elongated plates, *3:6:8-trichloro-7-hydroxy-4-methylcoumarin*, m. p.  $268^\circ$ , and *3:5:6:6:8:8-hexachloro-7-keto-4-methyl-5:6:7:8-tetrahydrocoumarin*,  $CO \cdot CCl_2 \cdot C \cdot O \cdot CO$   
 $\begin{array}{c} | \quad | \quad | \\ CCl_2 \cdot CHCl \cdot C \cdot CMe \cdot CCl \end{array}$ , m. p.  $186^\circ$ , prisms. This keto-chloride liberates iodine from potassium iodide, loses hydrogen chloride only with difficulty, and is reduced by stannous chloride and glacial acetic acid to the preceding *3:6:8-trichloro-7-hydroxy-4-methylcoumarin*, in which the distribution of the chlorine atoms between the two nuclei is proved by its conversion by boiling 33% potassium hydroxide (and subsequent acidification) into *5:7-dichloro-6-hydroxy-3-methylcoumarilic acid*,  $OH \cdot C_6HCl_2 \cdot \begin{array}{c} \diagup CMe \\ O \diagdown \end{array} \cdot CO_2H$ , m. p.  $268^\circ$  (decomp.); the last substance is shown to be a coumarone derivative by developing with concentrated sulphuric acid a violet coloration changing to deep blue.

*8-Bromo-7-hydroxy-4-methylcoumarin* in boiling glacial acetic acid yields by treatment with nitric acid (D 1.4), *8-bromo-6:7-dinitro-7-hydroxy-4-methylcoumarin*, m. p.  $236$ — $239^\circ$ , yellow prisms. Under similar conditions, *8-chloro-7-hydroxy-4-methylcoumarin* yields *8-chloro-6-nitro-7-hydroxy-4-methylcoumarin*, m. p.  $225^\circ$ , elongated prisms, in which the position of the nitro-group is assumed from analogy to *6:8-dichloro-7-hydroxy-4-methylcoumarin*. By nitration, *7-hydroxy-4-methylcoumarin* yields *8-nitro-7-hydroxy-4-methylcoumarin*, in which the position of the nitro-group is proved by the fact that its product.

of reduction is identical with the 8-amino-7-hydroxy-4-methylcoumarin obtained by the condensation of 2-aminoresorcinol and ethyl acetoacetate.

The chlorination of 6-hydroxy-4-methylcoumarin in glacial acetic acid on the water-bath yields successively 5-chloro-6-hydroxy-4-methylcoumarin, m. p. 195—201°, prisms or needles, and 5:7-dichloro-6-hydroxy-4-methylcoumarin, m. p. 246°, prisms, whilst at the ordinary temperature 3:5:5:7:7:8-hexachloro-6-keto-4-methyl-5:6:7:8-tetrahydrocoumarin,  $\begin{array}{c} \text{CO}\cdot\text{CCl}_2-\text{C}\cdot\text{CMe}\cdot\text{CCl} \\ \text{CCl}_2\cdot\text{CHCl}\cdot\text{C}\cdot\text{O}-\text{CO} \end{array}$ , m. p. 138—140°, hexagonal plates, is obtained by prolonged chlorination. The keto-chloride yields 3:5:7-trichloro-6-hydroxy-4-methylcoumarin, m. p. 197°, needles (and a little 3:5:7:8-tetrachloro-6-hydroxy-4-methylcoumarin), by reduction with stannous chloride, and readily loses hydrogen chloride by keeping in the air or by boiling with sodium acetate and glacial acetic acid, yielding 3:5:5:7:8-pentachloro-6-keto-4-methyl-5:6-dihydrocoumarin, m. p. 135—136°, yellow plates. The last substance is reduced to 3:5:7:8-tetrachloro-6-hydroxy-4-methylcoumarin, m. p. 227—230°, faintly yellow prisms, by stannous chloride and glacial acetic acid.

5-Chloro-6-hydroxy-4-methylcoumarin in boiling glacial acetic acid is converted by nitric acid (D 1.4) into 5-chloro-7-nitro-6-hydroxy-4-methylcoumarin, m. p. 187° (decomp.), yellow needles, which forms a red sodium salt, but is decomposed by 2*N*-sodium hydroxide at 60° into the blue sodium salt of 6-chloro-4-nitro-2:5-dihydroxy- $\beta$ -methylcinnamic acid,  $\text{NO}_2\cdot\text{C}_6\text{HCl}(\text{OH})_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , m. p. 155° (decomp.), yellow prisms.

7:8-Dihydroxy-4-methylcoumarin (methyldaphnetin) is oxidised by lead peroxide and boiling acetone to 4-methyl-7:8-coumarinoquinone,  $\begin{array}{c} \text{C}_6\text{H}\cdot\text{CH}\cdot\text{C}\cdot\text{CMe}\cdot\text{CH} \\ \text{CO}\cdot\text{CO}-\text{C}\cdot\text{O}-\text{CO} \end{array}$ , m. p. 200° (decomp.), red prisms (which is very readily reduced to the dihydroxymethylcoumarin), and by exhaustive chlorination in glacial acetic acid, followed by reduction of the resulting keto-chloride, yields 3:5:6-trichloro-7:8-dihydroxy-4-methylcoumarin, m. p. 245—249° (decomp.), needles containing  $\text{H}_2\text{O}$ . 3:5:7:8-Tetrachloro-6-hydroxy-4-methylcoumarin in hot glacial acetic acid is oxidised by nitric acid (D 1.4) to 3:7:8-trichloro-4-methyl-5:6-coumarinoquinone, decomp. 270°, stout, red prisms, which is reduced to 3:7:8-trichloro-5:6-dihydroxy-4-methylcoumarin, m. p. 212° (decomp.), colourless needles.

The exhaustive chlorination of 6:7-dihydroxy-4-methylcoumarin (methylæsculetin) in glacial acetic acid produces a keto-chloride which is reduced by stannous chloride to 3:5:8-trichloro-6:7-dihydroxy-4-methylcoumarin, m. p. 225° (decomp.); this in acetic acid is oxidised by nitric acid (D 1.2) to 3:5:8-trichloro-4-methyl-6:7-coumarinoquinone, m. p. 179°, dark red prisms. C. S.

Coefficients of Precipitability of Quinine Salts in Saline Solutions of Various Concentrations. I. N. TARUGI (*Gazzetta*, 1914, 44, i, 131—151).—The author has investigated the precipitability of basic quinine hydrochloride,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ , by sodium, potassium, and calcium chloride and by sodium nitrate, the



quinine solution being run into the inorganic salt solution until turbidity resulted; all the experiments were made at 16°, and the concentrations are given in grams per 100 c.c.

The solubility coefficient of the quinine salt varies regularly from 2.6 in a 2.02% sodium chloride to 0.085 in a 19.83% solution, the product of the coefficient and the concentration of the salt diminishing from 5.2 to 1.48.

With sodium nitrate, the solubility coefficient similarly diminishes from 2.85 to 0.0663 as the concentration of the nitrate increases from 0.677 to 31.78%, the value of the product, coefficient  $\times$  concentration diminishing from 1.9 to 1.34, then increasing to 2.97, and finally falling to 2.09.

With potassium chloride, the solubility coefficient diminishes from 2.545 to 0.0997 as the concentration of the potassium salt increases from 2.63 to 25.74%, the product of concentration and coefficient falling regularly from 6.69 to 2.56.

In the case of calcium chloride, the product of the solubility coefficient and the concentration of the calcium salt for different values of the latter is as follows: 6.37%, 6.5; 7.03%, 6.67; 7.75%, 6.82; 7.96%, 6.08; 34.42%, 6.22. This product is hence virtually constant and has the mean value 6.43, so that by employing a calcium chloride solution of known concentration, the concentration of a solution of the quinine salt can be estimated. This can also be done with solutions of the other salts used, but here the relations are more complicated.

The presence of either cinchonine or cinchonidine hydrochloride in the quinine salt may be detected as follows. Twenty-five c.c. of the quinine hydrochloride solution are saturated in the cold with sodium nitrate, and are allowed to remain for at least three hours. With 5 c.c. of the filtered liquid, 1.5 c.c. of concentrated ammonia solution (0.880) are carefully mixed without excessive shaking. If the quinine salt contains 3% of cinchonine or cinchonidine hydrochloride, this procedure yields a turbid solution, but the test does not serve for the detection of quinidine hydrochloride.

T. H. P.

**Preparation of a Compound of Quinine and Dipropylbarbituric Acid.** E. MERCK (Swiss Patent 63032).—A compound of quinine and dipropylbarbituric acid is prepared by the interaction of quinine hydrochloride and sodium dipropylbarbiturate in aqueous solution.

J. C. C.

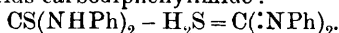
**Preparation of Ethylhydrocupreine Salicylate.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (Swiss Patent 63031).—*Ethylhydrocupreine salicylate*, a colourless and tasteless powder, m. p. 50°, is prepared by heating ethylhydrocupreine with phenyl salicylate for six hours to 130—135°.

J. C. C.

**Action of Pyridine on Certain Organic Sulphur Compounds.** I. M. RAFFO and G. ROSSI (*Gazzetta*, 1914, **44**, i, 104—108).—Pyridine is an excellent solvent for many organic and inorganic compounds, but sometimes reacts with the solutes. Sulphur itself dissolves completely when heated with pyridine, hydrogen sulphide

being liberated; if the solution is subjected to prolonged boiling, it assumes a colour varying from intense red to blackish-brown, and, on cooling, deposits a black pitchy substance, which has not yet been investigated. Pyridine solutions of organic sulphur compounds also yield hydrogen sulphide when boiled, but in such cases the hydrogen of the evolved gas is not furnished by the pyridine, which seems to act simply as a catalyst.

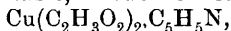
In this way, thioacetamide gives acetonitrile, and thiobenzamide, benzonitrile. With diphenylthiocarbamide, the first phase of the reaction, which proceeds until the whole of the diphenylthiocarbamide has disappeared, yields carbodiphenylimide:



The latter then reacts further with the hydrogen sulphide, thus:  $3\text{C}(\text{NPh})_2 + 3\text{H}_2\text{S} = \text{CS}(\text{NHPh})_2 + \text{NH}_2\text{Ph} + \text{NPh}:\text{C}(\text{NHPh})_2 + \text{CS}_2$ ; this reaction proceeds at a temperature slightly above  $116^\circ$ , the boiling point of pyridine, whereas in absence of the latter a temperature of  $170^\circ$  is necessary. In a similar manner, di-*o*-tolylthiocarbamide and pyridine give first carbodi-*o*-tolylimide and hydrogen sulphide, these products then reacting to form tri-*o*-tolylguanidine, *o*-toluidine, and carbon disulphide as first products.

T. H. P.

**Equilibrium in the System Copper Acetate-Pyridine.** J. HOWARD MATHEWS and ERNEST BADEN BENDER (*J. Physical Chem.*, 1914, 18, 264—268).—The solubility of copper acetate in pyridine has been determined between the temperatures  $-11.6^\circ$  and  $95.4^\circ$ . From the curves it is shown that there is a transition point at  $44.7^\circ$ . Below this temperature the substance  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ , a blue, crystalline compound, is stable, and above this temperature



a green, crystalline compound, is stable. These results confirm those of Foerster (A., 1893, i, 131)

J. F. S.

**Complex Iron Salts. II.** G. SPACU (*Ann. Sci. Univ. Jassy.*, 1914, 8, 24—32).—*Aquopentapyridine ferrous bromide*,  $[\text{OH}_2, \text{Fe}, \text{Py}_5]\text{Br}_2$ , is obtained similarly to the tetrapyridine ferrous chloride (A., 1912, i, 494), by the action of pyridine on ferrous bromide at  $-15^\circ$  in an atmosphere of carbon dioxide. It forms canary-yellow crystals, which lose pyridine on exposure to the air. When dissolved in hydrobromic acid (D 1.38), garnet-red crystals of the compound  $[\text{Fe}_2, 3\text{Py}, \text{HBr}]\text{Br}_6$  (*loc. cit.*) are obtained. When the aquopentapyridine bromide is kept over sulphuric acid in a desiccator, which is opened to the air from time to time, it loses water and four molecules of pyridine and the iron is oxidised to the ferric condition, giving the compound,  $\text{FePyOBr}_2$ , which is reddish-brown in colour, and corresponds with the chloride previously described (*loc. cit.*). When dissolved in hydrobromic acid and the solution evaporated in a vacuum over concentrated sulphuric acid, brown leaflets of the compound,  $\text{FeBr}_3\text{Py}, \text{HBr}, \text{H}_2\text{O}$ , are obtained.

When boiling pyridine (100 grams) is treated with anhydrous ferric bromide (10 grams) in small portions at a time, reduction takes place and brownish-yellow crystals of *hexapyridine ferrous bromide*,  $[\text{FePy}_6]\text{Br}_2$ , are obtained, which rapidly decompose on exposure to the

air. Similarly, ferric iodide and pyridine at  $-15^{\circ}$  give clear yellow crystals of *hexapyridine ferrous iodide*,  $[\text{FePy}_6]\text{I}_2$ , the reaction being accompanied by considerable elevation in temperature. When excess of pyridine (110 grams) at  $-20^{\circ}$  is treated with anhydrous ferric chloride (12 grams), vigorous reaction takes place; by a complicated method of procedure, deep red crystals of *tetrapyridine ferric chloride*,  $[\text{FePy}_4]\text{Cl}_3$ , can be obtained from the reaction mixture. They are exceedingly deliquescent, and can only be preserved over phosphoric oxide. When dissolved in anhydrous ether, they lose pyridine, giving the reddish-brown compound,  $[\text{Fe}_2\text{Py}_8]\text{Cl}_6$ .

On treating a 50% solution of ferric chloride with an excess of a solution of ethylenediamine hydrochloride and evaporating on the water-bath, orange-red crystals of the compound,  $[\text{Fe en 2HCl}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ , are obtained. When hydrated ferric sulphate is heated at  $60^{\circ}$  with an excess of pyridine and the mixture kept for ten to fifteen days, the compound,  $[\text{Fe}_2\text{Py}_4](\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ , is obtained as an amorphous, yellowish-brown powder. T. S. P.

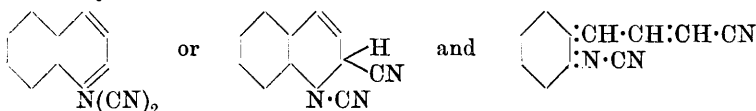
**Complex Chromium Fluorides. IV.** N. COSTĂCHESCU (*Ann. Sci. Univ. Jassy*, 1914, 8, 16—23).—The following salts have been prepared by double decomposition of difluorotetrapyridinechromium nitrate (compare A., 1912, i, 493) with the appropriate potassium salts. *Difluorotetrapyridinechromium bromide*,  $\text{YBr} \cdot 2\text{H}_2\text{O}$ , where  $\text{Y} = [\text{F}_2\text{CrPy}_4]$ , is a rose-violet, crystalline powder. The *perchlorate*,  $\text{YClO}_4$ , forms small, rose-violet, acicular crystals. The *permanganate*,  $\text{YMnO}_4 \cdot 2\text{H}_2\text{O}$ , is a crystalline, indigo-coloured powder, giving a solution resembling that of potassium permanganate in colour; the *dichromate*,  $\text{Y}_2\text{Cr}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ , forms slender, yellowish-orange needles. With a solution of potassium cuprocyanide,  $\text{K}_6\text{Cu}_2(\text{CN})_8$ , the bromide gives stable, rose-violet crystals of *potassium difluorotetrapyridinechromium cuprocyanide*,  $\text{K}_2\text{Y}_2\text{Cu}_2(\text{CN})_6 \cdot 7\text{H}_2\text{O}$ . T. S. P.

**Pyridine-2-aldehyde.** GEORG LÉNÁRT (*Ber.*, 1914, 47, 808—810).—Pyridine-2-aldehyde is conveniently prepared by the oxidation of 2-styrylpyridine by ozone; the styrylpyridine was dissolved in ten times its bulk of concentrated hydrochloric acid and treated with a stream of 6—8% ozone for approximately two hours per gram of base. The pyridine-2-aldehyde obtained has b. p.  $62-63^{\circ}/13-14$  mm.,  $180^{\circ}/750$  mm. (compare Kaufmann and Vallette, A., 1912, i, 655; 1913, i, 293),  $D_4^{18.5}$  1.1255,  $n_D^{18.5}$  1.53886; phenylhydrazone, pale yellow needles or leaflets, m. p.  $173-176^{\circ}$ , according to the rate of heating; hydrochloride, red, silky needles, m. p.  $196^{\circ}$ ; *oxime*, colourless needles, m. p.  $113.5^{\circ}$ ; *semicarbazone*, microscopic needles, m. p.  $195-199^{\circ}$ , according to the rate of heating. D. F. T.

**Quinoline Dicyanide and Allied Substances.** OTTO MUMM and ERNST HERRENDÖRFER (*Ber.*, 1914, 47, 758—765).—The formation of additive compounds of quinoline with hydrogen cyanide and imino-chlorides (this vol., i, 534) has been investigated. In the first place, experiments were made in order to determine whether the chloride or hydrogen cyanide could be replaced by similar agents, and it was found

(Hesse, *Diss.*, 1911) that quinoline, bromocyanogen, and hydrogen cyanide react, with elimination of hydrogen bromide, to form a compound which readily passes into an isomeride. The constitution of these isomerides is the subject of the present paper.

Of substituted quinolines, only those in which the substituent is in the benzene ring, in a position which is not ortho to the nitrogen atom, give such compounds. *iso*Quinoline does not form a second isomeride. The primary product is re-converted into the base by boiling with glacial acetic acid, but not so the isomeride. This led to the supposition that the pyridine ring is still intact in the primary product, but opened out in the isomeride, and the substances are therefore represented by the formulæ :



No transformation products could be obtained, so the number of double linkings was estimated by catalytic reduction. As was expected, all the second isomerides required four atoms of hydrogen, whereas the primary naphthylquinoline and *iso*quinoline dicyanides absorbed only two atoms. Unfortunately, the quinoline and tolylquinoline compounds required four atoms, but it may be that they undergo the isomeric change during the reduction.

Quinoline, bromocyanogen, and anhydrous hydrogen cyanide were left for a day in benzene, when the hydrobromide of the base was filtered, the excess of base was washed out by dilute acid, and the dry extract was evaporated. *Quinoline dicyanide* forms colourless crystals, m. p.  $100^\circ$ , and the *isomeride* separates in white needles, m. p.  $136^\circ$ , when a few drops of methyl-alcoholic ammonia are added to the cold saturated solution. *3-Methylquinoline dicyanide* has m. p.  $96\cdot5^\circ$ , and the *isomeride*, m. p.  $153\text{--}154^\circ$ ;  *$\beta$ -naphthaquinoline dicyanide* forms colourless, quadratic columns, m. p.  $150\text{--}151^\circ$ , and its *isomeride*, colourless needles, m. p.  $210^\circ$  (decomp.); *isoquinoline dicyanide* crystallises in colourless needles, m. p.  $137^\circ$ .  
J. C. W.

**Preparation of Quinolyl Ketones.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R. P. 268830).—Esters of quinolinecarboxylic acids condense with esters of the general formula  $\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}'$  (where  $\text{R}$ =hydrogen or alkyl and  $\text{R}'$ =alkyl) under the influence of alkaline condensing agents, such as sodium ethoxide, to form  $\beta$ -ketonic esters which on decomposition with 25% sulphuric acid yield quinolyl ketones. Ethyl quinoline-4-carboxylate and ethyl acetate, by this reaction, condense to form *ethyl 4-quinoloylacetate*,  $\text{C}_9\text{H}_6\text{N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , a yellow oil which forms a sparingly soluble *hydrogen sulphate*, and yields, on heating with 25% sulphuric acid, 4-quinolyl methyl ketone, b. p.  $153\text{--}155^\circ/8$  mm. (Kaufmann, Peyer, and Kunkler, A., 1912, i, 1017). Similarly, ethyl 6-methoxyquinoline-4-carboxylate condenses with ethyl propionate to form *ethyl  $\alpha$ -6-methoxy-4-quinoloylpropionate*,  $\text{OMe}\cdot\text{C}_9\text{H}_5\text{N}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$  (*picrate*, yellow needles, m. p.  $137\text{--}138^\circ$ ; *picrolonate*, orange needles, decomp.  $136^\circ$ ), from which 6-methoxy-

4-quinolyl ethyl ketone, pale yellow needles, m. p. 57—58°, is obtained, and the above ester, with ethyl acetate, furnishes ethyl 6-methoxy-4-quinoloylacetate, a yellow powder, m. p. 79—80°, from which 6-methoxy-4-quinolyl methyl ketone (Kaufmann, Peyer, and Kunkler, *loc. cit.*) is produced. J. C. C.

Preparation of Sulpho-compounds of 2-Phenylquinoline-4-carboxylic Acid or its Derivatives. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 270994).—Sulpho-2-phenylquinoline-4-carboxylic acid and sulpho-2-phenyl-6-methylquinoline-4-carboxylic acid are prepared by the action of fuming sulphuric acid on the corresponding carboxylic acids. The introduction of the sulphonic group has scarcely any effect on the therapeutical action of the carboxylic acids. J. C. C.

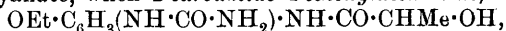
Action of Acetic Anhydride on Some Benzylideneanthranilic Acids. III. JOHN B. EKELEY and L. CECIL SLATER (*J. Amer. Chem. Soc.*, 1914, **36**, 603—606).—In continuation of the work of Ekeley and Dean (A., 1912, i, 211) and Ekeley and Clinton (A., 1913, i, 395), benzylideneanthranilic acids have been prepared from *o*-, *m*-, and *p*-chlorobenzaldehydes, *m*- and *p*-tolualdehydes, and *m*-hydroxybenzaldehyde, and have been converted into the respective oxazines by the action of acetic anhydride.

*o*-, *m*-, and *p*-Chlorobenzylideneanthranilic acids, m. p. 130°, 174°, and 136°, form colourless crystals, and yield 4-acetyl-3-*o*-, -*m*-, and -*p*-chlorophenyldihydro-2:4-benzoxazine-1-ones,  $C_6H_4 \begin{smallmatrix} CO-O \\ \diagdown \diagup \\ NAc \cdot CH \cdot C_6H_4Cl \end{smallmatrix}$  m. p. 154°, 171°, and 187°. *m*- and *p*-Tolylideneanthranilic acids, m. p. 149° and 131°, form colourless and yellow crystals respectively, and furnish 4-acetyl-3-*m*- and -*p*-tolylidihydro-2:4-benzoxazine-1-ones, m. p. 145° and 121°, which are both colourless. *m*-Hydroxybenzylideneanthranilic acid, m. p. 175° (decomp.), forms yellow crystals, and gives 4-acetyl-3-*m*-acetoxyphenyldihydro-2:4-benzoxazine-1-one, m. p. 124°. Attempts to prepare oxazines from anisaldehyde, piperonaldehyde, and furfuraldehyde were not successful. E. G.

Acylation of Aromatic *o*-Diamines by Different Acid Residues. D. MARON and J. J. BLOCH (*Ber.*, 1914, **47**, 717—724).—The acyl derivatives would offer promising material for the preparation of substitution compounds of the *o*-diamines, or for the application of those bases in syntheses, but, owing to the tendency to condensations between the amino-groups, very few of them are known. It has now been found that *o*-nitroamides can very generally be reduced to monoacylated *o*-diamines, which may readily be transformed into simple or mixed di-acyl derivatives or condensed to benzimidazoles. In the present communication, some typical transformations are illustrated in the case of *o*-aminolactophenin [2-amino-4-ethoxylactanilide].

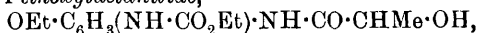
A good yield of 2-nitro-4-ethoxylactanilide (Elbs and Mette, A., 1911, i, 192) was obtained by warming a solution of 4-ethoxylactanilide in acetic acid with 16% nitric acid for a few minutes at 35—45°. The compound is quantitatively reduced by iron powder and acetic acid to

2-amino-4-ethoxylactanilide,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{NH}_2)\text{NH} \cdot \text{CO} \cdot \text{CHMe} \cdot \text{OH}$ , m. p. 135—136°. The hydrochloride of the base was left with a solution of potassium cyanate, when 2-carbamido-4-ethoxylactanilide,



was deposited in white needles, with  $1\text{H}_2\text{O}$ , m. p. 174—175°. The anhydrous substance melts at 157—158° and passes into ethoxybenziminazolone (Cohn, A., 1899, i, 944). The same change occurs when the solution of the derivative is boiled, especially with acetic acid

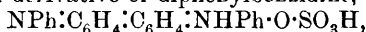
2-Urethano-4-ethoxylactanilide,



was obtained as a white powder, m. p. 108—109°, by leaving a benzene solution of the base with ethyl chloroformate. 2-Acetyl-amino-4-ethoxylactanilide,  $\text{C}_{13}\text{H}_{18}\text{O}_4\text{N}_2$ , was obtained by the action of acetic anhydride in the cold. It forms unstable, slender, white needles when crystallised rapidly from water, but stable tablets when the solution is cooled slowly, m. p. 139°. 2-Chloroacetyl-amino-4-ethoxylactanilide has m. p. 140—141°, and is converted by alcoholic ammonia into 2-glycyl-amino-4-ethoxylactanilide,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2) \cdot \text{NH} \cdot \text{CO} \cdot \text{CHMe} \cdot \text{OH}$ . This melts at 168° in a previously warmed bath, but also loses ammonia, forming what is probably a cyclic compound, m. p. 203—204°. The same change occurs at 100—110° in a vacuum. The chloroacetyl derivative also reacts with piperidine to give 2-piperidinoacetyl-amino-4-ethoxylactanilide,  $\text{C}_{18}\text{H}_{27}\text{O}_4\text{N}_3$ , m. p. 115°.

When aminolactophenin is boiled with acetic acid, it is condensed to 5-ethoxy-2- $\alpha$ -hydroxyethylbenziminazole, m. p. 171—172°. J. C. W.

**Reactions of Diphenylamine. Preparation of Diphenylbenzidine.** MARQUEYROL and HENRI MARAOUR (*Bull. Soc. chim.*, 1914, [iv], 15, 186—197).—The blue coloration produced by the action of oxidising agents on solutions of diphenylamine in sulphuric acid has been attributed to the formation of an acid sulphate of diphenyl-dihydrophenazonium (Wieland, A., 1911, i, 569). Kehrman and Micewicz (A., 1912, i, 1020) have shown that it is more probably due to a quinonoid derivative of diphenylbenzidine,



and this explanation has been accepted by Wieland (A., 1913, i, 1386). The authors have investigated the reaction in a slightly modified manner, and are led to conclusions differing in some respects from those of Wieland.

On repetition of Wieland's experiments on the oxidation of diphenylamine, the authors find that the yield of diphenylbenzidine does not exceed 20% of that theoretically possible, and consider that no definite proof can be deduced that the blue coloration is due solely to a quinonoid derivative of diphenylbenzidine. They have therefore altered the mode of procedure, and by oxidising diphenylamine, dissolved in an aqueous solution of sulphuric and acetic acids, by means of sodium dichromate and reduction of the product with sodium hydrogen sulphite solution, have obtained diphenylbenzidine in 60% yield, or, on addition of the portion of the product which is insoluble in toluene (shown to be a derivative of diphenylbenzidine), in a total yield of 79.5%. The diphenylbenzidine has m. p. 250.5—251.5° (Maquenne

block), but the discrepancy between this figure and that quoted by Wieland (242°) is attributed to difference in the mode of determination. If it is thus admitted that the blue coloration is mainly due to a quinonoid derivative of diphenylbenzidine, this theory is only true if the sulphuric acid is not too concentrated. The yield of diphenylbenzidine decreases with increasing concentration of the acid, whilst, on the other hand, the proportion of residue, insoluble in boiling toluene, increases. The nature of this residue has not been definitely ascertained; it is, however, derived from diphenylbenzidine, since it can be obtained by oxidation of the latter in sulphuric-acetic acid solution and reduction of the product by sulphurous acid. When treated with oxidising agents in sulphuric acid solution, it yields a blue coloration. Hence, the blue coloration obtained from diphenylamine is attributed to a superposition of the blue tint of the quinonoid derivative of diphenylbenzidine and the duller tint of the quinone of the condensation product, the latter being formed in greater quantity as the acid increases in concentration. At great concentrations of acid, only small quantities of the above products are formed, and the colorations are less intense.

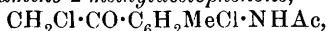
With regard to the mechanism of the change, the authors agree with Wieland that tetraphenylhydrazine is not an intermediate product. Wieland has assumed a direct union of the benzene nuclei without formation of intermediate products, and, in support of the assumption, has shown that a similar blue coloration is formed by the oxidation of triphenylamine. According to the authors, the evidence is not conclusive, since the oxidation of the latter is effected in acetic acid solution, whilst in the case of diphenylamine, the presence of sulphuric acid is necessary. Further, acetyldiphenylamine is not oxidised by dichromate in acetic acid solution to diacetyldiphenylbenzidine. The authors also find that diphenylamine, when dissolved in concentrated sulphuric acid, resists the attack of oxidising agents, whilst in more dilute solution, excellent yields of diphenylbenzidine are obtained. They are therefore led to the conclusion that the primary attack occurs at the :NH group, the sulphuric acid being only necessary in that it causes the transformation of the intermediate product; in concentrated sulphuric acid solution, the :NH group is so far protected that oxidation cannot occur. Further investigation is necessary to establish the nature of the intermediate product. The authors recommend the substitution of diphenylbenzidine for diphenylamine in the detection of small quantities of oxidising agents, such as nitrites.

H. W.

**Solubility of Indigotin in Methyl Sulphate.** S. J. PEACHEY (*J. Soc. Dyers*, 1914, **30**, 84).—Indigotin dissolves very readily, even in the cold, in methyl sulphate containing a very small quantity of sulphuric acid, but is soluble in the pure ester only when warm.

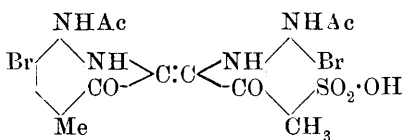
W. H. G.

**Some New Derivatives of Indigotin.** FRANZ KUNCKELL (*J. pr. Chem.*, 1914, [ii], **89**, 324–328. Compare A., 1912, i, 1027).—*ω*-4-Dichloro-5-acetyl-amino-2-methylacetophenone,



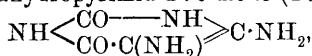
prepared by the interaction of chloroacetyl chloride and *m*-chloro-*p*-acetotoluidide in carbon disulphide solution in the presence of aluminium chloride, crystallises in white needles, m. p. 129°, and, on nitration, yields *ω*-4-dichloro-6-nitro-5-acetylamino-2-methylacetophenone, which forms slender, yellow, lustrous, silky needles, m. p. 199°, and is converted by reduction with zinc and acetic acid into 6:6'-dichloro-7:7'-diacetylamino-4:4'-dimethylindigotin.

*ω*-Chloro-4-bromo-5-acetylamino-2-methylacetophenone, obtained from *m*-bromo-*p*-acetotoluidide in a similar manner, forms slender, pale yellow needles, m. p. 116°, and on nitration yields *ω*-chloro-4-bromo-6-nitro-5-acetylamino-2-methylacetophenone, which crystallises in soft, light yellow needles, m. p. 222°, and is reduced by zinc and acetic acid to 6:6'-dibromo-7:7'-diacetylamino-4:4'-dimethylindigotin. The latter compound dissolves in cold strong sulphuric acid to form a *sulphonic acid* of the annexed constitution. F. B.



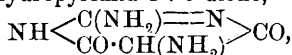
**Pyrimidines. LXVIII. Structure of Ritthausen's Divicine.** TREAT B. JOHNSON and CARL O. JOHNS (J. Amer. Chem. Soc., 1914, 36, 545—550).—Johnson (this vol., i, 366) has pointed out that divicine, obtained by Ritthausen by hydrolysing vicine with sulphuric acid, may be a pyrimidine compound. It is now shown that divicine is probably identical with 4:5-diaminouracil.

4:5-Diaminotetrahydropyrimid-2:6-dione (4:5-diaminouracil),



has been prepared by Traube's method (A., 1900, i, 416) and found to respond to all the tests which Ritthausen has described as characteristic of divicine. When the compound is heated with carbamide at 170—180°, it is converted quantitatively into uric acid.

2:5-Diaminotetrahydropyrimid-4:6-dione,



has also been prepared by Traube's method (*loc. cit.*); it is not so stable as divicine and is much less soluble in water. E. G.

**Quinazolines. XXXII. Some Quinazolones, Benziminazoles, and Related Compounds, Derived from *s*- $\psi$ -Cumidine.** MARSTON TAYLOR BOGERT and ANDREW BENDER (J. Amer. Chem. Soc., 1914, 36, 568—584).—Attempts have been made to prepare 5-amino-benzene-1:2:4-tricarboxylic acid (1) by acetylating *s*- $\psi$ -cumidine and oxidising the acetyl derivative, and (2) by converting  $\psi$ -cumene into the 5-nitro-derivative, oxidising the latter to the nitro-1:2:4-carboxylic acid, and reducing this to the amino-compound. Neither method proved successful.

The acetyl derivative of *s*- $\psi$ -cumidine has m. p. 164.5° (corr.); its 6-nitro-derivative, m. p. 199.5° (corr.), yields on reduction 2:4:5:7-tetramethylbenziminazole,  $\text{C}_6\text{HMe}_3 \text{---} \text{N} \text{---} \text{CMe}$ , m. p. 232° (corr.).



2:4:5:7-Tetramethylbenziminazole methiodide forms colourless needles, which darken above 330°, but are not melted at 350°. When the tetramethylbenziminazole is heated with methyl iodide and sodium in presence of xylene, 1:2:4:5:7-pentamethylbenziminazole methiodide,

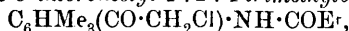
$C_6HMe_3 \begin{smallmatrix} \text{NMe} \\ \text{N(MeI)} \end{smallmatrix} \text{CMe}$ , m. p. 274—275° (corr.), is obtained as minute, straw-coloured crystals. 2-Styryl-4:5:7-trimethylbenzimin-

azole,  $C_6HMe_3 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{CHPh}$ , m. p. 257.5° (corr.), prepared by heating 2:4:5:7-tetramethylbenziminazole with benzaldehyde, forms colourless crystals; the corresponding 2-p-nitrostyryl compound has m. p. 303—305° (uncorr.). 2:4:5:7-Tetramethylbenziminazole-

2-phthalone,  $C_6HMe_3 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{CH} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C_6H_4$ , m. p. 296—297° (corr.), obtained by the action of phthalic anhydride on the benziminazole, forms yellow crystals.

Propionyl-ψ-cumidine,  $C_6H_2Me_3 \cdot NH \cdot COEt$ , m. p. 144° (corr.), crystallises in colourless needles, and when treated with fuming nitric acid is converted into 6-nitro-5-propionylamino-1:2:4-trimethylbenzene,  $C_6HMe_3(NO_2) \cdot NH \cdot COEt$ , m. p. 167° (corr.). This compound, on reduction with tin and hydrochloric acid, yields the hydrochloride of 4:5:7-trimethyl-2-ethylbenziminazole,  $C_6HMe_3 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{CEt}$ , HCl, m. p. 318—320° (decomp.); the base, m. p. 197° (corr.), forms colourless crystals; its platinichloride and methiodide have m. p. 245—246° (corr.) and 345—346° (corr.) respectively.

5-Propionylamino-3-chloroacetyl-1:2:4-trimethylbenzene,

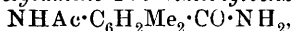


m. p. 181° (corr.), obtained by the action of chloroacetyl chloride on propionyl-ψ-cumidine in presence of aluminium chloride, crystallises in silky needles, and when boiled with hydrochloric acid is converted into chloroacetyl-ψ-cumidine (Kuncell, A., 1900, i, 664). 6-Nitro-5-propionylamino-3-chloroacetyl-1:2:4-trimethylbenzene, m. p. 193.2° (corr.), forms slender, colourless needles.

6-Acetylamino-3:4-dimethylbenzoic acid,  $NHAc \cdot C_6H_2Me_2 \cdot CO_2H$ , m. p. 248—250° (decomp.), obtained as one of the products of oxidation of acetyl-ψ-cumidine by potassium permanganate, forms minute, colourless crystals; its methyl ester has m. p. 120° (corr.). By the action of acetic anhydride on this acid, 3:4-dimethylacetylanthranil,

$C_6H_2Me_2 \begin{smallmatrix} \text{CO} \\ \text{N} \\ \text{N}Ac \end{smallmatrix}$ , m. p. 263.5° (corr.), is produced, which is converted

by ammonia into 2-acetylamino-4:5-dimethylbenzamide,

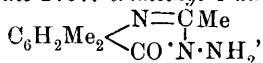


which does not melt at 340°; the corresponding methylamide has m. p. 320—322° (decomp.). When 3:4-dimethylacetylanthranil is heated with methylamine and potassium hydroxide, 2:3:6:7-tetramethyl-4-

dihydroquinazolone,  $C_6H_2Me_2 \begin{smallmatrix} \text{N} \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{CMe} \\ \text{CMe} \end{smallmatrix}$ , m. p. 210—212° (corr.) is

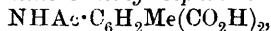
produced, which forms minute, colourless needles. By the action of aniline on the acetylanthranil, a quinazolone is not formed, but 2-acetyl-

*amino-4 : 5-dimethylbenzanilide*,  $\text{NHAc} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CO} \cdot \text{NHPh}$ , m. p.  $307^\circ$  (decomp.), is obtained. *2-Acetyl-amino-4 : 5-dimethylbenzhydrazide*,  $\text{NHAc} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , m. p.  $297^\circ$  (decomp.), produced by the action of hydrazine hydrate on the acetylanthranil, forms minute, colourless needles, and when boiled with potassium hydroxide solution is converted into *3-amino-2 : 6 : 7-trimethyl-4-dihydroquinazalone*,



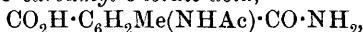
m. p.  $215^\circ$  (uncorr.).

When aceto- $\psi$ -cumidide is oxidised with potassium permanganate, a small quantity of 6-acetyl-amino-3 : 4-dimethylbenzoic acid is produced, together with a larger quantity (not exceeding 25% of the theoretical) of 6-acetyl-amino-4-methylisophthalic acid,

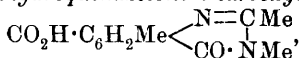


m. p.  $278-280^\circ$  (decomp.); its *dimethyl* and *diethyl* esters have m. p.  $138^\circ$  (corr.) and  $116.5^\circ$  (corr.) respectively. By the hydrolysis of this acid with dilute sulphuric acid, 6-amino-4-methylisophthalic acid,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{CO}_2\text{H})_2$ , m. p.  $305-308^\circ$  (corr.), is obtained, which crystallises in long, colourless needles; its *hydrochloride* has m. p.  $196-197^\circ$  (decomp.), and the *dimethyl* and *diethyl* esters, m. p.  $150^\circ$  (corr.) and  $103.5^\circ$  (corr.) respectively. By the action of acetic anhydride on 6-acetyl-amino-4-methylisophthalic acid, the *acetyl-anthranil*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2\text{Me} \begin{array}{c} \text{CO} \\ \text{N} \text{Ac} \end{array}$ , m. p.  $285-286^\circ$  (corr.), is produced,

which forms yellow needles and is converted by solution of ammonia into 4-acetyl-amino-5-carbamyl-o-toluic acid,

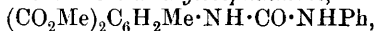


m. p.  $303-305^\circ$  (corr.). If the acetylanthranil is boiled with solution of ammonia in presence of potassium hydroxide, *2 : 7-dimethyl-4-dihydroquinazalone-6-carboxylic acid*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2\text{Me} \begin{array}{c} \text{N}=\text{CMe} \\ \text{CO} \cdot \text{NH} \end{array}$ , is obtained which chars at  $340^\circ$  without melting. By the action of methylamine on the acetylanthranil in presence of potassium hydroxide, *2 : 3 : 7-trimethyl-4-dihydroquinazalone-6-carboxylic acid*,



m. p.  $299.5^\circ$  (corr.), is produced. *2 : 7-Dimethyl-3-ethyl-4-dihydroquinazalone-6-carboxylic acid* has m. p.  $250.8^\circ$  (decomp.), and the corresponding *3-phenyl* compound, m. p.  $300-301^\circ$  (corr.). *3-Amino-2 : 7-dimethyl-4-dihydroquinazalone-6-carboxylic acid*, m. p.  $306^\circ$  (decomp.), obtained by the action of hydrazine hydrate on the acetylanthranil, yields an *acetyl* derivative, m. p.  $220^\circ$  (uncorr.), and a *benzylidene* derivative, m. p.  $237.5^\circ$  (corr.).

*Methyl 6-phenylcarbamido-4-methylisophthalate*,



m. p.  $192.5^\circ$  (corr.), obtained by the action of phenylcarbimide on methyl methylaminoisophthalate, forms colourless, microscopic needles; the *ethyl* ester has m. p.  $177-178^\circ$  (corr.).

In one experiment on the oxidation of aceto- $\psi$ -cumidide, a small quantity of the *anhydride* of 5-acetylaminobenzene-1 : 2 : 4-tricarboxylic

acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2(\text{NHAc})\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\rangle\text{O}$ , m. p. 240—242° (corr.), was produced, which crystallises in transparent prisms. E. G.

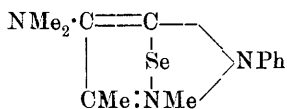
**Behaviour of Diphenyltriketones towards Amino-compounds.** II. G. GASTALDI and F. CHERCHI (*Gazzetta*, 1914, **44**, i, 287—290).—The course followed by the reaction between *o*-phenylenediamine and diphenyltriketone (A., 1913, i, 767) rendered it possible that the interaction of 1:8-naphthylenediamine and diphenyltriketone would yield a heptatomic heterocyclic compound. The latter reaction is found, however, to be quite different from the former, and is similar to that occurring between diacetyl and 1:8-naphthylenediamine (compare Sachs, A., 1909, i, 426), the product being *dibenzoyldihydroperimidine* (annexed formula), which forms orange-yellow prisms, m. p. 215°.

The action of 1:8-naphthylenediamine on dibenzoylmethane (*loc. cit.*) yields 2-phenylperimidine (compare Sachs, *loc. cit.*; Noelting, A., 1902, i, 314). T. H. P.

**Selenopyrazolone and Selenopyramidone.** A. MICHAELIS and PAUL LANGENKAMP (*Annalen*, 1914, **404**, 21—36).—5-Chloro-4-benzoyl-1-phenyl-3-methylpyrazole, which is best prepared by heating 4-benzoyl-1-phenyl-3-methyl-5-pyrazolone with an excess of phosphoryl chloride on the water-bath, reacts with potassium hydroselenide in alcohol in an atmosphere of hydrogen to form 4-benzoyl-1-phenyl-3-methyl-5-selenopyrazolone,  $\text{NPh}\langle\begin{smallmatrix}\text{N}=\text{CMe}\\\text{CSe}\cdot\text{CHBz}\end{smallmatrix}\rangle$ , which has been obtained in two modifications, red needles, m. p. 96°, and yellow needles, m. p. 116°. Both forms are easily soluble in aqueous sodium hydroxide, but by acidifying the solutions the red modification only is obtained from both. It forms a mercuric salt,  $\text{Hg}_2(\text{C}_{17}\text{H}_{13}\text{ON}_2\text{Se})_2$ , m. p. 195°, colourless crystals, mercurichloride,  $\text{C}_{17}\text{H}_{13}\text{ON}_2\text{SeHgCl}$ , m. p. 220°, colourless crystals, Se-benzoyl derivative,  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_2\text{Se}$ , m. p. 111°, colourless needles, and methyl, ethyl and benzyl ethers, m. p. 70°, 84°, and 146° respectively, all colourless crystals. A faintly alkaline solution of the 5-selenopyrazolone and aqueous chloroacetic acid yield after acidification 4-benzoyl-1-phenyl-3-methylpyrazole-5-selenolactic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{Se}\cdot\text{C}\langle\begin{smallmatrix}\text{NPh}\cdot\text{N}\\\text{CBz}-\text{CMe}\end{smallmatrix}\rangle$ , m. p. 157°, colourless needles.

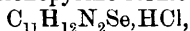
The 5-selenopyrazolone oxidises extremely easily, best by merely dissolving in alcohol, to form bis-4-benzoyl-1-phenyl-3-methyl-5-selenopyrazole,  $\text{Se}_2(\text{C}\langle\begin{smallmatrix}\text{NPh}\cdot\text{N}\\\text{CBz}-\text{CMe}\end{smallmatrix}\rangle)_2$ , m. p. 141°, golden-yellow needles, which is insoluble in aqueous alkalis. The latter is oxidised to 4-benzoyl-1-phenyl-3-methylpyrazole-5-selenonic acid,  $\text{N}\langle\begin{smallmatrix}\text{NPh}\cdot\text{C}\\\text{CMe}\cdot\text{CBz}\end{smallmatrix}\rangle\cdot\text{SeO}_3\text{H}$ , m. p. 152°, colourless needles, by 30% hydrogen peroxide and glacial acetic acid, and reacts with chlorine, bromine, and iodine in chloroform at 0° to form a tetrachloride, m. p. 125°, colourless needles, tetrabromide,

m. p. 201°, yellowish-red needles, and *tetra-iodide*, m. p. 78°, reddish-brown needles, respectively,  $\text{Se}_2\text{X}_4\left(\text{C}\begin{smallmatrix} \text{NPh}\cdot\text{N} \\ \text{||} \\ \text{CBz}-\text{CMe} \end{smallmatrix}\right)_2$ . By reduction with aqueous sulphurous acid, an alcoholic solution of the selenonic acid yields the *diselenoxide*,  $\text{Se}_2\text{O}_2\left(\text{C}\begin{smallmatrix} \text{NPh}\cdot\text{N} \\ \text{||} \\ \text{CBz}-\text{CMe} \end{smallmatrix}\right)_2$ , m. p. 126°, golden-yellow crystals, which is probably identical with the yellow substance, m. p. 126°, obtained by warming the preceding tetrabromide with dilute sodium hydroxide.

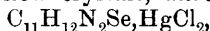


*Selenopyramidone* (4-dimethylaminoselenopyrine or 4-dimethylamino-1-phenyl-2:3-dimethyl-2:5-selenopyrazolone) (annexed formula), m. p. 196°, pale yellow needles, is easily prepared by the addition of an aqueous solution of pyramidone chloride to aqueous potassium hydroselenide. It forms a *hydrochloride*,  $\text{C}_{13}\text{H}_{17}\text{N}_3\text{Se}\cdot\text{HCl}$ , m. p. 177°, colourless crystals, *methiodide*, m. p. 208°, faintly yellow crystals, *ethiodide*, m. p. 170°, pale yellow needles, *dichloride*, m. p. 197°, yellow crystals, *dibromide*, m. p. 203°, reddish-yellow powder, and *di-iodide*,  $\text{C}_{13}\text{H}_{17}\text{N}_3\text{SeI}_2$ , reddish-brown powder; the *iodide*,  $\text{C}_{26}\text{H}_{34}\text{N}_6\text{Se}_2\text{I}_2$ , yellowish-red needles, has m. p. 190°. C. S.

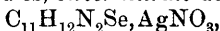
*ψ- and bis-Selenopyrine*. A. MICHAELIS and ERNST DUNTZE (*Annalen*, 1914, 404, 36—45).—By dry distillation under 11 mm. pressure, selenopyrine methiodide yields *ψ-selenopyrine* (5-methylselenol-1-phenyl-3-methylpyrazole),  $\text{SeMe}\cdot\text{C}\begin{smallmatrix} \text{NPh}\cdot\text{N} \\ \text{||} \\ \text{CH}-\text{CMe} \end{smallmatrix}$ , b. p. 181°/11 mm., pale yellow liquid, which is quantitatively decomposed into selenium, methyl chloride, and 1-phenyl-3-methylpyrazole by concentrated hydrochloric acid at 200°. *ψ-Selenopyrine* forms a *hydrochloride*,



m. p. 81°, crystals, *nitrate*, colourless crystals (both of these salts are decomposed by water), *platinichloride*,  $2\text{C}_{11}\text{H}_{12}\text{N}_2\text{Se}\cdot\text{H}_2\text{PtCl}_6$ , decomp. above 147°, brownish-yellow crystals, *mercurichloride*,



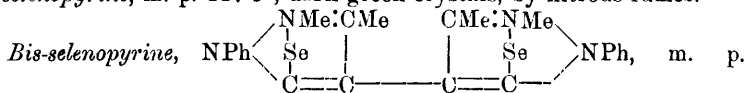
m. p. 125°, colourless needles, *silver nitrate derivative*,



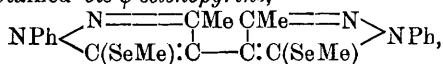
m. p. 175—176°, colourless needles, *dichloride*, m. p. 128°, yellow crystals, *dibromide*, m. p. 110°, red needles, and *methiodide*, m. p. 197°, the last compound being identical with that formed by the union of methyl iodide and selenopyrine at the ordinary temperature. The *ethiodide*, m. p. 185°, colourless leaflets, prepared from its components at 110°, loses chiefly methyl iodide by dry distillation and yields *ethyl-ψ-selenopyrine* (5-ethylselenol-1-phenyl-3-methylpyrazole), b. p. 182°/15 mm. By heating with aqueous sodium carbonate, the preceding dibromide yields 4-bromo-*ψ-selenopyrine*,  $\text{SeMe}\cdot\text{C}\begin{smallmatrix} \text{NPh}\cdot\text{N} \\ \text{||} \\ \text{CBr}-\text{CMe} \end{smallmatrix}$ , m. p. 147°, golden-yellow leaflets, in which the halogen atom is very firmly retained.

*ψ-Selenopyrine* in glacial acetic acid is converted into the *selenone*,

$\text{SeO}_2\text{Me}\cdot\text{C}\begin{array}{l} \nearrow \text{NPh}\cdot\text{N} \\ \searrow \text{CH}-\text{CMe} \end{array}$ , m. p.  $126^\circ$ , colourless needles, by an excess of 30% hydrogen peroxide, and in hydrochloric acid at  $0^\circ$  into 4-nitroso- $\psi$ -selenopyrine, m. p.  $117.5^\circ$ , dark green crystals, by nitrous fumes.



$270-271^\circ$ , pale yellow needles, is obtained by treating a hot aqueous solution of bis-5-chloro-1-phenyl-3-methylpyrazole methiodide with potassium hydroselenide. It forms a *methiodide*,  $\text{C}_{24}\text{H}_{28}\text{N}_4\text{Se}_2\text{I}_2$ , m. p.  $249^\circ$ , yellow needles, by the distillation of which under reduced pressure is obtained *bis- $\psi$ -selenopyrine*,



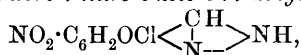
m. p.  $115^\circ$ , colourless needles.

C. S.

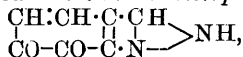
**Indazoles.** K. FRIES and E. ROTH (*Annalen*, 1914, **404**, 81—92. Compare this vol., i, 569).—The following reactions of 6-hydroxyindazole are to be compared with the corresponding reactions of  $\beta$ -naphthol and of phenol.

6-Hydroxyindazole in glacial acetic acid yields 7-bromo-6-hydroxyindazole, m. p.  $182^\circ$ , needles, by bromination at  $0^\circ$ , and 7-chloro-6-hydroxyindazole, m. p.  $184^\circ$ , needles, by chlorination. The latter, by further chlorination, yields a mixture of 5:7-dichloro-6-hydroxyindazole, m. p.  $203^\circ$ , needles, and a keto-chloride, by the reduction of which 7-chloro-6-hydroxyindazole is regenerated.

7-Bromo-6-hydroxyindazole in cold glacial acetic acid is converted by nitric acid (D 1.52) into 7-bromo-5-nitro-6-hydroxyindazole, m. p.  $239^\circ$  (decomp.), yellow needles, whilst under the same conditions 7-chloro-6-hydroxyindazole yields, after the mixture has been warmed on the water-bath, 7-chloro-7-nitro-6-keto-6:7-dihydroindazole,



decomp.  $80-98^\circ$ , unstable, yellow crystals, and a little 7-chloro-5-nitro-6-hydroxyindazole, m. p.  $281^\circ$  (decomp.), yellow crystals. By boiling in an indifferent solvent, such as benzene, 7-chloro-7-nitro-6-keto-6:7-dihydroindazole is converted into 6:7-indazolequinone,



decomp.  $160-300^\circ$ , red prisms, which by reduction with sulphurous acid yields 6:7-dihydroxyindazole, colourless crystals blackening by heating.

C. S.

**Hydrazidines.** M. BUSCH and CHR. SCHNEIDER (*J. pr. Chem.*, 1914, [ii], **89**, 310—323).—Busch and Ruppenthal (A., 1911, i, 86) have shown that the interaction of benzanilide imide chloride and phenylhydrazine gives rise to two isomeric  $\alpha$ - and  $\beta$ -diphenylbenzenylhydrazidines,  $\text{NH}_2\cdot\text{NPh}\cdot\text{CPh}\cdot\text{NPh}$  and  $\text{NHPh}\cdot\text{NH}\cdot\text{CPh}\cdot\text{NPh}$ . The reaction has now been extended to other arylhydrazines, and it is found that the relative proportions of the two isomerides depend on the nature

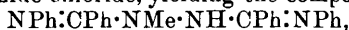
of the hydrazine employed. Thus, *p*-tolylhydrazine resembles phenylhydrazine in yielding both the  $\alpha$ - and  $\beta$ -isomerides, the latter being formed in greater amount, whilst *o*-tolylhydrazine gives rise almost exclusively to the  $\beta$ -form.

The interaction of benzanilide imide chloride with hydrazine, semicarbazide, thiosemicarbazide, and diphenylthiosemicarbazide has also been investigated, but, except in the case of thiosemicarbazide, the resulting hydrazidines could not be isolated owing to the ease with which they undergo internal condensation.

*$\beta$ -Phenyl-*p*-tolylbenzenylhydrazidine*,  $C_7H_7 \cdot NH \cdot NH \cdot CPh \cdot NPh$ , obtained from benzanilide imide chloride and *p*-tolylhydrazine in ethereal solution, crystallises in yellow needles, m. p. 127—128°, and is oxidised by mercuric oxide in alcoholic solution to the corresponding *azo*-compound; the accompanying  *$\alpha$ -isomeride*,  $C_7H_7 \cdot N(NH_2) \cdot CPh \cdot NPh$ , forms long, colourless needles, m. p. 109—110°, and is much more basic in character than the  $\beta$ -compound.

*$\beta$ -Phenyl-*o*-tolylbenzenylhydrazidine*, prepared from *o*-tolylhydrazine, crystallises in yellow prisms, m. p. 134—136°.

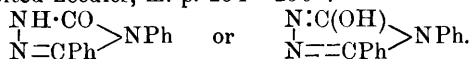
The interaction of benzanilide imide chloride and methylhydrazine in alcoholic solution yields diphenylbenzenylamidine and the *benzoyl* derivative of *phenylbenzenylmethylhydrazidine*,  $NHBz \cdot NMe \cdot CPh \cdot NPh$  or  $NMeBz \cdot NH \cdot CPh \cdot NPh$ , which crystallises in lustrous, transparent needles, m. p. 185—186°. The authors explain the formation of these compounds by assuming that the methylhydrazine reacts with two molecules of the imide chloride, yielding the compound



which is subsequently hydrolysed to the above benzoyl derivative, the aniline simultaneously produced in the hydrolysis then reacting with the unchanged imide chloride to form diphenylbenzenylamidine.

Benzanilide imide chloride and hydrazine hydrate in ice-cold, alcoholic solution give rise to 3:6-diphenyl-1:2:4:5-tetrazine and 3:4:5-triphenyl-1:2:4-triazole, which crystallises in colourless prisms, m. p. 291°, forms a reddish-yellow *platinichloride*, and is identical with the compound, m. p. 304—305°, obtained by Pellizzari and Alciatore (A., 1901, i, 571) by condensing aniline with dibenzoylhydrazide.

*Carbamylphenylbenzenylhydrazidine*,  $NPh \cdot CPh \cdot NH \cdot NH \cdot CO \cdot NH_2$ , prepared from the imide chloride and semicarbazide in alcoholic solution, crystallises in colourless prisms, m. p. 189° (decomp.), yields a *hydrochloride*, crystallising in colourless prisms, and is oxidised by mercuric oxide in alcoholic solution to the corresponding *azo*-compound, which separates in orange-yellow, leafy crystals. When heated at 200°, it is converted by loss of ammonia into 3:4-diphenyldihydrotriazolone, colourless, felted needles, m. p. 254—256°:



Benzanilide imide chloride reacts with thiosemicarbazide to form 3:4:5-triphenyl-1:2:4-triazole. With diphenylthiosemicarbazide,



it yields 5-thion 1:3:4-triphenyl-1:2:4-triazolone,  $\begin{array}{c} N = CPh \\ || \\ NPh \cdot CS \end{array} > NPh,$

together with the *hydrochloride* of a red base,  $C_{20}H_{16}N_3Cl$ , crystallising in lustrous, citron-yellow needles, m. p. above  $290^\circ$ . The red base is very unstable, and rapidly passes into 1:4:5-triphenyl-3:5-endothiodihydro-1:2:4-triazole.

5-Thion-1:3:4-triphenyl-1:2:4-triazolone crystallises in slender, colourless needles, m. p.  $190^\circ$ , and is identical with the compound obtained by Busch and Holzmann (A., 1901, i, 234) by the oxidation of  $\alpha$ -diphenylbenzylidenethiosemicarbazone, and considered by them to have the formula 
$$\begin{array}{c} N \cdot NPh \\ || \\ CPh-S \end{array} > C:NPh.$$

Its constitution has been established by its conversion into 1:3:4-triphenyltriazolone by the action of mercuric oxide at  $140^\circ$ . F. B.

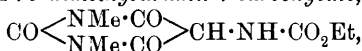
**1:3-Dimethyluric Acid 4:5-Diglycol.** HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1914, **404**, 131—137. Compare Biltz and Topp, A., 1911, i, 692).—A suspension of theophylline (not more than 2 grams in one operation) in water is treated vigorously with chlorine until solution is complete. (Without this precaution, dimethylalloxan is obtained.) After removing the excess of chlorine by a current of air and concentrating the solution under diminished pressure, 1:3-dimethyluric acid 4:5-diglycol, 
$$\begin{array}{c} NMe \cdot CO \cdot C(OH) \cdot NH \\ CO \cdot NMe \cdot C(OH) \cdot NH \end{array} > CO, \text{ m. p. } 183^\circ$$

(decomp.), rhombic or monoclinic plates, is obtained in 40% yield. The same substance can be synthesised in about 90% yield from dimethylalloxan dihydrate and carbamide in boiling water or hot glacial acetic acid. In accordance with previous observations on methylated uric acid glycols (Biltz, A., 1910, i, 524), 1:3-dimethyluric acid 4:5-diglycol, being methylated in the pyrimidine but not in the glyoxaline nucleus, does not undergo the caffolide degradation, prolonged heating with water or acetic acid resulting in the rupture of the 5-ring and the elimination of carbamide; however, caffolide degradation can be effected after the imino-groups have been methylated (Biltz and Heyn, A., 1912, i, 589). The hydroxyl groups in 1:3-dimethyluric acid 4:5-diglycol cannot be etherified by means of alcoholic hydrogen chloride.

8-Bromotheophylline is produced when theophylline is brominated in anhydrous alcohol or glacial acetic acid; 8-chlorotheophylline cannot be prepared in a similar manner. C. S.

**Degradation of Theophylline.** HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1914, **404**, 137—170).—The increase in the stability of the pyrimidine nucleus, caused by the presence of methylimino-groups therein and already illustrated by the behaviour of 1:3-dimethyluric acid 4:5-diglycol (preceding abstract), is further shown by the behaviour of theophylline itself towards chlorine under suitable conditions. By passing a rapid stream of chlorine into a mixture of theophylline, chloroform, and ethyl alcohol at the ordinary temperature, a substance,  $C_{11}H_{17}O_6N_3$ , m. p.  $110^\circ$ , elongated, hexagonal plates, is obtained. The same substance is obtained, although not so satisfactorily, in the absence of chloroform. A corresponding substance,

$C_9H_{13}O_6N_3$ , m. p.  $167^\circ$ , stout plates, is obtained when methyl alcohol is used in place of ethyl alcohol. These substances are proved to be *ethyl* (or *methyl*) 5-ethoxy(or methoxy)-1:3-dimethyluramil-7-carboxylate,  $CO \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix} > C(OR) \cdot NH \cdot CO_2R$  (where R is Et or Me), by the following evidence. Ethyl 5-ethoxy-1:3-dimethyluramil-7-carboxylate is remarkably stable to nitric acid, alcoholic hydrogen chloride, and acetic anhydride, is converted into dimethylparabanic acid and amalic acid by boiling 2*N*-hydrochloric acid, and yields dimethylparabanic acid by oxidation with chromic acid. By energetic reduction with hydriodic acid (D 1.96) and phosphonium iodide on the water-bath, it yields 1:3-dimethyluramil, but by milder treatment with hydriodic acid (D 1.5) at  $80^\circ$ , a substance,  $C_9H_{13}O_5N_3$ , m. p.  $134^\circ$ , is obtained, which is shown to be *ethyl* 1:3-dimethyluramil-7-carboxylate,



by its synthesis from 1:3-dimethyluramil and ethyl chlorocarbonate in aqueous sodium hydroxide.

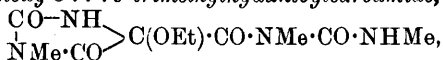
Ethyl 1:3-dimethyluramil-7-carboxylate has pronounced acid properties. It liberates carbon dioxide from carbonates and forms an *ammonium* salt,  $C_9H_{16}O_5N_4$ , decomp.  $290^\circ$ , hexagonal leaflets, which is not hydrolysed by water; the *methylammonium* salt, m. p.  $210^\circ$ , needles, and *potassium* and *silver* salts are described. It yields 1:3-dimethyluramil by energetic reduction with hydriodic acid, and is converted into ethyl 5-ethoxy-1:3-dimethyluramil-7-carboxylate or *ethyl* 5-methoxy-1:3-dimethyluramil-7-carboxylate, m. p.  $138^\circ$ , by treatment with chlorine and chloroform and ethyl or methyl alcohol respectively. By treatment with boiling acetic anhydride, ethyl 1:3-dimethyluramil-7-carboxylate yields *ethyl* 7-acetyl-1:3-dimethyluramil-7-carboxylate,  $CO \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix} > CH \cdot NAc \cdot CO_2Et$ , m. p.  $76^\circ$ , quadratic prisms, in which the position of the acetyl group is deduced by the fact that the substance still has acid properties and forms an *ammonium* salt, m. p.  $212^\circ$ . *Methyl* 1:3-dimethyluramil-7-carboxylate, m. p.  $178^\circ$ , rhombic leaflets, can be prepared by the same methods as the ethyl ester and forms an *ammonium* salt, m. p.  $211^\circ$  (decomp.), leaflets, *methylammonium* salt, m. p.  $206^\circ$ , prisms, and *silver* salt, needles. It yields methyl 5-methoxy-1:3-dimethyluramil-7-carboxylate by treatment with chlorine and methyl alcohol, *methyl* 5-ethoxy-1:3-dimethyluramil-7-carboxylate, m. p.  $150^\circ$ , needles, by treatment with chlorine and ethyl alcohol, and is converted by boiling acetic anhydride into *methyl* 7-acetyl-1:3-dimethyluramil-7-carboxylate, m. p.  $134^\circ$ , leaflets (*ammonium* salt, m. p.  $217^\circ$  [decomp.]; *methylammonium* salt, m. p.  $205^\circ$ ). *Methyl* 7-acetyl-1:3-dimethyluramil-7-carboxylate is converted into methyl 5-methoxy-1:3-dimethyluramil-7-carboxylate by treatment with chlorine and methyl alcohol.

Unsuccessful attempts have been made to convert esters of 1:3-dimethyluramil-7-carboxylic acid into 1:3-dimethyl- $\psi$ -uric acid, and vice versa.

Methylamine or ethylamine, reacting with the esters of 5-alkyloxy-1:3-dimethyluramil-7-carboxylic acid in alcoholic solution on the



water-bath, displaces both alkyloxy-groups; at the ordinary temperature, however, only the alkyloxy-group of the carbalkyloxy-group is displaced, a reaction which is also effected by ammonia at the low or the high temperature. The substances thus obtained were at first thought to be derivatives of  $\psi$ -uric acid, but could not be converted into this or obtained from it. They have now been proved to be derivatives of 3-methylhydantoin by conversion into this by energetic reduction. The action of ammonia or of an alkylamine on methyl or ethyl 5-alkyloxy-1:3-dimethyluramil-7-carboxylate, therefore, causes a rupture of the pyrimidine ring; the initially-formed, additive compound loses methyl or ethyl alcohol with the consequent formation of the hydantoin nucleus. The following substances have thus been obtained: 5-ethoxy-3:7:9-trimethylhydantoylcarbamide,



m. p. 150°, hexagonal plates; 5-ethoxy-3:7-dimethyl-9-ethylhydantoylcarbamide, m. p. 137°, leaflets; 5-ethoxy-3:7-dimethylhydantoylcarbamide, m. p. 218°, leaflets; 5-methoxy-3:7-dimethylhydantoylcarbamide, m. p. 198°, rhombic leaflets; 5-methylamino-3:7:9-trimethylhydantoylcarbamide, m. p. 186°, rhombohedra (hydriodide,  $\text{C}_9\text{H}_{15}\text{O}_4\text{N}_5 \cdot \text{HI}$ , m. p. 135° [decomp.], hydrochloride, m. p. 217°), and 5-ethylamino-3:7-dimethyl-9-ethylhydantoylcarbamide, m. p. 169°, elongated leaflets.

By treatment with boiling aqueous barium hydroxide, the preceding alkylated 5-alkyloxyhydantoylcarbamides yield methylamine or ammonia and a white substance which decomposes by acidification into carbon dioxide and mesoxalic acid (identified as the phenylhydrazone); methylated carbamides could not be detected.

5-Ethoxy-3:7:9-trimethylhydantoylcarbamide is converted into isocaffuric acid (A., 1913, i, 1376) by boiling concentrated hydrochloric acid, into 3-methylhydantoin-5-carboxymethylamide (*loc. cit.*) by hydriodic acid (D 1.5) and phosphonium iodide at 60–70°, and into 3-methylhydantoin by hydriodic acid (D 1.96), and phosphonium iodide at 130°. It is oxidised to methylparabanic acid by chromic acid.

1:3-Dimethyluramil yields dimethylalloxan dihydrate by treatment with chlorine in the presence of methyl alcohol, and 5:5-dichloro-1:3-dimethylbarbituric acid by treatment with chlorine and water.

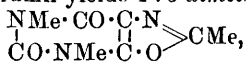
The action of chlorine on an aqueous solution of methyl 1:3-dimethyluramil-7-carboxylate yields a substance,  $\text{C}_{16}\text{H}_{20}\text{O}_{10}\text{N}_6$ , m. p. 230°, quadratic prisms, which is also produced from methyl iodide and the silver salt of methyl 1:3-dimethyluramil-7-carboxylate at 100°, and is regarded as methyl bis-1:3-dimethyluramil-7-carboxylate; the corresponding ethyl ester,  $\text{C}_{18}\text{H}_{24}\text{O}_{10}\text{N}_6$ , m. p. 175°, crystallises in stout, hexagonal plates. The methyl ester is unchanged by chlorine and methyl alcohol, yields 1:3-dimethyluramil by reduction with hydriodic acid, and is converted into the ammonium salt and the methylammonium salt of methyl 1:3-dimethyluramil-7-carboxylate by alcoholic ammonia and alcoholic methylamine respectively. C. S.

**7-Acyltheophyllines and their Degradation.** HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1914, 404, 170–180).—7-Acetyl- or benzoyl-theophylline, like theophylline itself (preceding abstract), but

unlike caffeine, shows a special tendency to undergo rupture in the glyoxalite nucleus. 7-Acetyltheophylline, m. p. 158°, long needles, prepared from theophylline and boiling acetic anhydride, is converted by chlorine and ethyl alcohol into 7-acetyl-5-ethoxy-1:3-dimethyluramil,

$\text{CO} \begin{array}{c} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CO} \end{array} \text{C}(\text{OEt}) \cdot \text{NHAc}$ , m. p. 215°, prisms. This substance, which is stable to concentrated nitric acid and is reduced to 1:3-dimethyluramil by hydriodic acid (D 1.5) can also be prepared by the action of chlorine and ethyl alcohol on 7-acetyl-1:3-dimethyluramil, m. p. 208° (decomp.), elongated leaflets. 7-Acetyl-5-methoxy-1:3-dimethyluramil, m. p. 251°, is obtained by the action of chlorine and methyl alcohol on 7-acetyltheophylline or 7-acetyl-1:3-dimethyluramil.

7-Benzoyltheophylline, m. p. 202°, 7-benzoyl-5-ethoxy-1:3-dimethyluramil, m. p. 167°, and 7-benzoyl-5-methoxy-1:3-dimethyluramil, m. p. 162°, are also described. By boiling with acetic anhydride and a little pyridine, 1:3-dimethyluramil yields 1:3-dimethyl-thenyluramil,

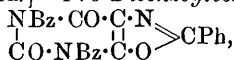


m. p. 149°, long needles, which is easily converted into 7-acetyl-1:3-dimethyluramil by hot dilute hydrochloric acid. Benzenyl-1:3-dimethyluramil, m. p. 237°, prepared from 1:3-dimethyluramil and boiling benzoyl chloride, is not attacked even by boiling concentrated hydrochloric acid, but is converted into 7-benzoyl-5-methoxy- or -ethoxy-1:3-dimethyluramil by chlorine and methyl or ethyl alcohol.

Benzenyl-1:3-dimethyluramil can also be prepared by boiling 1:3-dimethyl-ψ-uric acid with benzoyl chloride; on the contrary, 1:3-dimethyl-ψ-uric acid and boiling acetic anhydride yield, not 1:3-dimethylethenyluramil, but diacetyl-1:3-dimethyl-ψ-uric acid, m. p. 201°. C. S.

**Benzenyluramil and Benzenyl-1-methyluramil.** HEINRICH BILTZ (*Annalen*, 1914, **404**, 180—185).—Uramil and 1-methyluramil behave like 1:3-dimethyluramil towards boiling benzoyl chloride (preceding abstract).

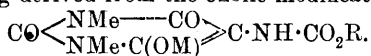
[With JOSEF KARTER.]—1:3-Dibenzoylbenzenyluramil,



m. p. 186°, colourless prisms, is converted in acetone by 2*N*-sodium hydroxide on the water-bath into benzenyluramil, m. p. 314° (decomp.), prisms, which yields 7-benzoyl-5-ethoxyuramil, m. p. 225° (decomp.), rhombic plates, and 7-benzoyl-5-methoxyuramil, m. p. 244° (decomp.), by treatment with chlorine and ethyl and methyl alcohol respectively. The methoxy-compound is reduced to uramil by hydriodic acid (D 1.96) and phosphonium iodide on the water-bath.

[With KARL STRUBE.]—Benzenyl-1-(or 3-)-methyluramil, m. p. 324° (decomp.), hexagonal plates, is obtained by boiling 1-methyluramil or 1-methyl-ψ-uric acid with benzoyl chloride; by prolonged action, the benzoyl derivative, C<sub>19</sub>H<sub>13</sub>O<sub>4</sub>N<sub>3</sub>, m. p. 246°, colourless needles, is obtained. By the action of chlorine and methyl or ethyl alcohol on benzenylmethyluramil, 7-benzoyl-5-methoxy-1-methyluramil, m. p. 190°, or 7-benzoyl-5-ethoxy-1-methyluramil, m. p. 200°, is obtained. C. S.

**Salt Formation with Barbituric Acid and its Derivatives.** HEINRICH BILTZ (*Annalen*, 1914, **404**, 186—199).—Derivatives of 1:3-dimethyluramil containing a carbethoxy-group in position 7 possess strongly acidic properties (Biltz and Strufe, preceding abstracts), the metallic salts being derived from the enolic modification :



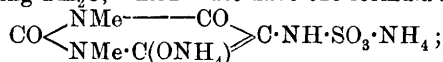
For this reason the author has examined the formation of salts of barbituric acid and its derivatives, particularly those containing alkyl groups in positions 1 and 3. The non-formation of metallic derivatives or the formation of mono-, di-, and tri-metallic derivatives of barbituric, 1:3-dimethylbarbituric, 5-bromobarbituric, 5:5-dibromobarbituric, 5-nitrobarbituric, hydurilic, dialuric, and dimethyldialuric acids has been described by many investigators, and in all cases the facts are satisfactorily explicable by enolic formulæ. Particularly important is the case of tetramethylhydurilic acid, which is dibasic according to the calorimetric measurements of Matignon; this has been confirmed by the preparation of a *dipotassium* and a *diammonium* salt, m. p. 272° (decomp.),  $\text{CO} \begin{array}{c} \text{NMe} \text{---} \text{CO} \\ \text{NMe} \cdot \text{C(OM)} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{CO} \text{---} \text{NMe} \\ \text{C(OM)} \cdot \text{NMe} \end{array} \text{CO}$ . At variance with theory, however, is Baeyer's dichlorohydurilic acid. This acid, which on account of its great stability doubtless contains its chlorine atoms in positions 5 and 5', has been described as a strong, dibasic acid; such a property is not in harmony with the formula, and the acid is being re-investigated.

The acidic character of the methylene hydrogen atoms in barbituric acid is greatly diminished when one of the hydrogen atoms is replaced by an amino-group; the uramils, therefore, are only feeble acids. From the fact that uramil, even with 50% potassium hydroxide, forms only a dipotassium salt (which reacts with methyl iodide to yield 1:3-dimethyluramil [Piloty and Finckh, A., 1904, i, 824]), it has been assumed that the hydrogen atom in position 5 is no longer replaceable by metals. This is incorrect. The imino-hydrogen atoms are far more strongly acidic than that in position 5, but the latter exhibits its feeble acid character when the imino-hydrogen atoms are replaced by alkyl groups; thus, with 50% potassium hydroxide, 1:3-dimethyluramil forms a *potassium* salt,  $\text{C}_6\text{H}_8\text{O}_3\text{N}_3\text{K}$ , hexagonal plates, and 1-methyluramil forms a *dipotassium* salt,  $\text{C}_5\text{H}_5\text{O}_3\text{N}_3\text{K}_2$ , prisms.

The formation of benzenyl derivatives from uramils (preceding abstracts) is readily explicable by means of the enolic formulæ of the latter. The enolic formula of 4-thiouramils is definitely proved by the fact that these strong, monobasic acids form alkali salts which can be converted into thio-ethers.

The diminution in the acid character of the barbituric acids caused by the introduction of an amino-group in position 5 is more than compensated when a hydrogen atom of the amino-group is replaced by an acyl, carboxyl, or sulpho-group. 7-Acetyluramil (Piloty and Finckh, *loc. cit.*) and the esters of 1:3-dimethyluramil-7-carboxylate (Biltz and Strufe, preceding abstract) are strong monobasic acids which decompose carbonates. Analogous to these are the dibasic thionuric acids, the formulæ of the salts of which are determined by

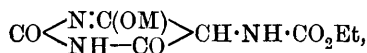
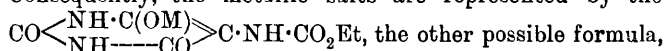
the fact that 1:3-dimethylthionuric acid yields a *diammonium* salt, needles containing  $2\text{H}_2\text{O}$ , which must have the formula:



1-methylthionuric acid also forms a *diammonium* salt,  $\text{C}_5\text{H}_{13}\text{O}_6\text{N}_5\text{S}$ , long prisms.  
C. S.

**Esters of Uramilcarboxylic Acid and of 1-Methyluramil-carboxylic Acid.** HEINRICH BILTZ [with JOSEF KARTTE and KARL STRUFE] (*Annalen*, 1914, 404, 199—218).—For comparison with the esters of 1:3-dimethyluramil-7-carboxylic acid and of its 5-alkyloxy-derivatives (Biltz and Strufe, preceding abstracts), the corresponding derivatives of uramil and of 1-methyluramil have been prepared.

Uramil and ethyl chlorocarbonate readily condense in 2*N*-sodium hydroxide to form, after acidification, *ethyl uramil-7-carboxylate*,  $\text{C}_7\text{H}_9\text{O}_5\text{N}_3$ , m. p.  $228^\circ$ , long prisms. This ester has pronounced acid properties and yields a *potassium*, *ammonium*, *methylammonium*, and *silver* salt. The last salt reacts with methyl iodide at  $100^\circ$  to form an *O-ether*,  $\text{C}_8\text{H}_{11}\text{O}_5\text{N}_3$ , m. p.  $224^\circ$ , leaflets, which is readily hydrolysed by aqueous ammonia and yields uramil by reduction with hydriodic acid. Consequently, the metallic salts are represented by the formula:



being rejected on the ground that the hydrogen atom in position 5 is more reactive than the imino-hydrogen atom. Ethyl uramil-7-carboxylate is reduced to uramil hydriodide by hydriodic acid (D 1.96) and phosphonium iodide on the water-bath.

*Methyl uramil-7-carboxylate*, m. p.  $237\text{—}238^\circ$  (decomp.), is prepared in a similar manner as the ethyl ester. These esters cannot be converted into the corresponding amide,  $\psi$ -uric acid. They react with chlorine and methyl or ethyl alcohol to form 5-alkyloxy-derivatives. *Ethyl 5-ethoxyuramil-7-carboxylate*, m. p.  $198\text{—}199^\circ$  (decomp.), *ethyl 5-methoxyuramil-7-carboxylate*, m. p.  $210^\circ$  (decomp.), *methyl 5-ethoxyuramil-7-carboxylate*, m. p.  $215^\circ$  (slight decomp.), and *methyl 5-methoxyuramil-7-carboxylate*, m. p.  $212^\circ$ , are described. These alkyloxy-derivatives react with ammonia or an amine in alcoholic solution to form ammonium or alkylammonium salts, which are readily decomposed into their generators by acids; the *ammonium* salt,  $\text{C}_9\text{H}_{16}\text{O}_6\text{N}_4$ , m. p.  $152\text{—}155^\circ$ , and the *methylammonium* salt,  $\text{C}_{10}\text{H}_{18}\text{O}_6\text{N}_4$ , m. p.  $155^\circ$  (decomp.), of ethyl 5-ethoxyuramil-7-carboxylate, and the *ethyl-ammonium* salt,  $\text{C}_{10}\text{H}_{18}\text{O}_6\text{N}_4$ , m. p.  $168\text{—}170^\circ$  (decomp.), of ethyl 5-methoxyuramil-7-carboxylate are described.

*Ethyl 1-methyluramil-7-carboxylate*, m. p.  $205^\circ$ , rhombic leaflets, prepared from 1-methyluramil and ethyl chlorocarbonate in aqueous sodium hydroxide, behaves like the uramilcarboxylate. The *ammonium* salt, m. p.  $256^\circ$  (decomp.), long prisms, *methylammonium* salt, m. p.  $240^\circ$  (decomp.), leaflets, and *silver* salt, white powder, have been prepared. The last salt and methyl iodide at  $100^\circ$  yield a *methyl ether*,  $\text{C}_9\text{H}_{13}\text{O}_5\text{N}_3$ , m. p.  $206^\circ$  (decomp.), stout prisms, which is not hydrolysed

by aqueous ammonia, but is converted into 1-methyluramil by reduction with hydriodic acid; consequently, the new methyl group is not attached to a nitrogen atom.

*Methyl 1-methyluramil-7-carboxylate*, m. p. 232° (slight decomp.), elongated leaflets, forms an *ammonium* salt, m. p. 255° (decomp.). *Ethyl 5-ethoxy-1-methyluramil-7-carboxylate*, m. p. 146°, long prisms, *ethyl 5-methoxy-1-methyluramil-7-carboxylate*, m. p. 130°, stout prisms, *methyl 5-ethoxy-1-methyluramil-7-carboxylate*, m. p. 185°, rhombic plates, and *methyl 5-methoxy-1-methyluramil-7-carboxylate*, m. p. 212°, react with concentrated aqueous ammonia or with 33% alcoholic methylamine to form additive compounds which do not lose ammonia or methylamine by treatment with acids and yield methylamine, not ammonia, by treatment with sodium hydroxide. The assumption is made that the ring is ruptured, the additive compounds being substances of the type  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{OR})(\text{NH}\cdot\text{CO}_2\text{R})\cdot\text{CO}\cdot\text{NHMe}$ ; they are, therefore, stable analogues of the unstable, intermediate products formed during the conversion of methyl or ethyl 5-alkyloxy-1:3-dimethyluramil-7-carboxylates into derivatives of hydantoylcarbamide (Biltz and Strufe, preceding abstract). The following substances of this type have been prepared: *ethyl  $\alpha$ -methylamino- $\gamma$ -carb-amido- $\beta$ -ethoxymalonylcarbamate*,

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{OEt})(\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NHMe}$ , m. p. 198° (decomp.), *ethyl  $\alpha$ -methylamino- $\gamma$ -methylcarb-amido- $\beta$ -ethoxymalonylcarbamate*,

$\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{OEt})(\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NHMe}$ , m. p. 190° (decomp.), *ethyl  $\alpha$ -methylamino- $\gamma$ -carb-amido- $\beta$ -methoxymalonylcarbamate*,  $\text{C}_9\text{H}_{16}\text{O}_6\text{N}_4$ , m. p. 177°, *ethyl  $\alpha$ -methylamino- $\gamma$ -methylcarb-amido- $\beta$ -methoxymalonylcarbamate*, m. p. 208° (decomp.), and *methyl  $\alpha$ -methylamino- $\gamma$ -methylcarb-amido- $\beta$ -ethoxymalonylcarbamate*, m. p. 214°.

1:7-Dimethyluramil does not react with ethyl chlorocarbonate in the presence of aqueous sodium hydroxide. C. S.

**Some Derivatives of Hydrazidicarboxylhydrazide and Carbohydrazide.** R. STOLLÉ and K. KRAUCH (*Ber.*, 1914, **47**, 724—729).—The anisaldehyde condensation product of hydrazidicarboxylhydrazide described earlier (A., 1910, i, 790) was really the *cinnamylidene* compound,  $\text{C}_{20}\text{H}_{20}\text{O}_2\text{N}_6$ , m. p. 218°, for the aldehyde used was wrongly labelled. The true *p-anisylidene* compound,  $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_6$ , has m. p. 222°. *Cinnamylidenecarbohydrazide*,  $\text{C}_{19}\text{H}_{18}\text{ON}_4$ , has m. p. 205°, and its alcoholic solution develops a fugitive yellow coloration with bleaching powder solution. *Cinnamylideneaminourazole*,  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_4$ , forms small leaflets, m. p. 234°.

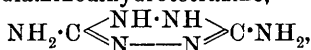
*Dibenzoylhydrazidicarboxylhydrazide*,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{NH}\cdot\text{NHBz})_2$ , may be prepared, either by shaking the hydrochloride of hydrazidicarboxylhydrazide with benzoyl chloride and sodium carbonate, or by warming hydrazidicarboxylazoimide and benzhydrazide with dry toluene and pyridine in a sealed tube. It crystallises from water in rectangular tablets with  $2\text{H}_2\text{O}$ , m. p. 197°, and from alcohol in anhydrous, elongated leaflets. It is soluble in alkaline and ammoniacal solutions, and gives a *disilver* salt. The addition of sodium hypochlorite to the alkaline solution precipitates the sodium salt of the oxidation product,

*dibenzoylazodicarboxylhydrazide*,  $C_{16}H_{14}O_4N_6$ , which forms yellowish-red needles, m. p.  $172^\circ$ . *Dibenzoylcarbohydrazide*,  $C_{15}H_{14}ON_4$ , also forms shining, rectangular leaflets with  $2H_2O$  from water, m. p.  $205^\circ$ , and anhydrous leaflets from alcohol, but the corresponding azo-compound must be very unstable, for only a fugitive red coloration is produced by sodium hypochlorite.

Hydrazidicarboxylazoimide (*ibid.*) is best prepared by adding a solution of the hydrochloride of hydrazidicarboxylhydrazide in several portions to a solution of sodium nitrite which is just frozen after each addition. Attempts were made to deprive it of azoimide in order to arrive at the compound  $CO:N:N:CO$ , but no definite results were obtained, and the experiments have been abandoned owing to a serious explosion. J. C. W.

*s*-Diaminotetrazine [3:6-Diamino-1:2:4:5-tetrazine]. II. and III. G. PONZIO and C. GASTALDI (*Gazzetta*, 1914, **44**, i, 257—268, 277—282.)—II. Study of the reduction of 3:6-diamino-1:2:4:5-tetrazine confirms the structure of this compound (compare A, 1913, i, 1109) and, in consequence of rupture of the tetrazine nucleus, leads to a new method for the preparation of formazyl compounds. Further, the formation of such a tetrazine derivative is also observed with *s*-diaminoguanidine,  $NH:C(NH:NH_2)_2$ , and seems to be general in character.

Reduction of 3:6-diamino-1:2:4:5-tetrazine by means of hydrogen sulphide yields the diaminodihydrotetrazine,



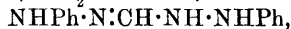
but subsequent oxidation of the resultant products gives but little of the original compound, since the diaminodihydrotetrazine undergoes further reduction, with liberation of part of the nitrogen as ammonia. This reduction is, however, quite different in character from that observed by Pinner (A., 1897, i, 637) with *s*-diphenyldihydrotetrazine,

$CPh \begin{array}{c} \nwarrow NH \cdot NH \\ \nearrow N \text{---} N \end{array} CPh$ , which gives ammonia and diphenyltriazole,

$CPh \begin{array}{c} \nwarrow NH \\ \nearrow N \cdot N \end{array} CPh$ . The addition of 2 mols. of hydrogen to the tetrazine compound results in its resolution into aminoguanidine and the unstable formamidine, which is decomposed by the water present into formic acid and ammonia. The formation of aminoguanidine in this way was confirmed by its conversion into *o*-nitrobenzylidene-aminoguanidine and into benzylideneaminoguanidine, m. p.  $182^\circ$ , and its nitrate, m. p.  $178^\circ$  (decomp.); preparation of these compounds by Thiele's method (A., 1892, 1295) demonstrates the inaccuracy of the melting points,  $178^\circ$  and  $158^\circ$  respectively given by this author.

The action of phenylhydrazine on 3:6-diamino-1:2:4:5-tetrazine yields formazyl hydride,  $NHPh:N:CH:N:NPh$ , which, contrary to the statements of previous authors (compare Bamberger and Wheelwright, A., 1893, i, 84, 156), crystallises with  $1H_2O$ . The formation of formazyl hydride in this reaction seems to be preceded by fission of the tetrazine into aminoguanidine and formamidine, the latter then undergoing hydrolysis into ammonia and

formic acid, which then passes through the following transformations:  
 $\text{H}\cdot\text{CO}_2\text{H} + \text{NH}_2\cdot\text{NHPh} \rightarrow \text{COH}\cdot\text{NH}\cdot\text{NHPh} + \text{NH}_2\cdot\text{NHPh} \rightarrow$



this, like all hydrazonehydrazides, being readily oxidised by phenylhydrazine to formazyl hydride.

Similarly, the action of *p*-bromophenylhydrazine on 3:6-diamino-1:2:4:5-tetrazine gives formyl-*p*-bromophenylhydrazine (compare Ruhemann, T., 1890, 57, 56) and di-*p*-bromophenylformazyl hydride (compare Busch and Wolbring, A., 1905, i, 493).

III. If the hydrolysis of 3:6-diamino-1:2:4:5-tetrazine were to proceed similarly to that of 3:6-diphenyl-1:2:4:5-tetrazine (compare Pinner, A., 1897, i, 637), it should result in the initial formation of nitrogen and aminoformaldehydesemicarbazone, whereas in reality it yields aminoguanidine. Hydrolyses made with dilute sulphuric and hydrochloric acids show that the first products detectable include ammonia, nitrogen, and carbon dioxide, but no trace of hydrazine, the hydrogen of which reduces a portion of the original compound to the

corresponding diaminodihydropyrimidine:  $\text{NH}_2\cdot\text{C} \begin{smallmatrix} \nwarrow \text{NH}\cdot\text{NH} \\ \text{N} \text{---} \text{N} \end{smallmatrix} \nearrow \text{C}\cdot\text{NH}_2$ ,

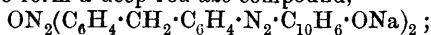
whilst the nitrogen of the hydrazine is liberated in the free state. The diaminodihydropyrimidine subsequently undergoes further reduction and hydrolysis, the tetrazine ring being broken and aminoguanidine,

formic acid and ammonia formed:  $\text{NH}_2\cdot\text{C} \begin{smallmatrix} \nwarrow \text{NH}\cdot\text{NH} \\ \text{N} \text{---} \text{N} \end{smallmatrix} \nearrow \text{C}\cdot\text{NH}_2 + 2\text{H}_2 + 2\text{H}_2\text{O} = \text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{NH}_2 + \text{H}\cdot\text{CO}_2\text{H} + 2\text{NH}_3$ .

This stage is reached immediately the liquid boils. If the heating is continued, the aminoguanidine is hydrolysed to carbon dioxide, ammonia and hydrazine (compare Thiele, A., 1892, 1295).

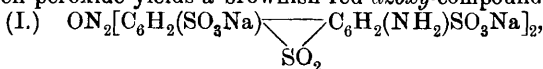
T. H. P.

**Some Azoxy-compounds and the Action of Dinitrophenylpyridinium Chloride on Sulphonated Compounds.** FRITZ REITZENSTEIN and ROBERT FITZGERALD (*J. pr. Chem.*, 1914, [ii], 89, 271—289).—In continuation of previous work (A., 1910, i, 702) on the formation of azoxy-compounds by the oxidation of benzidine-sulphonic acids with potassium ferricyanide in alkaline solution, the authors have examined the oxidation of 4:4'-diaminodiphenylmethane and find that the reaction proceeds in a similar manner to that occurring with the benzidinesulphonic acids. The resulting yellowish-brown azoxy-compound,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , has m. p. 74—75°, and after diazotisation couples with  $\beta$ -naphthol in aqueous sodium hydroxide solution to form a deep red azo-compound,



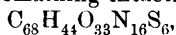
on distillation with iron filings it is reconverted into 4:4'-diaminodiphenylmethane.

Oxidation of sodium benzidinesulphonedisulphonate with potassium ferricyanide in alkaline solution, lead peroxide, ammonium persulphate, or hydrogen peroxide yields a brownish-red azoxy-compound,



from which, the corresponding acid is liberated by hydrochloric acid. The free acid is yellow, and after diazotisation combines with  $\beta$ -naphthol to form an *azo-dye* which dyes wool and silk an intense red.

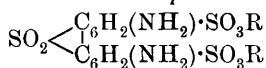
The azoxy-compound (I) differs from the simpler primary amines in its behaviour towards dinitrophenylpyridinium chloride. Instead of giving rise to a dianilide, the action of this reagent simply leads to the replacement of the two sodium atoms by the dinitrophenylpyridinium residue, the amino-groups remaining intact. The compound,



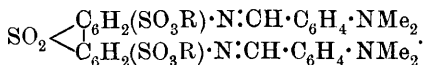
thus formed crystallises in red leaflets and condenses with *p*-dimethylaminobenzaldehyde (2 mols.), yielding a magenta-red *tetramethyl-p-diaminodibenzylidene* derivative,  $\text{C}_{86}\text{H}_{62}\text{O}_{33}\text{N}_{18}\text{S}_6$ , having a green, metallic lustre.

A similar stability of the amino-groups has also been observed with the sodium salts of benzidinesulphonedisulphonic, diaminostilbenedisulphonic, benzidinesulphonic, and benzidine-*m*-disulphonic acids; the action of dinitrophenylpyridinium chloride gives rise to the corresponding dinitrophenylpyridinium salts, the amino-groups remaining unattacked.

*Dinitrophenylpyridinium benzidinesulphonedisulphonate,*



(R = dinitrophenylpyridinium,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NC}_5\text{H}_5$ ), formed by the interaction of dinitrophenylpyridinium chloride and sodium benzidine-sulphonedisulphonate, crystallises in deep red leaflets, and condenses with *p*-dimethylaminobenzaldehyde, yielding the compound,



It resembles dinitrophenylpyridinium chloride in that it reacts with aniline in hot alcoholic solution to form dinitroaniline and Zincke's dianilide,  $\text{NPh} : \text{CH} : \text{CH} : \text{CH} : \text{CH} : \text{CH} \cdot \text{NHPh}, \text{HCl}$ .

Sodium diaminostilbenedisulphonate and dinitrophenylpyridinium chloride give rise to the compound,  $\text{C}_2\text{H}_2[\text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{SO}_3\text{R}]_2$ , which yields a condensation product,  $\text{C}_{54}\text{H}_{46}\text{O}_{14}\text{N}_{10}\text{S}_2$ , with *p*-dimethylaminobenzaldehyde (2 mols.).

When oxidised with alkaline potassium ferricyanide and the resulting azoxy-compound treated with dinitrophenylpyridinium chloride, sodium diaminostilbenedisulphonate yields a brownish-violet compound,  $\text{ON}_2[\text{C}_6\text{H}_3(\text{SO}_3\text{R}) \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{SO}_3\text{R}]_2$ .

The dinitrophenylpyridinium salts of benzidine-*m*-disulphonic and benzidinemonosulphonic acids are also described. Successive oxidation of sodium benzidinemonosulphonate with alkaline potassium ferricyanide and treatment with dinitrophenylpyridinium chloride gives rise to the compound,  $\text{ON}_2[\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{SO}_3\text{R}]_2$  which forms a deep red powder.

Sodium  $\beta$ -naphthylamine-6-sulphonate, on oxidation with alkaline potassium ferricyanide, yields sodium 2 : 2'-naphthazine-6 : 6'-disulphonate.

F. B.

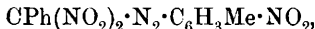


**Chloro-*p*-aminobenzeneazobenzene.** MARIO MAYER (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 353—357).—This substance (compare Betti, A., 1898, i, 656) exists in two forms. The yellow *isomeride* crystallises in scales, m. p. 116°, and yields on fusion a red liquid, which solidifies at 120° in the form of the other *isomeride*. The red *isomeride*, m. p. 136°, is the more stable form and is always obtained first in the preparation of the substance, the yellow form being produced when it is recrystallised from light petroleum. The two substances have the same composition and molecular weight and behave similarly in their reactions.

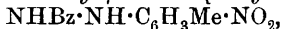
Betti's formula for the substance requires the existence of an asymmetric carbon atom, and in fact two brucine salts can be obtained, although the regeneration of the active chloralaminobenzeneazobenzenes could not be effected. One *brucine* salt (containing 1 mol. brucine, 1 mol. chloralaminobenzeneazobenzene, and 2 mol. benzene of crystallisation) forms red, prismatic crystals, m. p. 45—50°,  $[\alpha] - 45.7^\circ$ ; the other brucine salt is more soluble and was not isolated. R. V. S.

**Polysubstituted Diazonium Salts of Phenylidinitromethane [ $\omega$ -Dinitrotoluene].** G. PONZIO and C. MACCIOTTA (*Gazzetta*, 1914, 44, i, 269—277).—It has been shown previously (A., 1908, i, 482; 1909, i, 338; 1910, i, 192, 194) that, under the influence of moist ether, para-substituted benzenediazonium salts of  $\omega$ -dinitrotoluene undergo conversion into benzoylazoaryl compounds, the formation of which is preceded by isomeric change into benzoylarylnitronitrosohydrazines, these losing 2 atoms of nitrogen and 3 of oxygen spontaneously. It is now found that a similar change occurs in general with polysubstituted diazonium salts of  $\omega$ -dinitromethane, provided that one of the substituents occupies the para-position with respect to the  $N_2$  group. Since benzoylazoaryls are readily reduced by means of phenylhydrazine to the corresponding *s*-benzoylarylhvdrazines, the latter may be prepared, conveniently and in good yield, from  $\omega$ -dinitrotoluene.

The *o*-nitro-*p*-toluenediazonium salt of  $\omega$ -dinitrotoluene,



prepared by treating the diazo-compound of *m*-nitro-*p*-toluidine [ $CH_3 : NO_2 : NH_2 = 1 : 3 : 4$ ], in presence of sodium acetate, with the equivalent quantity of the potassium derivative of  $\omega$ -dinitrotoluene, forms an amorphous, yellow precipitate, m. p. 67° (decomp.). With moist ether it gives *benzoylazo-o-nitro-p-toluene*,  $NBz : N \cdot C_6H_3Me \cdot NO_2$ , which forms orange-yellow, flattened plates, m. p. 82°, and is reduced by phenylhydrazine to *a*-benzoyl- $\beta$ -*o*-nitro-*p*-tolylhvdrazine,



which forms brownish-yellow, shining plates, m. p. 164°, and dissolves in aqueous alkali hydroxide to an intensely blue solution.

The *p*-nitro-*o*-toluenediazonium salt of  $\omega$ -dinitrotoluene,  $C_{14}H_{11}O_6N_5$ , similarly prepared from *m*-nitro-*o*-toluidine [ $CH_3 : NH_2 : NO_2 = 1 : 2 : 5$ ], is a pale yellow, amorphous precipitate, and is converted by moist ether into *benzoylazo-p-nitro-o-toluene*,  $C_{14}H_{11}O_3N_3$ , which forms brownish-red prisms, m. p. 99°, and is transformed by alcohol and potassium hydroxide solution into the corresponding hydrazo-derivative, this dissolving with an intense, wine-red coloration.

*α-Benzoyl-β-p-nitro-o-tolylhydrazine*,  $C_{14}H_{13}O_3N_3 \cdot H_2O$ , forms flat, orange-yellow needles, m. p. 151—152° (anhydrous), and gives an intense, wine-red solution with aqueous alkali hydroxide.

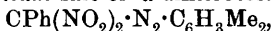
The *m-nitro-p-toluenediazonium* salt of *ω*-dinitrotoluene,

$C_{14}H_{11}O_6N_5$ , prepared from *o*-nitro-*p*-toluidine [ $CH_3:NO_2:NH_2 = 1:2:4$ ], forms an amorphous, yellow precipitate.

*Benzoylazo-m-nitro-p-toluene*,  $C_{14}H_{11}O_3N_3$ , crystallises in brownish-red needles, m. p. 90°.

*α-Benzoyl-β-m-nitro-p-tolylhydrazine*,  $C_{14}H_{13}O_3N_3$ , separates in pale yellow plates, m. p. 141°, and is insoluble in aqueous alkali hydroxide, but gives a brown solution with alcoholic potassium hydroxide.

The *m-4-xylenediazonium* salt of *ω*-dinitrotoluene,

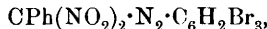


prepared from *m-4*-xylidine, forms a yellow, amorphous precipitate.

*4-Benzoylazo-m-xylene*,  $NBz \cdot N \cdot C_6H_3Me_2$ , crystallises in large, brown prisms, m. p. 53—54°.

*α-Benzoyl-β-m-4-xylylhydrazine*,  $NHBz \cdot NH \cdot C_6H_3Me_2$ , forms slender, pale straw-yellow needles, m. p. 160°, and forms a yellowish-red solution in alcoholic potassium hydroxide.

The 2:4:6-tribromobenzenediazonium salt of *ω*-dinitrotoluene,



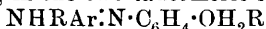
prepared from 2:4:6-tribromocaniline, is a flocculent, orange-yellow precipitate.

*Benzoylazo-2:4:6-tribromobenzene*,  $NBz \cdot N \cdot C_6H_2Br_3$ , crystallises in shining, coffee-coloured prisms, m. p. 123°.

*α-Benzoyl-β-2:4:6-tribromophenylhydrazine*,  $NHBz \cdot NH \cdot C_6H_2Br_3$ , crystallises in flat, sulphur-yellow needles, m. p. 172°, and forms a brownish-red solution in alcoholic potassium hydroxide. T. H. P.

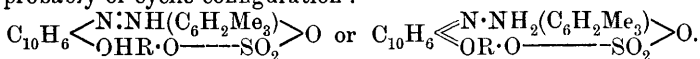
**Salts of *s-ψ*-Cumeneazo-β-naphthol and its Methyl and Ethyl Ethers.** G. CHARRIER and G. FERRERI (*Gazzetta*, 1914, 44, i, 120—131).—The authors have previously observed the limited stability of the salts of benzeneazo-β-naphthol (A., 1913, i, 1111). The hydrochlorides of a number of similar azo-β-naphthols, which can be obtained readily by saturating anhydrous ethereal solutions of the hydroxyazo-compounds with dry hydrogen chloride, have now been prepared; these salts crystallise well, and exhibit a golden or green metallic lustre, but they decompose immediately they are removed from the acid liquid. A marked exception is *s-ψ*-cumeneazo-β-naphthol hydrochloride, which is relatively stable. The same is the case with its nitrate and sulphate, obtained from the hydrochloride, in ether and chloroform respectively, by the action of ethereal solutions or suspensions of nitric and sulphuric acids. The nitrates of benzeneazo-β-naphthol and *p*-benzeneazophenol have been prepared similarly, and, on heating, undergo diazo-scission analogous to that occurring with nitrates of ethers.

For salts in which the hydroxyazo-compound functions as a diacid base, the only possible structures are those of oxonium or ammonium salts capable of existing in the two tautomeric forms:

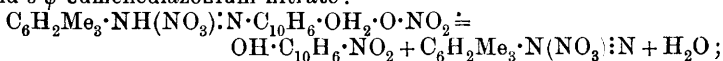


and  $NH_2RAr \cdot N \cdot C_6H_4 \cdot OHR$ , in which R represents an acid residue or

halogen atom. With the hydrochloride and sulphate of *s*- $\psi$ -cumeneazo- $\beta$ -naphthol, it is difficult to decide whether the two tautomeric forms have the structures  $\text{NHR} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$  and  $\text{NAr} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}_2\text{R}$ , or  $\text{NH}_2\text{R} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O}$  and  $\text{NHR} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OHR}$ . The fact that these salts contain one molecule of acid, whilst with ethers the hydrochlorides contain two molecules of acid and the sulphuric acid of the sulphates functions most probably as a bibasic acid, shows that the substitution of the hydrogen atom by the alkyl radicle doubles the basicity of the hydroxyazo-compound, and this increased basicity would seem to originate in the oxygen atom, the latter assuming basic properties on account of its union with the alkyl radicle. If, then, the salts of the ethers are considered to be ammonium or oxonium salts, those of non-etherified hydroxyazo-compounds, which contain but one equivalent of acid, must be regarded as possessing the structure of ammonium salts. Especially on account of their great stability, the sulphates of the ethers containing one molecule of sulphuric acid are probably of cyclic configuration :

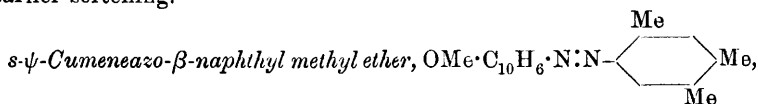


*s*- $\psi$ -Cumeneazo- $\beta$ -naphthol forms cherry-red needles with golden-yellow reflection, m. p. 160—161°; Meldola and Burls (T., 1893, 63, 934) gave m. p. 163—164°. The *hydrochloride*,  $\text{C}_{19}\text{H}_{18}\text{ON}_2 \cdot \text{HCl}$ , forms reddish-brown needles with green metallic reflection, becomes vivid red at about 100°, softens at 158°, and has m. p. 160—161°. The *nitrate*,  $\text{C}_{19}\text{H}_{18}\text{ON}_2 \cdot 2\text{HNO}_3$ , forms reddish-brown needles with green metallic lustre, and becomes bright red at 54—55°, after which it softens until at about 80° it melts and decomposes with evolution of gas. On long storing, especially under diminished pressure, or on heating at 55—60°, the nitrate decomposes, giving 1-nitro-2-naphthol and *s*- $\psi$ -cumenediazonium nitrate :



its spontaneous decomposition yields, in addition, a small proportion of nitro- $\psi$ -cumeneazo- $\beta$ -naphthol (?), m. p. 196—197°.

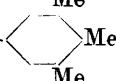
The *sulphate*,  $\text{C}_{19}\text{H}_{18}\text{ON}_2 \cdot \text{H}_2\text{SO}_4$ , forms red, hygroscopic needles with golden or green metallic lustre, and decomposes rapidly in the air. The *platinichloride*,  $(\text{C}_{19}\text{H}_{18}\text{ON}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , forms large, red, stable needles with golden metallic reflection, m. p. 167—168°, with somewhat earlier softening.



obtained by the action of methyl sulphate on the hydroxyazo-compound in presence of excess of 30% sodium hydroxide solution, forms bright red leaflets or flattened needles, m. p. 89—90°. The *hydrochloride*,  $\text{C}_{20}\text{H}_{20}\text{ON}_2 \cdot 2\text{HCl}$ , which forms mammillary masses of brick-red needles with golden lustre, and the *hydrobromide*, which forms deep, garnet-red needles, decompose rapidly at about 100° into *s*- $\psi$ -cumeneazo- $\beta$ -naphthol, methyl haloid, and halogen hydracid. The *nitrate*,  $\text{C}_{20}\text{H}_{20}\text{ON}_2 \cdot 2\text{HNO}_3$ , forms a dark green, crystalline powder, or minute, cantharides-green

leaflets, m. p.  $83^{\circ}$  (decomp., with evolution of gas), and with water yields *s*- $\psi$ -cumeneazo- $\beta$ -naphthyl methyl ether and nitric acid; on spontaneous decomposition or when heated, it is resolved similarly to *s*- $\psi$ -cumeneazo- $\beta$ -naphthyl nitrate, nitro- $\psi$ -cumeneazo- $\beta$ -naphthol (?), m. p.  $196$ — $197^{\circ}$ , being obtained in the former case. The *sulphate*,  $C_{20}H_{20}ON_2 \cdot H_2SO_4$ , forms non-hygroscopic, cantharides-green needles, m. p.  $162$ — $163^{\circ}$ , and is decomposed by water, very slowly in the cold, or more rapidly in the hot, into *s*- $\psi$ -cumeneazo- $\beta$ -naphthyl methyl ether and sulphuric acid. The *platinichloride* forms highly stable, red, metallic-looking crystals, m. p.  $182$ — $183^{\circ}$ , the ether functioning as a monoacid base.

*s*- $\psi$ -Cumeneazo- $\beta$ -naphthyl ethyl ether,  $C_{21}H_{22}ON_2$ , forms flat, garnet-red needles, m. p.  $91^{\circ}$ . Its *hydrochloride* forms a red, crystalline powder with green metallic lustre, and its *hydrobromide*, garnet-red needles. The *nitrate*,  $C_{21}H_{22}ON_2 \cdot 2HNO_3$ , forms green, metallic-looking crystals, m. p.  $76$ — $77^{\circ}$  (decomp., with evolution of gas); when heated at about its melting point, it undergoes diazo-scission, yielding 1-nitro-2-naphthyl ethyl ether and *s*- $\psi$ -cumenediazonium nitrate, which gives *s*- $\psi$ -cumeneazo- $\beta$ -naphthol with  $\beta$ -naphthol

and *s*- $\psi$ -cumeneazo- $\beta$ -naphthylamine,  $NH_2 \cdot C_{10}H_6 \cdot N:N$ —Me, in

orange-red needles, m. p.  $161^{\circ}$ , with  $\beta$ -naphthylamine. The *sulphate*,  $C_{21}H_{22}ON_2 \cdot H_2SO_4$ , forms rosettes of stable, non-hygroscopic, metallic green needles, becoming opaque and dark green when powdered; it turns slightly brown at above  $150^{\circ}$ , melts at  $154$ — $155^{\circ}$ , and decomposes, with evolution of gas, at  $159$ — $160^{\circ}$ ; by water it is resolved into *s*- $\psi$ -cumeneazo- $\beta$ -naphthyl ethyl ether and sulphuric acid, and at  $160^{\circ}$  it undergoes a decomposition which is being investigated. The *platinichloride*,  $(C_{21}H_{22}ON_2)_2 \cdot H_2PtCl_6$ , forms stable, dark green, metallic-looking needles, m. p.  $185$ — $186^{\circ}$ . T. H. P.

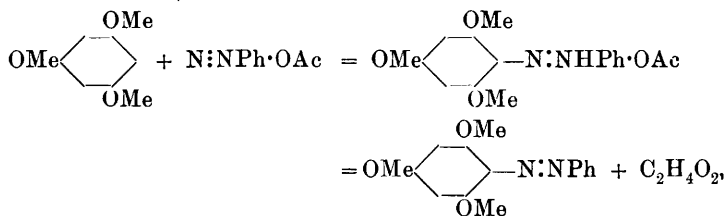
**Action of Nitric Acid on Hydroxyazo-compounds.** G. CHARRIER and G. FERRERI (*Gazzetta*, 1914, **44**, i, 165—182. Compare A., 1913, i, 1111, 1112, 1113, and preceding abstract).—According to its concentration, to the temperature, and to the nature of the hydroxyazo-compound, nitric acid may exert nitrating and oxidising effects to varying extents. The nitric acid is first added to give a nitrate of the hydroxyazo-compound, which then decomposes, giving a nitrophenol and a diazonium nitrate:

$NO_3 \cdot NHA r \cdot N \cdot C_6H_4 \cdot OH \cdot NO_3 = OH \cdot C_6H_4 \cdot NO_2 + NO_3 \cdot NAr \cdot N + H_2O$ .  
By means of excess of nitric acid, nitration of the nitrate of the hydroxyazo-compound may be effected before this decomposition occurs, a nitroaryldiazonium nitrate being thus obtained; the nitrophenol resulting from the decomposition may also undergo further nitration.

The results of a number of experiments on the action of nitric acid of different concentrations on hydroxyazo-compounds show that, in general, only nitrohydroxyazo-compounds with the nitro-group in the hydroxyl-free nucleus are formed before scission of the molecule takes place. In face of the resistance offered by a quinonoid ring to the

action of nitrating and other substituting agents, this behaviour seems most readily explainable by attributing a quinonoid structure to the hydroxyazo-nitrates. The sole exception to the above rule consists in the formation of benzeneazo-*o*-nitrophenol from *p*-benzeneazophenol and nitric acid (compare Hewitt, T., 1900, 99, 810).

The preparation of ethers of hydroxyazo-compounds by the coupling of diazonium acetates with phenolic ethers in acetic acid solution (compare Meyer and Lenhardt, A., 1913, i, 723) may be regarded as an additive reaction (see A., 1913, i, 1111).



and is hence strictly analogous to the coupling of phenolic ethers with diazonium nitrates in presence of nitric acid, with intermediate formation of nitrates of the ethers of the corresponding hydroxyazo-compounds (see A., 1913, i, 1113).

The action of 2*N*-nitric acid on benzeneazo-*p*-phenol gives *p*-benzeneazophenyl nitrate, which undergoes diazo-scission into *p*-nitrophenol and benzenediazonium nitrate; the latter is then decomposed into phenol, which is converted by the excess of nitric acid into *o*- and *p*-nitrophenols and 2:4-dinitrophenol. The action of nitric acid of D 1.4 yields, on the one hand, benzenediazonium and *p*-nitrobenzenediazonium nitrates, and, on the other, 2:4-dinitrophenol and *p*-2:4-dinitrobenzeneazophenol, and possibly a small proportion of *p*-4-nitrobenzeneazophenol. The action of a 20% solution of nitric acid of D 1.52 in glacial acetic acid gives 2:4-dinitrophenol and benzenediazonium nitrate.

With *p*-benzeneazophenyl methyl (or ethyl) ether, nitric acid of D 1.4 gives benzenediazonium nitrate and *p*-nitrophenol methyl (or ethyl) ether.

With 2*N*-nitric acid, benzeneazo- $\beta$ -naphthol reacts similarly to *p*-benzeneazophenol. With nitric acid of D 1.4, the products are 1:6-dinitro- $\beta$ -naphthol, *p*-nitrobenzeneazo- $\beta$ -naphthol, and *p*-nitrobenzenediazonium nitrate; if the filtered, diluted liquid resulting from this reaction is cooled in a freezing mixture, neutralised with 25% potassium hydroxide and treated slowly with 30% potassium iodide solution, pure *p*-iodonitrobenzene is obtained. With a 20% solution of nitric acid of D 1.52 in glacial acetic acid, benzeneazo- $\beta$ -naphthol gives 1:6-dinitro- $\beta$ -naphthol and benzenediazonium nitrate.

The action of nitric acid, D 1.4, on benzeneazo- $\beta$ -naphthol gives *p*-nitrobenzenediazonium nitrate, whilst with its methyl ether and with that of *p*-methoxybenzeneazo- $\beta$ -naphthol it yields 1:6-dinitro- $\beta$ -naphthol and benzenediazonium or *p*-methoxybenzenediazonium nitrate. A similar difference in behaviour is shown by *p*-benzeneazophenol and its ethers. It appears, then, to be a general rule that, with nitric acid of D 1.4, non-etherified hydroxyazo-compounds give nitro-substituted diazonium

nitrates, whereas the ethers give diazonium nitrates containing the same aromatic radicles as the hydroxyazo-compounds. This requires attention when the reaction with nitric acid is employed to establish the constitution of a hydroxyazo-compound.

The action of nitric acid of D 1.4 on *p*-tolueneazo- $\beta$ -naphthol gives *p*-toluenediazonium and dinitro-*p*-toluenediazonium nitrates. As with benzeneazo- $\beta$ -naphthol (see above), *p*-iodotoluene may be obtained from the products of this reaction.

T. H. P.

**Phthaleins. III. The Constitution of the Bisazophenolphthaleins and of the Coloured Salts of Phenolphthalein.** BERNARDO ODDO (*Ber.*, 1914, 47, 967—972\*. Compare A., 1913, i, 1110).—An adverse criticism of Schestakov and Nocken's experiments (this vol., i, 335) and a reiteration of the author's desire to reserve this field of work for himself.

J. C. C.

**Electrolysis of Proteins and Their Degradation Products.** JAMES P. ATKINSON (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxxiv—xxxv).—After varying periods of electrolysis in the presence of 5 to 10% sulphuric acid, protein solutions cease to give the biuret reaction. About 50% of the nitrogen of egg-white, Witte's peptone, and hydrolysed horse serum appear as ammonia. Amino-acids (except glycine), uric acid, and urea yield less than 50% of their nitrogen as ammonia in the same time. The amount of ammonia obtained from amino-acids is roughly inversely proportional to their molecular weights.

W. D. H.

**Preparation, Composition, and Properties of Caseinogenates of Magnesium.** LUCIUS L. VAN SLYKE and ORRIN B. WINTER (*J. Biol. Chem.*, 1914, 17, 287—291).—If base-free caseinogen is dissolved in magnesium hydroxide, containing magnesium oxide in fine suspension, and this is treated with hydrochloric acid under specified conditions and subjected to dialysis, four magnesium caseinogenates are obtainable: (1) basic caseinogenate containing 1.06% magnesium, soluble in water and neutral to phenolphthalein; (2) normal caseinogenate neutral to litmus containing 0.71% magnesium; (3) di-magnesium caseinogenate sparingly soluble in water containing 0.24% magnesium, and (4) mono-magnesium caseinogenate insoluble in water, containing 0.13% magnesium.

W. D. H.

**Development of the Amino-group on Wool.** M. FORT and L. L. LLOYD (*J. Soc. Dyers*, 1914, 30, 73—77).—Use has been made of potassium  $\beta$ -naphthaquinone-4-sulphonate to obtain information on the function of amido- and amino-groups in the reactions of wool.

Potassium  $\beta$ -naphthaquinone-4-sulphonate is known to react readily with aromatic amines with the formation of potassium hydrogen sulphite and an arylimino-derivative of  $\beta$ -naphthaquinone; it is now shown to react similarly with aromatic compounds containing an amino-group such as aminocarboxylic acids, amino-sulphonic acids, aminophenols, etc., also with certain alkaloids, aliphatic amino-acids, and certain compounds containing an imino-group, but not

\* and *Gazzetta*, 1914, 44, i, 389—396.

with ammonia, aliphatic amines, or acid amides. Carbamide does not condense with the quinonesulphonate, although thiocarbamide and biuret do so readily.

Wool reacts with potassium  $\beta$ -naphthaquinone-4-sulphonate and the formation of a fast brown condensation product on the fibre is taken as evidence of condensation with amino-groups of the wool in a manner similar to that observed with the compounds just cited. Treatment of wool with hot dilute solutions of alkalis increases the reactivity with the quinonesulphonate, from which it is inferred that free amino-groups are developed in the wool substance by this treatment and the increase in the affinity of the wool for acid dyes brought about at the same time must also be ascribed to the formation of free amino-groups in the wool substance. A cold, strong, aqueous solution of sodium hydroxide does not produce such a marked change as a hot dilute solution of sodium carbonate, whilst wool treated with cold, strong sulphuric acid does not react with the quinonesulphonate and its affinity for acid dyes is greatly diminished; dilute acids, however, render the wool more open to condensation with the quinonesulphonate.

General speaking, any treatment that brings about a decrease in the affinity of the wool for acid dyes also decreases the reactivity of the wool towards the quinonesulphonate and vice versa; consequently, it may be assumed that amino-groups are largely responsible for the affinity of wool for acid dyes applied from acid baths. W. H. G.

**The Introduction of Phosphoric Acid into Amino-acids, Peptones, Albumoses, and Proteins.** C. NEUBERG and W. OERTEL (*Biochem. Zeitsch.*, 1914, 60, 491—508).—The general method employed consists in treating the aqueous solution of the substance with phosphoryl chloride dissolved in carbon tetrachloride in the presence of magnesia usta. The phosphorus compound is slowly added to the cooled aqueous solution and magnesia, which are kept stirred with a turbine. From tyrosine, an amorphous substance corresponding with the formula  $\text{PO}_3\text{Mg} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{NH}(\text{PO}_3\text{Mg}) \cdot \text{CO}_2\text{H}$  was obtained. Corresponding substances from alanine and glycine could not be obtained in a pure state, as the phosphoric acid derivatives of the simpler amino-acids appear to be very unstable. More stable products were obtained from peptones (Witte's and silk peptones), from which scission of phosphoric acid takes place on treatment with ferments. Corresponding products from blood globulin and casein were obtained from solutions of these substances in sodium hydroxide. In these cases the free acids were obtained; they are insoluble in water. The product from globulin contained 1.77%, and that from casein 1.76% of phosphorus. They are both digestible on treatment with proteoclastic ferments, and give precipitates when dissolved in lime-water, on treatment with a few drops of strong solutions of rennin. S. B. S.

**"Tricresol" as a Substitute for Toluene in Enzyme Work.** SARA S. GRAVES and PHILIP ADOLPH KOBER (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxix—xxx; *J. Amer. Chem. Soc.*, 1914, 36, 757—758).—"Tricresol" (a mixture of *o*-, *m*-, and *p*-

cresols) is preferable, as it does not possess many disadvantages of toluene. It does not appreciably interfere with enzyme action, except in certain cases.

W. D. H.

**Action of Invertase on Sucrose in Methyl and Ethyl Alcohols of Different Strengths.** EM. BOURQUELOT and M. BRIDEL (*J. Pharm. Chim.*, 1914, [vii], 9, 321—327).—Invertase is much more resistant to the injurious action of ethyl alcohol than of methyl alcohol. In the case of the latter the ferment is destroyed when the strength of the alcohol reaches 60% by weight, whilst it is still active in ethyl alcohol, 90% by volume. The action of the invertase is, however, diminished by lower concentrations than these.

W. G.

**The Activity of the Lipodiasase of Castor Seeds at Low Temperatures.** A. BLANCHET (*Compt. rend.*, 1914, 158, 895—896).—A comparison of the activity of the lipodiasase, contained in the cytoplasm of castor seeds, at 17°, 0°, and -5°, by determining the amounts of castor oil saponified by this lipase at these temperatures. Saponification takes place at temperatures below 0°, but the activity of the enzyme diminishes progressively with the temperature. The temperature at which activity ceases must be considerably below -5°.

W. G.

**The Theory of Oxidation Ferments. Peroxydase and Catalase Reactions of Formaldehyde and Acetaldehyde.** GERTRUD WOKER (*Ber.*, 1914, 47, 1024—1029).—In a previous paper (*Zeitsch. allg. Physiol.*, 1914, 16, 340) the theory has been developed that the different ferment actions (oxygen transmission in the presence of hydrogen peroxide, decomposition of hydrogen peroxide into water and oxygen, reduction of solutions of dyes) are due to the same agent, which is identical with the oxygenase of Chodat and Bach (*A.*, 1904, i, 704), and has an aldehydic character. In all cases the primary product is a peroxide,  $\text{OH}\cdot\text{CHR}\cdot\text{O}\cdot\text{OH}$ , which can then be decomposed in such a manner that (1) in the presence of an excess of hydrogen peroxide, oxygen is evolved (catalase reaction), (2) that oxygen is transmitted to an oxidisable substance (peroxydase reaction), or (3) in absence of hydrogen peroxide and air, oxygen is withdrawn from an oxidising agent (reductase action). The first and second types of reaction can occur simultaneously, and the relative prominence of the one or the other depends on the nature and quantity of the substances present with the ferment.

Experiments on the identity of catalase and peroxydase in plant sap carried out in conjunction with Begemann (*Zeitsch. allg. Physiol.*, 1914, 16, 350) have shown that the catalase action and peroxydase actions are destroyed at practically the same temperature, that the content of catalase is practically always parallel with that of peroxydase, and that the relationship is not altered by dialysis. With mushroom sap, the sole material with which the peroxydase reaction has not been observed, the catalase action is very vigorous.

In support of the theory that the fermentative principle of these



three actions has an aldehydic character, the author has investigated the action of formaldehyde, and shows that, in addition to its well known reducing action, it can also produce the catalase and peroxydase effects. Thus, when treated with hydrogen peroxide and benzidine or with guaiacum tincture and oil of turpentine, a blue coloration is developed, the intensity and time of appearance of which depends on the concentration of the formaldehyde and varies in the same manner as that produced by natural peroxydase. Also, when mixed with hydrogen peroxide, formaldehyde causes an evolution of oxygen. Acetaldehyde behaves in a similar manner. After repeated fractionation, benzaldehyde gives a blue coloration in the presence of hydrogen peroxide; preserved benzaldehyde, in consequence of its content of peroxides, gives a blue colour with benzidine alone, which is hindered by hydrogen peroxide as a result of the rapid mutual decomposition of the peroxides. A catalase reaction has not been observed with benzaldehyde, the substance appearing to function rather as a preservative of hydrogen peroxide.

Dextrose does not show the peroxydase reaction. Hydroxy-aldehydes (salicylaldehyde, protocatechualdehyde, vanillin, ortho-vanillin, o-nitrovanillin, veratraldehyde, methylvanillin, and piperonal) either do not give a coloration, or the latter is masked by the intense yellow or orange-red colour which develops by the action of the aldehydes on benzidine without intervention of hydrogen peroxide. H. W.

**Carboxylase.** V. I. PALLADIN, N. N. GROMOV, and N. N. MONTEVERDE (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 297—315).—The action of the carboxylase of several preparations of dead yeast has been studied under various conditions at 18—20°, the amounts of carbon dioxide evolved being measured by means of a Pettenkofer's tube; toluene was employed as antiseptic.

Free pyruvic acid acts on zymine as a poison, retarding auto-fermentation; neutralisation with potassium hydroxide after twenty-three hours effects little improvement. Potassium pyruvate produces, however, a marked increase in the quantity of carbon dioxide evolved during auto-fermentation, this increase being especially large with zymine poor in glycogen. The presence of dipotassium hydrogen phosphate causes considerable acceleration of the decomposition of free pyruvic acid, this effect being explained by the following equations:  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{Na}_2\text{HPO}_4 = \text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{Na} + \text{NaH}_2\text{PO}_4$  and  $\text{CH}_3\cdot\text{CHO} + \text{NaHCO}_3 + \text{NaH}_2\text{PO}_4 = \text{CH}_3\cdot\text{CHO} + \text{Na}_2\text{HPO}_4 + \text{CO}_2 + \text{H}_2\text{O}$ .

Experiments were made with sucrose with a view to decide if the resolution of pyruvic acid and alcoholic fermentation are processes independent one of the other, but the results are not absolutely conclusive. The course of the action of carboxylase is quite different from that of zymase, since the latter displays its maximal activity after some hours, whereas the former functions most energetically at first and rapidly loses in activity.

Experiments with juice obtained from yeast dried by von Lebedev's method show that sucrose and pyruvic acid together give carbon dioxide in quantity less than the sum of the quantities given by

sucrose and pyruvic acid separately; also in the former case, the evolution of gas shows a second maximum, possibly owing to stimulation of alcoholic fermentation by the acetaldehyde formed.

An old specimen of zymín, devoid of the power to ferment sucrose, was found to retain considerable capacity for auto-fermentation, which was stopped by the introduction of sucrose, so that auto-fermentation cannot be regarded as typical alcoholic fermentation. This conclusion is confirmed by Lvov's results (A., 1913, i, 943), which showed that methylene-blue retards the evolution of carbon dioxide during the fermentation of sucrose and stimulates it during auto-fermentation.

The action on sucrose of hefanol which had almost entirely lost its fermenting power was found to be practically unaffected by boiled taka-diastrase solution, but addition of boiled hefanol juice restored the ability to ferment sucrose. When all three of these solutions had ceased to evolve gas, addition of potassium pyruvate in each case caused renewed activity. With the solution containing the boiled hefanol juice, which had given a large quantity of gas with the sucrose alone, this second evolution of gas exceeded that of the liquid containing only hefanol and sucrose, which previously gave practically no gas. Hence, carboxylase is either independent of alcoholic fermentation or is stimulated by the hefanol juice.

In absence of sucrose, carboxylase is stimulated not at all by boiled or unboiled taka-diastrase solution, and but slightly by boiled hefanol juice.

Extraction of hefanol with methyl alcohol virtually destroys its capacity of fermenting sucrose, but only slightly retards the activity of its carboxylase. Auto-fermentation seems to cease with hefanol extracted by means of methyl alcohol. Hence, in order to study the action of carboxylase in as pure a form as possible, this extraction should be carried out previously.

The resolution of free pyruvic acid is scarcely affected by extraction of the hefanol with either toluene or methyl alcohol. During autolysis carboxylase is destroyed gradually, and at about the same rate as is zymase.

In high concentration, glycerol paralyses the activity of carboxylase, but in weak solutions it extends the activity over an increased period.

Hydrogen peroxide decomposes pyruvic acid with the same velocity as does carboxylase, and in the former case this velocity is slightly diminished by addition of peroxydase from horse-radish. This observation furnishes a new proof that peroxydase oxidises only aromatic compounds. Indeed, the addition of peroxydase and catechol almost entirely arrests the decomposition of pyruvic acid by hydrogen peroxide, the peroxydase directing the action of the peroxide to the catechol. Consequently, the system peroxydase-respiratory chromogen serves for the removal of hydrogen:  $C_6H_6O_2 + O = C_6H_4O_2 + H_2O$  (compare Palladin, A., 1912, ii, 570).

T. H. P.

**The Fermentative Decomposition of Hydrogen Peroxide.**  
P. WAENTIG and O. STECHE (*Biochem. Zeitsch.*, 1914, 60, 463—471).—The authors' reply to certain criticisms of Michaelis and Pechstein

(Abstr., 1913, i, 1008) on their results on the effect on activity of agitation of ferment solutions, and point out the reasons why they have failed to reproduce these results. They object also to certain theoretical deductions of Michaelis and Pechstein, on the ground that such deductions are applicable only to homogeneous systems, and not to heterogeneous solutions containing colloids, such as catalase. In this case they regard the measured reaction as due to a diffusion process. S. B. S.

**Mode of Action of Soja Bean Urease.** DONALD D. VAN SLYKE and GLENN E. CULLEN (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxviii—xxix).—The concentration of a urea solution can be varied between 0.2 and 10% without influencing the rate at which ammonia is formed by a given concentration of urease. If the latter is varied, the initial rate of urea decomposition varies proportionately. These facts indicate that the enzyme combines with a definite maximum amount of urea, and the presence of excess of urea beyond this does not affect the rate of the reaction.

As the reaction proceeds, the ammonia formed causes a progressive retardation of the rate, until the latter has been depressed to about one-eighth of its original velocity; beyond this point the rate remains fairly constant. Between 10° and 50°, each 10° rise doubles the rate. The optimum temperature is about 60°. W. D. H.

**Soja Bean Urease; the Effect of Dilution, Acids, Alkalis, and Ethyl Alcohol.** E. K. MARSHALL, jun. (*J. Biol. Chem.*, 1914, 17, 351—362).—The velocity of the hydrolysis of urea by urease is proportional to the enzyme concentration; it increases with dilution to a maximum, and with further dilution decreases slightly. It is independent of the hydrogen or hydroxyl ion concentration within rather narrow limits. Hydrochloric acid and sodium hydroxide in sufficient amount inhibit and then destroy the enzyme. Ethyl alcohol exercises only a slight inhibitory and destructive action. W. D. H.

**o-Anisidinearsinic [4-Amino-3-methoxyphenylarsinic] Acid and Certain of its Derivatives.** L. BENDA (*Ber.*, 1914, 47, 995—1110).—The primary object of the investigation was the examination of therapeutic influence of the methoxy-group, which was found to be unfavourable.

The preparation of 4-amino-3-methoxyphenylarsinic acid is described. On nitration, it yields a mixture of 6-nitro-4-amino-3-methoxyphenylarsinic acid and 2-nitro-4-amino-3-methoxyphenylarsinic acid, which can be separated by taking advantage of their different solubility in water. The constitution of these acids cannot be directly determined, since boiling 10% sulphuric acid does not cause the elimination of the  $\cdot\text{AsO}(\text{OH})_2$  group, whilst treatment with water or acids at higher temperatures under pressure effects a profound decomposition. When, however, 4-acetyl-amino-3-hydroxyphenylarsinic acid is nitrated, 2-nitro-4-acetyl-amino-3-hydroxyphenylarsinic acid is obtained as sole product and the position of the nitro-group follows from its transformation by 10% sulphuric acid into 2-nitro-6-aminophenol (compare

Stuckenburg, *Annalen*, 1880, **205**, 86). On saponification with alkali, the acid is converted into 2-nitro-4-amino-3-hydroxyphenylarsinic acid, which with 10% sulphuric acid yields 2-nitro-6-aminophenol and on diazotisation yields intense yellowish-orange solutions giving characteristic colorations with R-salt and resorcinol. When, on the other hand, either of the nitroanisidinearsinic acids is diazotised, colourless or pale yellow solutions are obtained, which, when preserved or heated to 40–50°, do not evolve nitrogen and yield intensely yellow or yellowish-orange diazo-compounds, having colour reactions quite different from those of the original solutions. This change is shown to be due to the replacement of the methoxy- by the hydroxy-group, and since the orange-yellow diazo-compound obtained by warming diazotised solutions of the more readily soluble nitroanisidinearsinic acid is identical with that obtained from 2-nitro-4-amino-3-hydroxyphenylarsinic acid, the constitution of the former is fixed. Consequently, the sparingly soluble acid must be 6-nitro-4-amino-3-methoxyphenylarsinic acid. This is directly proved by reducing the acid by ferrous chloride (compare A., 1912, i, 62) to *diaminomethoxyphenylarsinic acid*, which yields arsenic-free azo-dyes identical with those obtained from 2:4-diaminoanisole. An analogous easy replacement of the  $-\text{AsO}(\text{OH})_2$  group by the group  $\text{R}'\text{N}:\text{N}-$  has been observed in the case of *p*-hydroxyphenylarsinic acid (A., 1912, i, 64).

It is remarkable that 2-nitro-4-amino-3-hydroxyphenylarsinic acid is the sole product of the nitration of 4-acetyl-amino-3-hydroxyphenylarsinic acid, and thus in this case the hydroxyl group exerts an influence only on the hydrogen atom in the ortho-position, whereas the nitration of 4-acetyl-amino-3-methoxyphenylarsinic acid yields two isomeric nitro-acids in which the  $-\text{NO}_2$  groups occupy the positions 2 and 6 respectively.

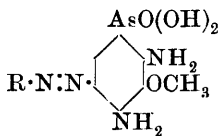
*4-Amino-3-methoxyphenylarsinic acid*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{AsO}(\text{OH})_2$ , cannot be advantageously prepared by the direct action of arsenic acid on *o*-anisidine (compare A., 1908, i, 591, 747), since the yield of product is small and difficulties are met in its extraction. It may, however, be obtained by the following process: a diazotised solution of 3-nitro-4-aminophenylarsinic acid (Berthelm, A., 1911, i, 1055) is poured into an alkaline solution of  $\beta$ -naphthol, when the dye is precipitated in the form of a crystalline *sodium* salt. This is alkylated by boiling its methyl-alcoholic solution with methyl *p*-toluenesulphonate and sodium carbonate until a portion of the solution remains red when diluted with water. The cinnabar-red dye thus obtained is reduced by sodium hyposulphite in the manner described for 3-nitro-4-aminophenylarsinic acid (A., 1912, i, 148), whereby 4-amino-3-methoxyphenylarsinic acid is obtained in centimetre-long, colourless needles, which are readily soluble in hot water, and have no sharp temperature of decomposition. The *diazo*-compound is colourless, and gives a bluish-red coloration with R-salt.

*4-Acetyl-amino-3-methoxyphenylarsinic acid*, white needles, darkening at 275° and decomposing at 285–287°, is prepared by the addition of acetic anhydride to a solution of 4-amino-2-methoxyphenylarsinic acid in *N*-sodium hydroxide solution. On nitration in sulphuric acid solution, it yields a mixture of 6-nitro-4-acetyl-amino-3-methoxyphenyl-

*arsinic acid* and 2-nitro-4-acetyl-amino-3-methoxyphenylarsinic acid, from which the former, yellow needles, is readily isolated by crystallisation of the crude product from water. For the isolation of both products (or of their derivatives) it is preferable to saponify the crude mixture with hot aqueous potassium hydroxide. The solution is cooled to  $40^{\circ}$  and sulphuric acid added until Congo-red paper is just turned brown, when 6-nitro-4-amino-3-methoxyphenylarsinic acid is precipitated. It forms orange needles, which dissolve in sodium carbonate, hydroxide or acetate, yielding intensely orange-coloured solutions. It is sparingly soluble in *N*-hydrochloric acid, and, on addition of sodium nitrite, yields a practically colourless solution which with R-salt and resorcinol gives a red and an orange coloration respectively. The diazo-solution, however, rapidly becomes lemon-yellow, and then gives reddish-violet and yellowish-red colorations with R-salt and resorcinol. 2-Nitro-4-amino-3-methoxyphenylarsinic acid is obtained by the further addition of sulphuric acid (until Congo-red paper is turned blue) to the filtrate obtained after separating the isomeride. It forms orange-yellow needles, which form pale yellow solutions in sodium carbonate, hydroxide or acetate. Its intensely yellow solution in *N*-hydrochloric acid is practically decolorised by addition of sodium nitrite, and the *diazo*-compound gives yellowish-red and orange-yellow colorations with R-salts and resorcinol respectively. Solutions of the *diazo*-compound rapidly become intensely orange-coloured and then yield bluish-violet and bluish-red colorations with R-salt and resorcinol. The orange-coloured *diazo*-compound is identical with that obtained from 2-nitro-4-amino-3-hydroxyphenylarsinic acid, giving the same reactions and, in particular, the same *azo*-dyes.

6-Nitro-4-amino-3-methoxyphenylarsinic acid is reduced by ferrous chloride and sodium hydroxide to 4:6-diamino-3-methoxyphenylarsinic acid, colourless needles. It dissolves in hydrochloric acid, yielding a colourless solution, which becomes orange-yellow on addition of nitrite; R-salt and resorcinol give intense bluish-red and orange colorations. When the acetic acid solution of the acid is treated with *p*-nitrodiazobenzene, a cinnabar-red *dye* is obtained, which does not contain arsenic and is identical with the compound prepared from *p*-nitrodiazobenzene and 2:4-diaminoanisole. A diazotised solution of sulphanilic acid also completely displaces the  $-\text{AsO}(\text{OH})_2$  group at the ordinary temperature.

2-Nitro-4-amino-3-methoxyphenylarsinic acid is similarly reduced by ferrous chloride and sodium hydroxide; in this case, the corresponding free acid could not be directly obtained, and was therefore isolated in the form of its *magnesium* salt, white powder. The latter dissolves in mineral acids, the solution becomes intensely yellow on addition of sodium nitrite, and couples with R-salt and resorcinol, yielding red and orange colorations respectively. The action of *p*-nitrodiazobenzene leads to the formation of a yellow *dye* which contains arsenic, whilst a diazotised solution of sulphanilic acid also yields a *dye* which is soluble in sodium carbonate and contains arsenic. These dyes have the annexed general formula.



4-Acetyl-amino-3-hydroxyphenylarsinic acid, colourless needles, is

prepared by the addition of acetic anhydride to a solution of 4-amino-3-hydroxyphenylarsinic acid (A., 1912, i, 148) in *N*-sodium hydroxide. When nitrated in sulphuric acid solution, it gives 2-nitro-4-acetyl-amino-3-hydroxyphenylarsinic acid, orange needles, darkening from 200°, m. p. about 220° (decomp.). The latter is hydrolysed by 2*N*-sulphuric acid with the formation of 2-nitro-6-aminophenol. When heated on the water-bath with aqueous potassium hydroxide and subsequently acidified, it yields 2-nitro-4-amino-3-hydroxyphenylarsinic acid, brownish-red needles, which gradually darken when heated, and are not melted at 280°. Its reactions with sodium nitrite and then with resorcinol and R-salt respectively are identical with those described for the diazotised and warmed solution of 2-nitro-4-amino-3-methoxyphenylarsinic acid. When boiled with 2*N*-sulphuric acid it yields 2-nitro-6-aminophenol. On reduction with ferrous chloride in alkaline solution, it gives a readily soluble diaminohydroxy-acid.

The conversion of 2-nitro-4-acetyl-amino-3-hydroxyphenylarsinic acid into 2-nitro-6-aminophenol is effected by boiling under reflux with 2*N*-sulphuric acid. The phenol is purified by sublimation, and forms long, red needles, m. p. 111–112°. The colourless solution in *N*-hydrochloric acid becomes intensely yellow on addition of sodium nitrite; the diazo-solution gives with R-salt a blue, with resorcinol a red coloration.

H. W.

**Preparation of Unsymmetrical Arseno-compounds.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270254. Compare A., 1913, i, 116, 415).—Unsymmetrical arseno-compounds are prepared by reducing a mixture of an arsenic acid (or oxide) and an inorganic arsenic compound. Examples are given illustrating the reduction of mixtures of the following substances: (1) phenylarsinic acid and sodium arsenite; (2) 3-amino-4-hydroxyphenylarsinic acid and sodium arsenite, and (3) *p*-aminophenylarsenious oxide and arsenic trichloride. The products contain from 45 to 57% and are of use in the treatment of trypanosomiasis.

J. C. C.

**Preparation of Mixed Arsenic-Phosphorus, Arsenic-Arsenic, Arsenic-Antimony, Arsenic-Selenium, and Arsenic-Tellurium Compounds.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269699).—The above compounds are obtained by the action of phosphorus, arsenic, antimony, selenium, and tellurium hydrides on aromatic arsine dichlorides, for example, phenylarsine dichloride or its derivatives. Examples are given of the preparation of compounds from (1) *p*-aminophenylarsine dichloride hydrate and hydrogen phosphide; (2) 3-amino-4-hydroxyphenylarsine dichloride and hydrogen phosphide; (3) 3-nitro-4-aminophenylarsine dichloride and hydrogen phosphide; (4) phenylarsine dichloride and arsenic trihydride; (5) *p*-aminophenylarsine dichloride and arsenic trihydride; (6) 3-amino-4-hydroxyphenylarsine dichloride hydrochloride and arsenic trihydride; (7) the preceding salt and antimony trihydride; (8) the same and hydrogen selenide, the product having the formula  $\text{HCl}, \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsSe}$ , and (9) the same and hydrogen telluride, the product having the formula  $\text{HCl}, \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsTe}$ .

J. C. C.

**Preparation of Antimony Compounds.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269743).—Arseno-stibino-compounds of the formula  $R \cdot As : Sb \cdot R''$ , are obtained by the interaction of aromatic arsines and antimony compounds of the formula  $SbRX_2$  ( $X$ =halogen and  $R$ =organic or inorganic group). 3-Amino-4-hydroxyphenylarsine and antimony trichloride give a brownish-red powder; the compound forms a sparingly soluble sulphate. The same arsenic compound and phenylstibine dichloride give a yellowish-brown substance,  $C_6H_5 \cdot Sb : As \cdot C_6H_3(OH) \cdot NH_2 \cdot HCl$ , and *p*-acetylaminophenylarsine and antimony tribromide yield a reddish-brown compound,  $NHAc \cdot C_6H_4 \cdot As : SbBr$ . J. C. C.

**Preparation of Arsenic-antimony Compounds.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269744. Compare preceding abstract).—In place of the antimony halogen compounds mentioned in the chief patent, compounds of antimony containing oxygen may be employed. 3-Amino-4-hydroxyphenylarsine and tartar emetic yield a brownish-yellow substance of the probable formula  $CH_3 \cdot CO_2 \cdot Sb : As \cdot C_6H_3(OH) \cdot NH_2 \cdot HCl$ , which forms a sparingly-soluble sulphate. Antimonyl chloride and 4-amino-3-carbomethoxyphenylarsine give a brown condensation product, and phenylstibine oxide and *p*-hydroxyphenylarsine yield a brown substance of the formula  $HO \cdot C_6H_4 \cdot As : SbPh$ . J. C. C.

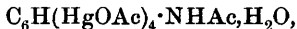
**Preparation of Arsenic-bismuth Compounds.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269745. Compare preceding abstracts).—Compounds analogous to those described in the chief patent (269743 above) are obtained by using bismuth compounds, such as the trichloride, tribromide, and tri-iodide, instead of the antimony compounds there mentioned. The condensation of 3-amino-4-hydroxyphenylarsine and bismuth trichloride yields a black compound, and of *p*-acetylaminophenylarsine and bismuth tribromide, also a black substance. These are slowly decomposed by acids or alkalis. J. C. C.

**Structure of Magnesium Organic Complexes and the Mechanism of their Formation.** V. TSCHELINCEV (*J. pr. Chem.*, 1914, [ii], 89, 86—92).—A criticism of Stadnikov's views on these subjects (*A.*, 1912, i, 109, 971). F. B.

**Colloidal Mercuri-organic Compounds. II.** M. RAFFO and G. ROSSI (*Gazzetta*, 1914, 44, 109—119; *Koll. Zeitsch.*, 1914, 14, 131—136).—The authors have studied further the colloidal properties of the acetate of pentamercuriacetanilide previously described (*A.*, 1912, i, 931) and of other similar compounds.

The acetate of 2:4-dimercuriacetanilide prepared by Pesci (*A.*, 1899, i, 908) exhibits no colloidal characters.

The acetate of 2:3:4:6-tetramercuriacetanilide,



obtained by heating an intimate mixture of mercuric acetate and acetanilide first at 120° and finally at 150°, is precipitated by alcohol

as a crystalline product, which dries to a vitreous mass resembling gum arabic; it gives a white powder, dissolving readily in water and decomposing at above  $195^{\circ}$ . Its solutions, unlike those of the acetate of pentamercuriacetanilide, give no precipitate with acetic acid, but heating at  $80^{\circ}$  produces a coagulum, which redissolves completely at ordinary temperatures. Its constitution is shown by its conversion into 2:3:4:6-tetrabromoacetanilide when treated with bromine and potassium bromide.

Prolonged dialysis of the acid solutions of tetra- and penta-mercuriacetanilide acetates results in coagulation in the dialyser, so that the presence of acetic acid is a necessary condition for obtaining stable colloidal solutions. Ultramicroscopic examination shows numerous small particles in the solutions before dialysis, but afterwards the coagulum presents crystalline structure.

The course of the successive stages, colloid-coagulum-crystals, was studied by ultrafiltration (compare Malfitano, A., 1912, ii, 240) combined with ultramicroscopic observation. The results show that, although in certain dilutions acetic acid acts as a colloid-former, when more concentrated it favours crystallisation.

T H. P.

**Mercuriation of Some Naphthalene Derivatives.** RICHARD BRIEGER and WERNER SCHULEMANN (*J. pr. Chem.*, 1914, [ii], 89, 97—183).—The authors have prepared a number of mercuriated derivatives of the naphthylamines, naphthols, and their sulphonic acids of the general formula  $R \cdot Hg \cdot X$  (where,  $X = OAc, Cl, I, Br$ ), and find that the stability of the carbon-mercury linking depends not only on the constitution of the aromatic residue,  $R$ , but also on the nature of the electronegative radicle attached to the mercury.

Thus, whilst sodium 1-acetoxymercuri- $\beta$ -naphthol-6-sulphonate is stable towards ammonium sulphide, the corresponding iodomercuri-compound readily yields mercuric sulphide; the stability of the chloromercuri- and bromomercuri-derivatives lies intermediately between those of the acetoxy- and iodo-compounds, the chloro-derivative being more stable than the bromo-compound.

These differences in the stability of the carbon-mercury linking are discussed from the point of view of the divisibility of the valency bond.

The addition of mercuric acetate to  $\alpha$ -naphthol in acetic acid solution results in the formation of a white, crystalline substance, which, when washed with water, acquires an intense yellow colour, and might be considered to be a quinonoid compound of the constitution  $C_6H_4 \begin{smallmatrix} \diagup C(=Hg) \\ \diagdown CH:CH \end{smallmatrix} > CO$ ; the analysis, however, agrees better with the formula  $C_{10}H_8O_2Hg$ .

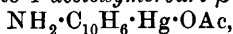
If excess of mercuric acetate is employed, 2:4-diacetoxymercuri- $\alpha$ -naphthol,  $C_6H_4 \begin{smallmatrix} \diagup C(OH) \\ \diagdown C(Hg \cdot OAc):CH \end{smallmatrix} \begin{smallmatrix} = \\ = \end{smallmatrix} C \cdot Hg \cdot OAc$ , is precipitated in colourless needles, which show the same behaviour towards water as the preceding compound.

In aqueous solution mercuric acetate reacts with sodium  $\beta$ -naphthol-6-sulphonate and sodium  $\alpha$ -naphthol-4-sulphonate, yielding sodium



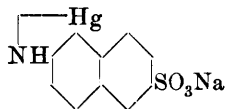
1-acetoxymercuri- $\beta$ -naphthol-6-sulphonate and sodium 2-acetoxymercuri- $\alpha$ -naphthol-4-sulphonate respectively.

The interaction of  $\beta$ -naphthylamine and mercuric acetate in acetic acid solution gives rise to 1-acetoxymercuri- $\beta$ -naphthylamine,

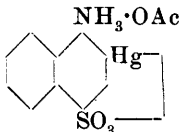


while  $\alpha$ -naphthylamine forms 2:4-diacetoxymercuri- $\alpha$ -naphthylamine,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_7(\text{Hg} \cdot \text{OAc})_2$ .

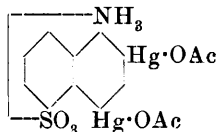
The action of sodium hydroxide on the product resulting from the interaction of sodium  $\beta$ -naphthylamine-6-sulphonate and mercuric acetate yields a yellow compound (I.), together with sodium 1-hydroxymercuri- $\beta$ -naphthylamine-6-sulphonate,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_7(\text{Hg} \cdot \text{OH}) \cdot \text{SO}_3\text{Na}$ , which forms colourless crystals containing  $1\text{H}_2\text{O}$ .



(I.)

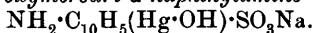


(II.)



(III.)

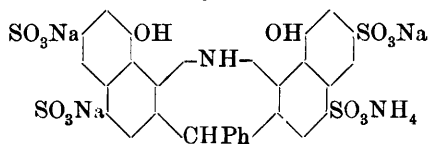
The sodium salt of  $\alpha$ -naphthylamine-4-sulphonic acid yields a colourless substance (II.), which is converted by sodium hydroxide into a yellow sodium 1-hydroxymercuri- $\alpha$ -naphthylamine-4-sulphonate,



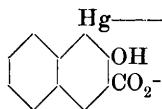
Sodium 8-amino- $\alpha$ -naphthylamine-5-sulphonate gives rise to a canary-yellow dimercuri-compound (III.).

The mercuriation of 8-amino- $\alpha$ -naphthol-3:5-disulphonic acid under various conditions was investigated, but the products had no definite composition. On benzoylation the sodium salt of the last-named acid yields a dibenzoyl derivative,  $\text{OBz} \cdot \text{C}_{10}\text{H}_7(\text{SO}_3\text{Na})_2 \cdot \text{NHBz}$ , which crystallises in white needles or leaflets and does not form a mercury derivative; partial hydrolysis of the dibenzoyl derivative yields sodium 8-benzoylamino- $\alpha$ -naphthol-3:5-disulphonate. This forms a white, crystalline powder, and couples with diazotised sulphanilic acid, benzidine, and *o*-tolidine, yielding red, violet and bluish-violet azo-dyes respectively. On treatment with mercuric acetate, it forms a mercuri-derivative, which, however, could not be isolated in a pure condition.

The disodium salt of 8-amino- $\alpha$ -naphthol-3:5-disulphonic acid reacts with benzaldehyde in aqueous solution to form a benzylidene derivative, whilst the monosodium salt gives rise to an acridine compound (formula IV), which crystallises in slender, orange needles.



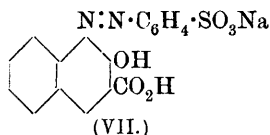
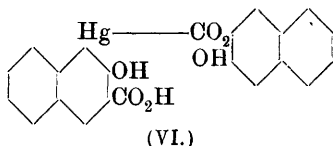
(IV.)



(V.)

The interaction of 3-hydroxy- $\beta$ -naphthoic acid and mercuric acetate yields a mixture of the compounds (V and VI), of which the former reacts with diazotised sulphanilic acid, yielding a brick-red azo-compound (VII) (identical with that obtained by directly coupling

3-hydroxynaphthoic acid with sulphanilic acid), and with iodine in aqueous potassium iodide to form 4-iodo-3-hydroxy- $\beta$ -naphthoic acid



This crystallises is slender, yellow needles, and on treatment with diazotised sulphanilic acid yields the same azo-derivative as the original mercuri-compound.

An account is given of the behaviour of the above mercury compounds towards potassium chloride, bromide and iodide, and of the stability of the resulting compounds toward ammonium sulphide.

The mercuriation of a number of other naphthol- and naphthylamine-sulphonic acids is described, but the products had no definite composition.

F. B.

## Physiological Chemistry.

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**A New Respiratory Chamber.** A. C. KOLLS and A. S. LOEVENHART (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxxviii—xxxix).—The chamber was designed for the purpose of estimating the effect of reducing the oxygen in the inspired air on the red corpuscles and hæmoglobin. In rabbits there is a distinct increase of both; increase of basophilic macrocytes in the blood indicates that this is due to stimulation of the red marrow.

W. D. H.

**A Respiration Incubator for the Study of Metabolism in New-born and Prematurely-born Infants.** JOHN R. MURLIN (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxxix—xl).—A Freas electric incubator was transformed into a respiration calorimeter by certain ingenious contrivances, which are described.

W. D. H.

**The Influence of Food and Posture on the Alveolar Carbon Dioxide Tension in Man.** HAROLD L. HIGGINS (*Amer. J. Physiol.*, 1914, **34**, 114—126).—The alveolar tension of carbon dioxide rises after the intake of food, and remains high whilst digestion is in progress; coffee causes vaso-constriction and a fall of the tension; vaso-dilatation coincides with a low tension. The tension also rises with the erect position, and is lowest in the lying posture. The variations, especially those due to alterations of position, can hardly be due to changes in the H-ion concentration of the blood; some other factor must affect the respiratory centre.

W. D. H.

**Hyperpnœa as a Result of Pain and of Ether in Man.** A. L. MEYER (*J. Physiol.*, 1914, 48, 47—52).—Y. Henderson's views on the relationship of acapnia to shock have been largely deduced from experiments on animals. The present work was done on man. Pain of moderate intensity (clamp screwed on to finger) and of short duration (two to three minutes) produces hyperpnœa and a lowering of the alveolar tension of carbon dioxide; the respiratory quotient is increased. Ether also in low concentration produces hyperpnœa of variable degree, usually in about a minute; with higher concentrations the breathing is diminished. W. D. H.

**Oxygen Requirements of Shell Fish.** PHILIP H. MITCHELL (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxxi—xxxii).—Oysters use from 7—35 dg. of oxygen per hour per 100 grams of body-weight; it varies with the temperature; when firmly closed they take no oxygen from the water. Data for *Mya arenaria* (clam) and *Venus mercenaria* (quahog) are also given. W. D. H.

**The Control of Oxygen Utilisation in Cases of Anæmia.** R. BIELING (*Biochem. Zeitsch.*, 1914, 60, 421—437).—When the power of combination with carbon dioxide of the blood of various animals is estimated by the tonometric method of Morawitz, it is found that this power is a constant for each individual animal (rabbits). It varies, however, with different individuals. After two days of starvation, the combining power diminishes as a result of acidosis. The blood of anæmic animals with 25—29% hæmoglobin has, in condition of rest, the normal combining power of carbon dioxide. In such cases of anæmia (produced experimentally) there is no want of oxygen. When, however, the hæmoglobin is reduced to below 20%, the combining power of the arterial blood for carbon dioxide is diminished, indicating a slightly diminished oxidation. S. B. S.

**Comparative Estimations of Oxygen and Carbon Dioxide in Arterial and Venous Blood at Paris, Chamonix, and Mont Blanc.** RAOUL BAYEUX and PAUL CHEVALLIER (*Compt. rend.*, 1914, 158, 958—961).—The determinations were made on the venous blood of the authors and the venous and arterial blood of rabbits. The results show that a high altitude produces a variation in the amount of oxygen and carbon dioxide in the blood, both increasing with the height. The increase in the amount of carbon dioxide is more marked than that of oxygen. Mountain sickness does not appear to appreciably modify the amount of carbon dioxide in the blood, but it is accompanied by a notable diminution of the oxygen in venous blood. W. G.

**Blood Pressure and Vaso-motor Irritability in the Anæsthetised Dog.** R. G. HOSKINS and HOMER WHEELON (*Amer. J. Physiol.*, 1914, 34, 81—88).—In various dogs the mean arterial

pressure, and the changes in it produced by given doses of adrenaline or nicotine, manifest certain variations, but their constancy is sufficient to permit of their being used as criteria of the activity and irritability of the sympathetic system.

W. D. H.

**A Tonometric Method for Determining the Equilibrium between Acids and Bases in the Organism.** P. MORAWITZ and J. CHANDLER WALKER (*Biochem. Zeitsch.*, 1914, 60, 395—420).—The authors give a detailed criticism of the general methods for determining the reaction of the blood. The method of analysis of the alveolar air appears to be a satisfactory one, provided that there is no change in the stimulability of the respiratory centre, and that the sample taken represents truly the alveolar air, which does not happen in certain cases of respiratory disturbance. The estimation of the carbon dioxide bound in the blood is also a satisfactory method, but the original method of determining this, as suggested by Walter (that is, simple carbon dioxide estimation in venous blood), contains certain sources of error. Under certain conditions, this carbon dioxide estimation gives more trustworthy results than physical chemical methods, and a process is now described by means of which such results can be obtained. The blood is shaken with an atmosphere of given carbon dioxide tension (3—5%) in a pear-shaped flask (which is figured in the text), which is kept at constant temperature in a thermos flask. The blood is then removed, and the carbon dioxide in it is then estimated in a Barcroft apparatus. The method is well adapted to animal experiments, but certain errors are apt to occur in the case of human blood when only venous blood is available. With certain precautions, however, these errors may be reduced to a minimum, or even eliminated altogether.

S. B. S.

**Diminished Blood-alkalinity in Experimental Uræmia.** FRITZ ELMENDORF (*Biochem. Zeitsch.*, 1914, 60, 438—446).—When uræmia is produced in animals by ligaturing the ureters or administration of uranium nitrate, the blood shows a diminished power of combining with carbon dioxide (as determined by the Morawitz tonometric method), and consequently a higher acidity.

S. B. S.

**The Uric Acid of the Blood.** ERNEST STEINITZ (*Zeitsch. physiol. Chem.*, 1914, 90, 108—123).—Folin's colorimetric method may be employed so that uric acid estimations may be easily made with 10 c.c. of blood or serum. On a purine-free diet, normal blood contains, on the average, 0·003% of uric acid; this endogenous uric acid may rise to 0·005% in gout, and nearly as much in "atypical gout" (Goldscheider). After an ordinary diet, a purine-free diet soon causes a fall to the normal level. Atophan diminishes the quantity markedly. Uric acid estimation in the blood may be employed for diagnostic purposes.

W. D. H.

**The Crystallisation of an Oxyhæmocyanin from an Arthropod.** CH. DHÉRÉ and A. BURDEL (*Compt. rend.*, 1914, 158, 978—981).—The authors have obtained an oxyhæmocyanin in a crystalline form from the blood of a spiny lobster by the following process. The blood was defibrinated, filtered, and dialysed until the greater part of the salts were removed, the dialysed blood having a specific conductivity of between  $44$  and  $58 \times 10^{-6}$ . This blood was then placed in an electrolytic cell and a current passed. The hæmocyanin travelled to the anode, and was precipitated there. To the liquid containing the precipitate, sodium chloride solution was added until the saline concentration was 1%. The oxyhæmocyanin dissolved immediately, but in a few moments a crystalline deposit began to form on the walls and base of the vessel, and consisted of rhombododecahedra of oxyhæmocyanin. Occasionally crystals of another form were found, consisting of hexagonal prisms combined with an inverse rhombohedron. Microphotographs of the crystals are given. W. G.

**Phenomena of Clot Formations. II. The Formation of a Gel from Cholate Solutions having many Properties Analogous to those of Cell Membranes.** S. B. SCHRYVER (*Proc. Roy. Soc.*, 1914, 87, B, 366—374).—Sodium cholate solutions containing 1% of the salt readily set to a gel at  $50^{\circ}$  in the presence of calcium chloride. The same result can also be produced by certain sodium, potassium, and magnesium salts, so that the clot production is not due to double decomposition between the calcium salts and the cholate. A method is described for measuring the clotting time, and it is shown that the calcium salts can be divided into two classes, viz., those which diminish the clotting time when their concentrations in the mixture are progressively increased, and those which, when the concentration exceeds a certain point, lengthen the clotting time; the former class increases the surface tension of water, whereas the latter diminishes it. The influence of various organic substances on the time of clot formation was also investigated, and it was found that, as a general rule, the more a substance diminishes the surface tension of water, the greater is its inhibitory action of clot formation. The rate is, however, by no means absolute, and it was found that those substances deviated from it, as regards clot formation, which formed the exceptions in Czapek's experiments on exosmosis of tannin from plant cells. There is a marked parallelism between inhibition of cholate clot formation and narcotic and exosmotic actions. In view of these results, the conception is advanced that the cell owes its semipermeability to the presence of a gel-forming substance, which need be neither lipid nor protein, and has many properties analogous to sodium cholate. The existence of such a substance would explain many of the actions, both of organic substances and salts, on the cell. S. B. S.

**Immunisation Against the Anti-coagulating Effect of Hirudin.** MIGUEL VERA and LEO LOEB (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxv—xxvi).—By injecting hirudin into mice on six successive days, the anti-coagulating effect of hirudin is no longer obtainable. The action is not altogether specific, for the anti-coagulating effect of sodium fluoride is also not obtained; other decalcifying agents (oxalate, citrate) act as usual. In mice with tumours the anti-substance does not appear quite so rapidly as in normal mice.

W. D. H.

**Anaphylactic Reactions.** H. C. BRADLEY and W. D. SANSUM (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxviii).—Hæmoglobins of different origins possess a high order of specificity; for example, guinea-pigs sensitised to dog's hæmoglobin react only to dog's hæmoglobin. Guinea-pigs injected with small amounts of guinea-pig "tissue-brei" are more severely intoxicated on subsequent injection than normal animals. A low order of specificity between different isogenous proteins is indicated.

W. D. H.

**Immunisation Experiments with Lipoproteins.** K. LANDSTEINER and E. PRÁŠEK (*Biochem. Zeitsch.*, 1914, **61**, 191—192).—In contradistinction to the results of Izar and Mammana (this vol., i, 355), who failed to produce immune sera with lipoproteins, the authors have succeeded in obtaining immune sera with preparations which have been obtained by treating proteins with acetyl chloride. The sera thus obtained reacted (with complement binding) on the acetylated, but not on benzoylated, sera. Similarly, sera produced by injection of benzoylated protein reacted with these protein derivatives, but not with acetylated proteins.

S. B. S.

**The Influence of the Blood-serum of Normal and Alcaptonuric Individuals on Homogentisic Acid.** OSCAR GROSS (*Biochem. Zeitsch.*, 1914, **61**, 165—170).—Normal sera of both man and rabbit contain a ferment which is capable of destroying homogentisic acid, acetone being a probable product of the reaction. This ferment was found to be absent in the sera of two alcaptonuric patients. Baumann's method for estimating the acid was employed, after the proteins had been precipitated from the hot diluted serum solutions by a few drops of concentrated zinc sulphate solution.

S. B. S.

**The Self-regulation of the Acidity of the Gastric Contents, and the Real Acidity of the Gastric Juice.** W. BOLDYREFF (*Quart. J. expt. Physiol.*, 1914, **8**, 1—12).—The acidity of freshly secreted gastric juice in men and animals is constant (0.5% hydrochloric acid). This acidity is rapidly lowered to a level which oscillates between 0.15 and 0.2%. The same thing happens when acids foreign to the stomach are introduced into it. This partial neutralisation is due to the reflux into the stomach of alkaline juices from the duodenum, the pancreatic juice being the

most important factor. Chlorine estimations show it is not due to absorption of the excess of acid. This lowering of acidity does not occur when the pancreatic ducts are ligatured, and clinical cases of hyperacidity are probably due to lack of pancreatic reflux. Neutral, alkaline, or feebly acid liquids introduced into the stomach provoke a secretion of acid juice which brings up the acidity to the normal level; this level (0.15 to 0.2%) is the optimum for protein digestion, and is that which can be borne by the sensitive duodenum.

W. D. H.

**The Stimulating Influence of Serum on Pancreatic Amylase** B. B. CROHN and A. A. EPSTEIN (*J. Biol. Chem.*, 1914, 17, 317—324).—Serum increases the amylolytic power of pancreatic extracts two-, three-, or even four-fold. The salts in serum are largely responsible for this activity; the serum salts are also largely present in the intestinal secretions, and so favour the digestion of starch.

W. D. H.

**The Action of Hitherto Unknown Constituents of the Pancreas on Sugar Katabolism. II.** E. VAHLEN (*Zeitsch. physiol. Chem.*, 1914, 90, 158—197).—By a complicated method of treating finely divided dried pancreas, in which treatment with zinc chloride at a high temperature plays a part, two substances of doubtful composition were separated. One of these hastens the activity, and the other delays the action, of yeast in the production of alcohol. The former is termed *metabolin*, the latter *antibolin*. Both are considered to act as catalytic agents, and by intramolecular rearrangement one can be converted into the other; acetic acid, for instance, converts metabolin into antibolin. These materials are further considered to play a part in metabolic changes in the tissues, and special regard is paid to their activity in relation to glycolysis; their action in furthering or retarding this process is stated to be similar to the action displayed in the alcoholic fermentation.

W. D. H.

**Action of Metabolin on Diabetic Dogs.** L. MOHR and E. VAHLEN (*Zeitsch. physiol. Chem.*, 1914, 90, 198—207).—Metabolin and antibolin (see preceding abstract) are only separated with difficulty from protein, and the present experiments were performed with metabolin and antibolin, which still gave the biuret reaction. When administered to dogs intravenously or subcutaneously suffering from diabetes, due to partial removal of the pancreas, they influenced the amount of sugar in the urine, metabolin diminishing and antibolin increasing it.

W. D. H.

**Metabolic Effects of Bathing in the Great Salt Lake.** HELEN I. MATTILL and H. A. MATTILL (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxxi).—The urine was examined quantitatively for various nitrogenous constituents in people who took the baths and a fixed diet; the interesting point is increased secretion of chlorides, due, possibly, to absorption of chlorides by the skin.

W. D. H.



**Production of Ammonia by Herbivora as a Protection Against Acidosis.** E. B. HART and V. E. NELSON (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xlv).—It is generally held that herbivora are unable to protect themselves against acidosis by ammonia production. This rests on experiments on rabbits. It is, however, not the case for cows and calves. W. D. H.

**The Chemistry of Gluconeogenesis. VII. The Fate of Pyruvic Acid in Metabolism.** A. I. RINGER (*J. Biol. Chem.*, 1914, 17, 281—285).—Whether pyruvic acid is glucogenetic appears unsettled; it has no toxic effect, and experiments here recorded show it to possess glucogenetic properties. Mayer's results to the contrary must have been due to some extraneous influence. Pyruvic acid yields acetoacetic acid, because of the intermediary formation of acetaldehyde, which undergoes aldol condensation, and it is glucogenetic because acetaldehyde and lactic acid are formed in its intermediary metabolism. In some experiments, however, scarcely any sugar was formed. It appears, therefore, that there are three ways in which pyruvic acid may behave: (1) by reduction, lactic acid and then sugar are produced; (2) by decarboxylation, acetaldehyde is formed and then sugar; and (3) an unknown intermediate substance is first produced, which does not yield sugar. W. D. H.

**The Influence of Underfeeding and of Subsequent Overfeeding on the Basal Metabolism of the Dog.** SERGIUS MORGULIS (*Biochem. Bull.*, 1914, 3, 264—268).—The respiratory metabolism fell during underfeeding, and was especially low with the onset of great debility. Four weeks of liberal feeding caused restoration in weight and respiratory exchange. The metabolic activity was raised during repair, but soon the basal metabolism returned to its original level. W. D. H.

**Utilisation of the Proteins of Cotton Seed by Man.** J. B. RATHER (*J. Amer. Chem. Soc.*, 1914, 36, 584—586).—Fraps and Fine (A., 1912, ii, 272) have stated, as the results of experiments on dogs, that the proteins of cotton-seed flour were utilised, on the average, to the extent of 71·6%. It has now been found that the utilisation of the proteins of cotton-seed meal and cotton-seed flour by man varies from 74·7 to 80·2%, with an average of 78·6%. Parallel experiments with meat showed that 96·6% of the proteins were utilised. E. G.

**The Influence of Cod-Liver Oil and Some Other Fats on Growth.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1914, 17, 401—408).—Young rats do not grow on isolated proteins, starch, lard, and protein-free milk; if the lard is replaced or supplemented by butter they grow, and symptoms of ill-health (diarrhoea, etc.) disappear. Other fats can take the place of butter in this respect, namely, fat of egg-yolk, and notably cod-liver oil. Almond oil is

here of no use. What the potent material is which is responsible for the good effect of butter and cod-liver oil is still unknown, but the experiments confirm clinical experience—that cod-liver oil is more than a mere nutrient. W. D. H.

**The Influence of Restricted Rations on Growth.** E. B. HART and E. V. McCOLLUM (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xliv—xlv).—With rats and pigs, a ration of wheat or wheat gluten with water stops growth. For a time growth goes on if potassium phosphate, potassium citrate, and calcium lactate are added. These results appear to harmonise with the view that wheat contains some toxic substance, and that the lack of growth is not due to the “incomplete” nature of the wheat protein.

W. D. H.

**Amino-acids in Nutrition and Growth.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1914, **17**, 325—350).—Certain amino-acids, especially those with cyclic nuclei, do not appear to be formed *de novo* by animal cells, as they are in plant life; hence proteins poor in tyrosine or tryptophan are of inferior value as foods, especially during growth, when new proteins are being formed; the question whether growth and maintenance in adult life (that is, repair of wear and tear) involve similar metabolic changes is discussed at length. On the experimental side it is shown that in growing rats, with gliadin as the sole protein, normal growth occurs if lysine is added. Tryptophan plays a unique rôle in preserving maintenance, and so contrasts with lysine, which is indispensable for growth. The addition of both to zein should lead to growth, and this expectation was fulfilled, and the experiments recorded are the first successful attempts to rear rats with zein as the sole food protein.

W. D. H.

**The Influence of Restricted Rations on Reproduction.** E. B. HART, E. V. McCOLLUM, and H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xlvii).—Wheat alone does not allow of normal reproduction in herbivora; corn (presumably maize) plus wheat straw does. Corn plus a salt mixture of the lactates and citrates (but not the carbonates) of potassium, magnesium, and calcium leads to a normal reproductive cycle. The substitution of wheat for corn leads to weak and undersized offspring. W. D. H.

**The Action of Various Anæsthetics in Suppressing Cell Division in Sea Urchin Eggs.** RALPH S. LILLIE (*J. Biol. Chem.*, 1914, **17**, 121—140).—The concentrations of various anæsthetics required for complete arrest of cleavage in the fertilised eggs of *Arbacia* were determined. The favourable anæsthetics (alcohols, urethanes, chloral hydrate) produce the effect in concentrations similar to those causing anæsthesia in *Arenicola* larvæ. In both cases increased resistance of the plasmatic membranes to the alterative or permeability-increasing action of salt solutions occurs.

W. D. H.

**Comparative Studies on the Amounts of the Constituents of the Ash in Different Types of Nervous Tissue.** ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1914, 89, 349—359).—This paper contains the results of a large number of ash analyses of different types of bovine and human nervous tissue. The central organ and the conducting paths contain the same amounts of calcium, magnesium, phosphorus, sulphur, and chlorine if the different quantities of water present are taken into account. In respect of these elements, therefore, the only differences are of concentration. Sodium, potassium, and iron, however, are present in these two types of tissue in the same concentration, but in different absolute quantity. R. V. S.

**Narcosis. II. The Influence of Narcosis on the Gaseous Metabolism of the Spinal Cord of Frogs.** HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1914, 61, 81—102).—The experiments on the respiratory exchange were carried out with the author's microspirometer. The isolated spinal cord of a frog which had been immersed in a urethane solution until its excitability was demolished, showed a diminution of the oxygen consumption, whereas a spinal cord treated with alcohol to produce the same effect showed an increased oxygen consumption. Excitability and rate of oxidation are therefore independent of one another, and diminution of oxidation by narcotics, when it exists, is therefore only a secondary phenomenon, which has nothing to do with the actual mechanism of narcosis. After a preliminary asphyxiation, alcohol narcosis causes no diminution of the oxygen respiration. During complete narcosis, electrical stimulation of the cord produces no increase in the oxidative processes; such an increase only results whilst stimulability still exists. The apparently contradictory facts, that alcohol narcosis does not inhibit oxidation, and that asphyxiated nervous centres cannot recover on access of oxygen during alcohol narcosis, indicate that between oxidative process and the processes concerned with stimulability and stimulation other phenomena must be interpolated which are influenced by narcosis. S. B. S.

**The Influence of Solutions of Inorganic Substances on the Oxidation Processes and the Reflex Irritability of the Spinal Cord of Frogs.** RUDOLF UNGER (*Biochem. Zeitsch.*, 1914, 61, 103—124).—The magnitude of oxygen consumption (measured by Winterstein's method) of the isolated cord in 0.7% sodium chloride under an oxygen pressure of 1 atmosphere is about 230 c.c. per gram per hour (at 0° and 760 mm.). Hypotonic sodium chloride solutions exert no influence on the oxidation process of the cord when surrounded by the pia mater, whilst they diminish or abolish reversely the reflex excitability. Hypertonic solutions of the salt cause an increased oxygen consumption of the cord when surrounded by the pia mater, and cause, first, an increased excitability, followed by inhibition. The pia mater exerts a marked influence on the above phenomena. When absent, the oxygen

consumption of the cord sinks in hypotonic solutions, whereas in hypertonic solutions the increased consumption noticed when the tissue is present is not observed. These facts are explained on the assumption that the pia inhibits mechanically the imbibition in hypotonic solutions, which finally leads to destruction of the tissue structure, and, further, that it acts as a semi-permeable membrane which is impermeable to sodium chloride, which in hypertonic solutions causes a shrinkage of the cord tissue, a change which is the immediate cause of increased oxygen consumption. If the pia is removed this shrinkage does not occur, as the sodium chloride can pass in both directions. Various experiments are quoted by the author in support of the above assumptions. Calcium salts in all concentrations cause a diminution of oxygen consumption; the reflex irritability is reversibly abolished in higher concentrations. Potassium salts have no very marked influence in either hypo- or hyper-tonic solutions on oxygen consumption. The irritability is reversibly abolished by moderate concentrations, but irreversibly by higher ones. Oxidation processes and stimulability are therefore to a large extent independent of one another. No kind of antagonistic action as regards oxygen consumption between sodium, calcium, and potassium ions was observed. S. B. S.

**The Influence of Various Ions on the Survival of the Central Nervous System of Mammals.** PAUL GERLACH (*Biochem. Zeitsch.*, 1914, 61, 125—148).—The method of experiment consisted in perfusing, by means of a technique due to Winterstein, the narcotised animal with the various solutions containing different salts, and determining at intervals the functioning capacity of the central nervous system by the twitch reactions, and in the case of older animals by the corneal reflex. It was found that calcium and sodium salts are, separately, capable of maintaining the central nervous system in a condition of survival. Minute quantities of potassium salts exert a deleterious action. The most efficient perfusion fluid was a solution containing 0.9% of sodium chloride and about 0.05% of calcium chloride (water-free). This solution is more effective for maintenance of the central nervous functions than either Ringer's or Tyrode's fluids. It is possible by its means to keep alive the central nervous systems of new-born animals of various species for two to three hours, and those of adult awakened hibernating animals for more than one hour. S. B. S.

**The Effect of Dextrose on Autolysis: a Possible Explanation of the Protein-sparing Action of Carbohydrates.** A. SHAFFER (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xlii—xliii).—In liver autolysis, the addition of 1% of dextrose solution slightly inhibits the action of proteolytic enzymes. It is suggested that the so-called protein-sparing action of carbohydrates is explained in a similar way. W. D. H.

**The Nerve Control of the Thyroid Gland.** JESSIE MOORE RABE, JOHN ROGERS, G. G. FAWCETT, and S. P. BEEBE (*Amer. J. Physiol.*, 1914, 34, 72—80).—Stimulation of the vagus of one side

produces on that side of the thyroid gland a loss of iodine which is sufficiently marked to lead to the conclusion that the organ is, in part, under nervous control. W. D. H.

**Calcium Metabolism after Thyro-parathyroidectomy.** F. T. STEWART, OLAF BERGEIM, and P. B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xlvii—xlvi).—In a patient after removal of thyroid and parathyroid, there was retention of calcium, and a small amount only in the urine. The calcium in the blood was also less than normal. The patient survived the operation thirty-nine days, but tetany did not occur. W. D. H.

**The Influence of Early Removal of the Thyroid and Parathyroid Glands on Nitrogenous Metabolism in the Sheep.** ANDREW HUNTER (*Quart. J. expt. Physiol.*, 1914, 8, 23—32).—Sheep deprived of their thyroid at an early age, and later of the parathyroids, excrete more nitrogen and rather more purine derivatives than normal; they are liable to succumb very early to inanition; they may fail to exhibit a high output of ammonia, and elimination of acetoacetic acid in hunger acidosis. The urine is usually alkaline, and contains more creatine than creatinine. There is no evidence of diminished oxidative power, but they have a sugar tolerance above the normal. W. D. H.

**Comparative Chemistry of Muscle: the Partition of Non-protein Water-soluble Nitrogen.** D. WRIGHT WILSON (*J. Biol. Chem.*, 1914, 17, 385—400).—The observations were made on extracts of the muscle of lampreys, limulus, and various shell-fish. Lamprey muscle contains a minimum of total extractive nitrogen, most of which is non-amino-nitrogen. The amino-nitrogen is only 4% of the total extractive nitrogen; in the clam and scallop this figure rises to over 50%. In the lamprey, as in other vertebrates, most of the amino-nitrogen is precipitable by phosphotungstic acid; in limulus about half is so precipitable, but in the lower forms the mono-amino-acid fraction is largely in excess. Lamprey muscle contains creatine; invertebrate muscle does not, but among the substances identified was betaine. W. D. H.

**Tricalcium Phosphate as a Bone-former for Human Infants.** ERNST SCHLOSS and LEONHARD FRANK (*Biochem. Zeitsch.*, 1914, 60, 378—394).—Experiments were carried out on two infants, one on a diet of human milk, and the other on a humanised milk (made by the method of Schloss). In the former case there was a normal nitrogenous metabolism, but the calcium and phosphorus retention were sub-normal. The addition of cod-liver oil alone caused an increased excretion of nitrogen in the urine and of alkali in the faeces, but a slight improvement in the phosphorus and calcium balance. The further addition of tricalcium phosphate caused a marked improvement in the nitrogen balance, and diminished the alkali excretion, and caused, furthermore, a very marked retention of calcium and phosphorus. When the medication was stopped,

the nitrogen metabolism became worse, and the alkali excretion increased, but the calcium metabolism was better than in the preliminary period before administration of the phosphate, and the phosphorus metabolism, relatively to the nitrogen metabolism, was also better. Similar results were obtained with the child on the artificial diet. S. B. S.

**Creatine- and Creatinine-free Foods.** RITA K. CHESNUT (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xli).—Creatine and creatinine are absent in crabs, lobsters, shrimps, clams, oysters, scallops, caviare, calves' brains, sweetbreads, and milk. In bloater-paste there is 0.12, in anchovy paste 0.085, in whitefish 0.19, and in halibut 0.36% of creatinine. W. D. H.

**Does a Destruction of Adrenaline by Iodine Occur in the Body?** ERNST FREY (*Arch. expt. Path. Pharm.*, 1914, **76**, 65—88).—The experiments recorded on rabbits and frogs show that a combination of iodine and adrenaline is formed in the body which renders the latter substance physiologically inactive as regards blood pressure, glycosuria, and the pupil. This occurs when iodine or iodine salts are given. Whether the salts are split up, and free iodine combines with the adrenaline in the circulation, is left uncertain, because of the difficulty of estimating iodine in the blood. Serum containing high concentrations of iodine destroys adrenaline. W. D. H.

**Chicken Fat. VI. The Factors Influencing the Acid Value of the Crude Fat.** M. E. PENNINGTON, J. S. HEPBURN, and E. L. CONNOLLY (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xliiv).—The acid value is an accurate measure of the decomposition of the fat. The hydrolysis is retarded by a low temperature. A large amount of fat in the body is usually accompanied by a low acid value. The degree of saturation of the fatty acids as measured by the iodine value, and the titre of the insoluble fatty acids, seem to be without influence on the acidity. W. D. H.

**Carotin; the Principal Natural Yellow Pigment of Milk Fat; its Relations to Plant Carotin and the Carotin of the Body Fat, Corpus Luteum and Blood Serum. I. The Chemical and Physiological Relation of the Pigments of Milk Fat to the Carotin and Xanthophylls of Green Plants.** LEROY S. PALMER and C. H. ECKLES (*J. Biol. Chem.*, 1914, **17**, 191—210).—The fat of cow's milk owes its yellow colour to the yellow pigments which accompany chlorophyll in all green plants; of these, xanthophyll, and more especially carotin, are the most important. The pigment is not made in the animal body, but is derived entirely from the food; fresh green grass contains most, and gives the highest coloured milk fat. There is a difference in breed, but this is not so important a factor as supposed. The highest colour is found in the colostral fat. W. D. H.

**Carotin. II. The Pigments of the Body-fat, Corpus Luteum, and Skin Secretions of the Cow.** LEROY S. PALMER and C. H. ECKLES (*J. Biol. Chem.*, 1914, **17**, 211—221).—The yellow lipochrome in the three situations mentioned is identical with that in butter-fat, and consists principally of carotin associated with one or more minor xanthophyll constituents in some cases. They are derived from the food. Jersey and Guernsey cows eliminate the pigment more slowly, hence the body fat is never highly coloured. On rations devoid of carotin and xanthophyll, the body-fat is devoid of colour. In the new-born Jersey calf, the blood is free from the pigments, and the body-fat is only faintly tinged.

W. D. H.

**Carotin. III. The Yellow Lipochrome of Blood-serum** LEROY S. PALMER and C. H. ECKLES (*J. Biol. Chem.*, 1914, **17**, 223—236).—This pigment is the same as in milk-fat, body-fat, etc., in cows, and is derived from the food in the same way. It is in the blood firmly combined with an albumin; the name *caroto-albumin* is suggested. It is doubtful whether this chromo-protein plays any part in respiration. In milk a corresponding compound with lactalbumin is probably present.

W. D. H.

**Carotin. IV. The Fate of Carotin and Xanthophylls during Digestion.** LEROY S. PALMER and C. H. ECKLES (*J. Biol. Chem.*, 1914, **17**, 237—243).—Carotin is assimilated from the food of the cow in preference to xanthophylls, because of its greater stability towards digestive juices. The latter are more soluble in bile than carotin, which probably accounts for their appearance in the fat of the blood. The xanthophylls do not appear to combine with proteins as carotin does.

W. D. H.

**Carotin. V. The Pigments of Human Milk Fat.** LEROY S. PALMER and C. H. ECKLES (*J. Biol. Chem.*, 1914, **17**, 245—249).—The fats of human milk have the same pigment as in cow's milk, but there is more xanthophyll. The colostrum is also more pigmented; and the pigment of the body fat is probably the same.

W. D. H.

**Lactochrome, the Yellow Pigment of Milk Whey; its Probable Identity with Urochrome.** LEROY S. PALMER and LESLIE H. COOLEDGE (*J. Biol. Chem.*, 1914, **17**, 251—263).—The yellow pigment of the whey of milk is different from that of the milk-fat. It gives reactions which are identical with those of urochrome. Urochrome may be transformed by action of acetaldehyde into a pigment resembling urobilin, as Garrod stated. The authors do not agree with Dombrowski's view that it is a protein decomposition product.

W. D. H.

**The Schardinger Formaldehyde-Methylene Blue and Other Ferment Reactions as Applied to Goat's Milk.** W. WEDEMANN (*Biochem. Zeitsch.*, 1914, **60**, 330—343).—Goat's milk does not decolorise the Schardinger reagent, either when fresh or when

some days old; 1% hydrogen peroxide solution is only decomposed to a very slight extent by fresh unboiled goat's milk, which contains, therefore, only a small amount of catalase. The reagents of Rothenfuss and of Storch, and the benzidine reagent, are decolorised by goat's milk in the same way as by cow's milk. No difference in the behaviour towards the Schardinger reagent could be detected between the first and last milkings, both from suckling and non-suckling goats, or from animals which had aborted. The cream of goat's milk is also without action on the reagent.

S. B. S.

**The Origin and Character of the Protein of Exudates which is Precipitated by Dilute Acetic Acid.** K. UJIHARA (*Biochem. Zeitsch.*, 1914, 61, 55—80).—Transudates of serous membranes produced by experimental methods contain no protein precipitable by acetic acid. It is, however, always present in experimental exudates. It is found in the urine in inflammatory conditions produced experimentally (by uranium salts), but not in cases of simple stasis in the kidneys. In normal gastric and intestinal juices and transudates of the alimentary tract it is always absent, although it is present in the exudates. Its amount bears no relationship to that of the pseudoglobulin, but there appears to be an intimate relationship to the fibrinoglobulin. In normal blood-serum, the protein precipitable by acetic acid is absent, but there are indications in blood-serum of animals with fever produced experimentally. It can be extracted by saline and water from almost all organs, and is found mixed with the transudate at the point of inflammation. It appears, therefore, that the protein content of an exudate is not derived only from the blood as a result of a change in the permeability of the capillary walls, but from juices issuing from the point of inflammation of tissues. The protein precipitable by acetic acid, which can be extracted from tissues, can be filtered through a Berkfeld filter. It appears to consist chiefly of a fibrinoglobulin mixed with a small quantity of euglobulin.

S. B. S.

**Variations in the Hydrogen-ion Concentration of the Urine of Man Accompanying Fasting, and the Low- and High-Protein Regeneration Periods.** PAUL E. HOWE and P. B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xlviii).—The man had a fast of seven days, then four days low-protein feeding, then five days high-protein feeding. The hydrogen-ion concentration rose during the first two days of the fast, and then remained stationary; it fell gradually on the low-protein diet, and continued to fall until the last two days of the experiment, when it returned to normal. There was no direct relation between the hydrogen-ion concentration and the ammonia output.

W. D. H.

**Diuresis.** DOUGLAS COW (*J. Physiol.*, 1914, 48, 1—17).—The mucous membrane of the stomach, and small intestine (especially the duodenum), contains a diuretic substance which can be extracted



with water or salt solution, especially if acidified. These extracts lose their activity by keeping, but not by boiling. Normal saline injected into a vein causes an immediate, slight, and transient diuresis; but the extract referred to produces not only this effect, but a delayed diuresis comparable to what occurs when water is given by the mouth. It is suggested that the delayed effect of water drunk is due to the water taking up the specific substance from the gastro-intestinal tract, which is then absorbed.

W. D. H.

**The Specific Rôle of Foods in Relation to the Composition of the Urine.** N. R. BLATHERWICK (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xl—xli).—Men were placed on a fixed ration, to which single articles of food were then added. Potatoes, oranges, bananas, apples, raisins, and other vegetables reduce the hydrogen-ion concentration and ammonia in the urine. Cranberries, plums, and prunes contain organic acids which are not easily burnt, and so lead to increase of urinary acidity. Benzoic acid produces the same result. When the hydrogen ion concentration is greater than  $1 \times 10^{-7}$ , uric acid is precipitated. The average hydrogen ion concentration of thirty specimens of urine from vegetarians was 6.63, as compared with 6.03 for normal urines.

W. D. H.

**The Nitrogen Excretion of Fasting Sheep.** ANDREW HUNTER (*Quart. J. expt. Physiol.*, 1914, 8, 13—20).—Tables are presented of the distribution of nitrogen in urea, uric acid, purine bases, creatine and creatinine, ammonia, etc., in normal fasting sheep.

W. D. H.

**Excretion of Kynurenic and Uric Acids in Dogs.** ANNIE HOMER (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, 48, ii—iii).—Feeding experiments show that dogs excrete an appreciable quantity of uric acid, contrary to the general belief. The amount of kynurenic acid eliminated is increased by giving tryptophan, but the relationship of the tryptophan administered and the kynurenic acid in the urine is not a simple one; the age and size of the dog influence the result. The direct formation of the one substance from the other involves the disruption of the pyrrole ring of an indole nucleus, and then the introduction of an extra carbon atom to form a quinoline compound. It is therefore possible that kynurenic acid is not formed directly from tryptophan, but it may result from more obscure metabolic processes induced by the administration of the tryptophan. In estimating kynurenic acid by Capaldi's method, it is contaminated with uric acid. On a meat-free diet traces only of both acids occur in the urine. The presence of kynurenic acid does not interfere with the estimation of uric acid.

W. D. H.

[The Relationship of] **Acidosis to Severe Muscular Work.** FRITZ SCHWYZER (*Biochem. Zeitsch.*, 1914, 60, 310).—The case is quoted of a youth who, during winter sports in Switzerland,

produced acetone in urine when on a sufficient diet. This effect is ascribed to the loss of sodium chloride in the sweat, which leads to abnormal metabolism. S. B. S.

**Albuminuria Following the Ingestion of Phenolphthalein.** J. L. HYDRICK (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxxvi—xxxvii).—Doses of 1—2 grains of phenolphthalein in man produced albuminuria of varying degrees; traces of the drug given were also found in the urine. In cats this did not occur. The sodium salt acts as a purgative, irritating the mucous membrane of the intestine and stimulating the nervous mechanism which controls peristalsis. W. D. H.

**Beriberi. XI. Function of Vitamines in Carbohydrate Metabolism.** CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1914, 89, 378—380. Compare this vol., i, 455).—The appearance of beriberi occurs the sooner the more food rich in carbohydrates is administered. The addition of carbohydrates to a standard diet hastens the appearance of beriberi, and this shows that the vitamins play an active part in carbohydrate metabolism. The influence of the vitamins is more marked in the katabolism of starch than in that of other food constituents. R. V. S.

**Synthetic Antigens for the Meicostigmin Reaction for Malignant Growths. IV. Simple and Mixed Glycerides of Myristic, Linolic and Ricinolic Acids.** GUIDO IZAR (*Biochem. Zeitsch.*, 1914, 60, 320—329).—The majority of the simple glycerides of the above acids give a positive meicostigmin reaction with sera of tumorous individuals. The magnitude of the reaction is smaller than that obtained by the acids themselves, and certain of the glycerides are inactive. The mixed glycerides are also generally active, the  $\alpha\alpha$ -diglycerides being more active than the  $\alpha\beta$ -derivatives. Of the triglycerides, the most active were those in which linolic and ricinolic acid residues occupied both the  $\alpha$ -positions.

S. B. S.

**Diabetes. I. Theory of Diabetes, with Consideration of the Probable Mechanism of Antiketogenesis and the Cause of Acidosis.** A. I. RINGER (*J. Biol. Chem.*, 1914, 17, 107—119).—It is well known that carbohydrates prevent acidosis, and lessen it when present. In some way dextrose prevents the formation of the acetone substances from fat; this is spoken of as antiketogenesis. By comparing the action in this direction of dextrose and gluconic acid, the conclusion is drawn that the action of the former is due to its aldehyde radicle; in the oxidation of  $\beta$ -hydroxybutyric acid to acetoacetic acid, the point of attack must be other than the  $\beta$ -carbon. The rôle of dextrose is to combine with the  $\beta$ -hydroxybutyric acid, and so change its configuration that it no longer yields acetone substances. There must therefore be enough carbohydrate in the diet to combine with the  $\beta$ -acid, and, what is more essential, the individual must be able to accom-

plish the "glucoside union" of the two. It is the latter faculty which is lacking in the diabetic person. The failure to form glycogen, with the consequent hyperglycæmia, the failure to burn dextrose, and the disturbance in the combustion of the lower fatty acids which are seen in diabetics, are all explicable on this theory.

W. D. H.

**A Peculiar Form of Glycosuria.** A. LOEWY and S. ROSENBERG (*Biochem. Zeitsch.*, 1914, **61**, 189—190).—Combined administration to dogs of pituitary substance or thyroid with moderate doses of morphine produced hyperglycæmia and glycosuria. Similar results were not obtained by a combination of the alkaloid with testicular or ovarian substance.

S. B. S.

**Formation of Dextrose from Citric Acid in Diabetes Mellitus and Phloridzin Glycosuria** ISIDOR GREENWALD (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxxiv).—The administration of sodium citrate to phloridzinised dogs, and in a case of diabetes mellitus, increases the excretion of dextrose, corresponding with a complete conversion of the six carbon atoms of citric acid into that substance.

W. D. H.

**Glycollaldehyde in Phloridzinised Dogs.** R. T. WOODYATT (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxix).—Glycollaldehyde was prepared from dihydroxymaleic anhydride, and given in doses of 5, 6, and 10 grams daily to fully phloridzinised dogs. This caused a rise in the sugar excreted, and also in the nitrogen, so that the D:N ratio remained practically the same.

W. D. H.

**The Influence of Inulin on the Output of Dextrose in Phloridzin Diabetes.** HOWARD B. LEWIS and EDWARD M. FRANKEL (*J. Biol. Chem.*, 1914, **17**, 365—367).—Inulin administered to phloridzinised dogs gives rise to no dextrose. Since lævulose under the same conditions is largely excreted as dextrose, it is not probable that inulin is converted into lævulose or into any substance which can give rise to dextrose in the diabetic organism.

W. D. H.

**Toxic Action of Phloridzin in Experiments with a Partly Excluded Liver (Eck's Fistula). The Formation of Urea.** P. ERDÉLYI (*Zeitsch. physiol. Chem.*, 1914, **90**, 32—59).—Phloridzin given to dogs with an Eck's fistula produces convulsive seizures; the body temperature remains normal even after exposure to great cold, or may rise during the convulsions; urobilin occurs in the urine, and sugar may entirely disappear from the blood, although the urine contains plenty; the production of acetone substances is diminished, so also is the output of urea. The muscles, being sugar-free, must utilise some other substance as a source of energy, and may thus lead to an abnormal form of nitrogenous katabolism, of which the drop in urea formation is an indication.

W. D. H.

**Toxic Conditions due to Phloridzin and their Relation to Complete Carbohydrate Starvation of the Organism and to the Liver.** FRITZ BURGHOLD (*Zeitsch. physiol. Chem.*, 1914, **90**, 60—74).—The toxic symptoms due to phloridzin and hunger are more easily elicited in dogs with an Eck's fistula; the whole organism becomes, in fistulous animals, extremely poor in carbohydrates, and the blood sugar sinks in amount until it disappears, the carbohydrate depôts of the body (liver, etc.) being exhausted. The time when sugar disappears from the blood is synchronous with the appearance of the signs of poisoning, and the epileptiform convulsions may be temporarily relieved by the injection of dextrose, or by abundant nutriment; the time from the beginning of the experiment until coma sets in is directly dependent on the nutritive condition of the animal. W. D. H.

**Metabolism in Osteitis Deformans.** J. C. DA COSTA, E. H. FUNK, OLAF BERGEIM, and P. B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, **17**, xxx).—In *O. deformans* there is retention of calcium, magnesium, and phosphorus, with a pronounced loss of sulphur. This indicates excess of osteoid formation and absorption of the highly sulphurised organic matrix. This is the reverse of what occurs in osteomalacia. W. D. H.

**The Elimination and Retention of Arsenic as Determined by the Koch-Norton Method.** R. ADAMS DUTCHER and MATTHEW STEEL (*J. Amer. Chem. Soc.*, 1914, **36**, 770—773).—Arsenious oxide was administered to two dogs, one of which was killed after twenty-four hours, and the other after twenty days; the distribution of the arsenic was tested by the method of Norton and Koch (*A.*, 1905, ii, 858). In both cases the largest quantity of the arsenic present in the body was found in the muscle, liver, and intestine. In the case of the second experiment, elimination of the arsenic ceased in about fifteen days, when approximately 71% had passed into the urine, none being found in the fæces. D. F. T.

**Retention of Nitrogen after Feeding on Ammonium Chloride.** E. GRAFF (*Zeitsch. physiol. Chem.*, 1914, **90**, 75—107).—The plan of the experiments was the same as in previous work by the author, and the results are presented in twenty pages of tables. They were conducted on men, dogs, and pigs. It is necessary, in order to obtain the retention of nitrogen previously noted, that care should be exercised that the concentration of ammonia in the blood should never reach a high level, otherwise toxic effects may set in; the ammonium salt should be given in very dilute solution, and in small quantities at intervals of from one to three hours. W. D. H.

**The Detection of Mercury in Urine and Organs, and the Behaviour of Certain Insoluble Mercury Compounds in the Organism.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1914, **61**, 27—40).—The author describes certain modifications in his method for detect-

ing mercury in the urine, etc. (A., 1911, ii, 771, 934), the chief of which consists in the method of destruction of the organic matter by evaporation on the water-bath with potassium chlorate and hydrochloric acid. Experiments were carried out on rabbits, to which were administered doses of various mercuric compounds (calomel, paranucleate, cholate with tannalbin, etc.), with the object of ascertaining the smallest doses which gave rise to detection of mercury in the urine. The conclusion was drawn that this factor depends, to a large extent, on the diet of the animal, and it is suggested that in mercury medication those diets should be avoided which give rise to mercaptan. S. B. S.

**Absorption and Fate of Tin in the Body.** WILLIAM SALANT, J. B. RIEGER, and E. L. P. TREUTHARDT (*J. Biol. Chem.*, 1914, 17, 265—273).—After the subcutaneous injection of soluble tin salts, the metal is found in the skin, a little in the liver, and excretion occurs mainly by the gastro-intestinal tract; the kidneys play a subordinate, although an important, rôle. Elimination is slow. Under certain conditions, absorption of tin may occur in the alimentary canal. W. D. H.

**Metabolism During Narcosis.** E. PAWEL (*Biochem. Zeitsch.*, 1914, 60, 352—369).—Paracetaldehyde in small, hypnotic doses slightly diminishes the amount of sugar in the blood, but in doses sufficient to cause general narcosis, it causes a rise in the blood-sugar, and eventually glycosuria. The smaller doses, furthermore, have no action on the nitrogenous metabolism, whereas larger doses increase the nitrogen output; the latter also cause a diminution of the body temperature and of the respiratory quotient. The conclusion is drawn that paracetaldehyde, in doses sufficient to produce general narcosis, causes a disturbance of the oxidative processes of the organism. The results are in accordance with those obtained by Oppermann with other narcotics. S. B. S.

**Physiological Action of *photo*-Acetophenine.** D. LO MONACO (*Ann. Chim. Applicata*, 1914, 1, 189—195).—The author has investigated the physiological properties of the synthetic alkaloid, *photo*-acetophenine,  $C_{18}H_{18}N_2$  (compare Paternò and Maselli, A., 1912, i, 295; this vol., ii, 321). This compound can be readily administered, since it forms soluble salts, and its hypnotic and markedly poisonous actions are similar to those of acetophenone itself, which is no longer employed, owing to the uncertainty of its effect and to the irritation it produces in the stomach. A striking feature of the new alkaloid is its extremely pronounced bitterness, which can be detected in 0.0001% solution; the most bitter alkaloid previously known was the monochloro-derivative of strychnine, which cannot be tasted in less concentration than 0.006%. The alkaloid is evidently formed by the union of two acetophenone residues by means of a nitrogenated group, the nature of the linking being, however, unknown. T. H. P.

**The Metabolic Relationship of the Acetone Substances.** W. McK. MARRIOTT (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxxii).—When acetoacetic acid is injected parenterally into young pigs, there is an increase of this acid, and also of  $\beta$ -hydroxybutyric acid, in the blood; the latter passes into the urine partly in the dextrorotatory form. If the latter acid is injected, there is a slight increase of the acetoacetic acid in the blood, but little or none in the urine. The optically inactive acid is more readily burnt than the lævorotatory form. If butyric acid is injected, an increase of the acetoacetic acid in the blood occurs, followed by an increase in  $\beta$ -hydroxybutyric acid. W. D. H.

**The Non-antigenic Properties of Racemised Egg-albumin.** CARL TEN BROECK (*J. Biol. Chem.*, 1914, 17, 369—376).—Antigens must be proteins; the ease with which they are broken down in some cases is proportional to their antigenic properties; compare, for instance, albumin with the conjugated proteins. Gelatin, however, is easily digestible, but fails to act as an antigen. After digestion, the cleavage products are non-antigenic. Dakin's racemised proteins are resistant to enzymic cleavage, and do not participate in metabolism when given by the mouth or under the skin. Racemised casein did not sensitise guinea-pigs, but good sensitisation with natural casein is also difficult; experiments were therefore tried with racemised egg-albumin; here also a negative result followed. In rabbits, the complement-binding and precipitin reactions were studied, but little or no antigenic properties of the racemised optically inactive egg-albumin were found. W. D. H.

**Formation of Creatine from Choline and Betaine** OTTO RIESSER (*Zeitsch. physiol. Chem.*, 1914, 90, 221—235).—The author has previously (this vol., i, 1135) expressed the view that creatine is formed by a synthesis of choline or its oxidation product, betaine, and urea. This hypothesis is confirmed by injecting choline or betaine into rabbits, and finding in the majority of experiments a rise in creatinine in the urine. W. D. H.

**Carbohydrate Metabolism. III. The Influence of Hydrazine on the Storage of Glycogen in the Organism and on the Composition of Blood.** FRANK P. UNDERHILL (*J. Biol. Chem.*, 1914, 17, 293—294).—Hydrazine salts cause hypoglycæmia and reduce the hepatic glycogen. This is not due to transference of glycogen to the muscles; the glycogen in these is also reduced, or may disappear. The solids of the blood may be very high, although the ash content is subnormal. W. D. H.

**Carbohydrate Metabolism. IV. Do Hydrazine Derivatives Show the Typical Hydrazine Effect on the Blood Sugar?** FRANK P. UNDERHILL (*J. Biol. Chem.*, 1914, 17, 295—298).—Hydrazine inhibits pancreatic diabetes, but is very toxic. Other hydrazine compounds were therefore investigated, but only a few (methyl-, phenyl-, phenylmethyl-, and diphenyl-hydrazine, and

-semicarbazide) could be employed, owing to the great insolubility of these substances. None had the effect on carbohydrate metabolism which hydrazine exerts.

W. D. H.

**Carbohydrate Metabolism. V. The Disappearance of Sugar from Solutions Perfused through the Heart of the Normal Rabbit, and of Animals Subjected to Inanition and to the Action of Hydrazine.** FRANK P. UNDERHILL and A. L. PRINCE (*J. Biol. Chem.*, 1914, **17**, 299—304).—Hydrazine given subcutaneously causes a greater quantity of sugar to disappear from a solution perfused through the heart than occurs in the heart of normal animals in a comparable nutritive condition. The nutritive condition, and hence the amount of glycogen in the tissues, is a factor to be reckoned with, as is shown by experiments on rabbits during inanition. The amount of sugar which disappears is but little influenced by the force of the heart-beat. The experiments fail to explain the cause of diminution of blood-sugar after administration of hydrazine.

W. D. H.

**Iodosobenzoic Acid.** FRIEDRICH JAHN (*Arch. expt. Path. Pharm.*, 1914, **76**, 16—39).—Iodosobenzoic acid has not the power to inhibit the agglutinating action of abrin. Iodosobenzoic acid in concentrations of 1 in 10,000 inhibits the growth of *Bacillus coli*, whereas iodobenzoic acid, one hundredfold more concentrated, has not this power. The lethal dose of the former acid in the frog is 15 to 17 mg. per 100 grams of body-weight; iodobenzoic acid is at least ten times less toxic. On the frog's heart, iodosobenzoic acid is negatively urotropic and chronotropic, and its action is irreversible; blood weakens its action. The pharmacodynamical limit value is about 0.001%. Iodobenzoic acid has a feeble action here also, and the effect is reversible. On isolated frog's muscle irritability is destroyed, and the same difference of action between the two acids is seen. Iodosobenzoic acid has no effect on isolated frog's nerve, but iodobenzoic acid in ten times greater concentration destroys conductivity. In rabbits the fatal dose of iodosobenzoic acid administered intravenously is 0.15 to 0.2 gram per kilo. of body-weight; convulsions and pauses in breathing occur before death. Extirpation of the thyroid gland has no effect on the result. Iodine in organic and inorganic union is found in the urine; the iodosobenzoic acid is probably hydrolytically split, and salicylic acid formed. A hydrolytic enzyme which acts thus is probably present in rabbit's urine, but not in human urine.

W. D. H.

**Purine Substances of Human Blood and the Action of 2-Phenylquinoline-4-carboxylic Acid (Atophan).** ROBERT BASS (*Arch. expt. Path. Pharm.*, 1914, **76**, 40—64).—Atophan produces a true increase in the excretion of uric acid by the kidneys, and the view taken is that this is not due to an increased new formation of the acid, but to an entrance into the circulation of certain unknown uric acid precursors from "purine depôts," although the

rapid excretion from the kidneys may not reveal any increase of uric acid in the blood. Uric acid itself, however, does not appear to be the only toxic agent towards joints in gouty conditions.

W. D. H.

**Biological Reactions of So-called Proteoses of Seeds.** H. GIDEON WELLS and THOMAS B. OSBORNE (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxvi—xxvii).—The proteoses of seeds act as antigens, and produce anaphylaxis. The proteoses obtained by hydrolysis of animal proteins are destitute of such power, or nearly so. The designation of the seed proteins as proteoses is therefore incorrect.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Methods in Soil Bacteriology. VII. Ammonification and Nitrification in Soil and Solution.** F. LÖHNIS and H. H. GREEN (*Centr. Bakt. Par.*, 1914, ii, **40**, 457—479).—An account of further experiments on the determination of factors influencing the rate and intensity of nitrogen metabolism under various laboratory conditions. In soil as well as in solution tests the following factors are stated to be of predominant importance: (a) nature and quantity of material used as substrate; (b) concentration and distribution of the substrate in the medium; (c) aeration; (d) diffusion, absorption, destruction, or evaporation of metabolic products; (e) reaction of the medium; (f) temperature; (g) duration of the experiment.

In ammonification tests, the concentration of material undergoing decomposition, and more particularly its distribution in the medium, is of consequence, while aeration plays a part. In nitrification tests in sand or solution, the concentration of ammonia is of vital importance, but this is largely reduced, if not completely eliminated, in soil tests. The transformation of nitrite into nitrate is adversely affected by the use of magnesium carbonate or by high temperatures (30—35°). Neutral chalk should always be used in place of basic magnesium carbonate. H. B. H.

**Hereditary Tolerance for Poisons in Inferior Organisms (the Lactic Ferment).** CHARLES RICHET (*Compt. rend.*, 1914, **158**, 764—770).—A comparison of the activities of lactic ferments repeatedly grown on pure milk and on milk containing various toxic substances, when sown on to pure milk and milk containing these same toxic substances at varying concentrations. The activity was measured by the acidity produced in the milk. The results lead to the following conclusions. A ferment which has

been grown on a medium containing a substance different from its normal medium becomes in a few days accustomed to this substance, so that in liquids containing this abnormal substance it grows more vigorously than the unaccustomed ferment. The ease with which a ferment becomes accustomed to a toxic substance varies with the nature of the substances. Of the substances tried, tolerance for arsenic is most readily produced, the tolerance being very rapidly established, and the maximum being reached at the end of eight days. The ferment becomes accustomed, not only to the toxic substance, but also to the particular degree of concentration of the substance. This tolerance rapidly disappears on growing the ferment for twenty-four hours on pure milk. W. G.

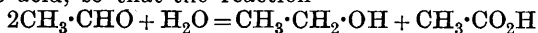
**Cell-free Fermentation of Polyhydroxymonocarboxylic Acids.** A. VON LEBEDEV (*Ber.*, 1914, 47, 965—967).—The author mentions that, in connexion with his recent work (this vol., i, 463), he has been partly anticipated, so far as glyceric and gluconic acids are concerned, by Neuberg (compare A., 1911, ii, 320, 520).

J. C. C.

**Is the Enzyme Theory of Fermentation to be Limited?** EDUARD BUCHNER and SIEGFRIED SKRAUP (*Ber.*, 1914, 47, 853—870).—An unfavourable review of Rubner's conclusions as to the existence of two concurrent processes, a vitalistic and an enzymatic, in the fermentation of sugar. Rubner's method of following the progress of fermentation by measurement of the heat-formation is criticised, and his experimental results are otherwise interpreted.

D. F. T.

**Alcoholic Fermentation. VI. Nature of the Reduction of Acetaldehyde by Living Yeast.** S. KOSTYTSHEV (*Zeitsch. physiol. Chem.*, 1914, 89, 367—372. Compare Kostytshev and Hübner, A., 1912, ii, 860; Neuberg and Kerb, this vol., i, 118).—Yeast produces from acetaldehyde equimolecular quantities of ethyl alcohol and acetic acid, so that the reaction



must occur.

R. V. S.

**Function of Glycogen in Fermentation by Living Yeast.** HANS EULER (*Zeitsch. physiol. Chem.*, 1914, 89, 337—344).—The author's experiments recorded in this paper do not lead him to any certain conclusion as to the function of glycogen as an intermediate product in fermentation, but they show that it is not the intermediate product responsible for the difference between the percentage diminution of rotation and the percentage of carbon dioxide evolved (compare Euler and Johansson, A., 1912, ii, 377).

R. V. S.

**Photochemical Reductions. I. The Conversion of the Nitro- into the Amino-group.** CARL NEUBERG and ERNST WELDE (*Biochem. Zeitsch.*, 1914, 60, 472—479).—When nitrobenzene is added to a yeast fermentation, an appreciable quantity is reduced to

aniline. Only minute traces of the latter were produced in control experiments in which the yeast had been killed. S. B. S.

**Chemical Composition and Formation of Enzymes. X.** Influence of Temperature and of Access of Air on the Formation of Invertase. HANS EULER and HARALD CRAMER (*Zeitsch. physiol. Chem.*, 1914, 89, 272—278. Compare this vol., i, 237).—Following the hypothesis that enzyme formation is closely correlated with the formation of fresh protoplasm, it is proved that invertase is produced much more rapidly at 16° than at 39°, although, in course of time, the quantity of enzyme produced is about the same in each case. Enzyme formation is not accelerated by an increased access of oxygen to the growing yeast: actually, a slight retardation is observed. The addition of hydrogen peroxide has an accelerating effect on enzyme formation.

Experiments with *S. thermantitonus* indicate that the rate of formation of enzyme in dextrose or sucrose solution is the same. E. F. A.

**Chemical Composition and Formation of Enzymes. XI.** HANS EULER and K. G. DERNBY (*Zeitsch. physiol. Chem.*, 1914, 89, 408—424. Compare this vol., i, 237).—The investigation of the effect of various methods of prior treatment on the amount of the enzymes in yeast has been extended to those proteoclastic enzymes which occasion autolysis. In order to measure these, the yeast was mixed with an equal quantity of glycerol, and after leaving for three hours at the ordinary temperature, chloroform water was added. The mixture was incubated at 37°, and at stated periods the total nitrogen and the amino-acid nitrogen determined. Both of these values increase at the same rate.

Autolysis is retarded by the presence of an excess of glycerol. It is slightly accelerated by the presence of oxidising agents, such as potassium nitrate and chlorate. The addition of boiled yeast extract, stated to contain an antiprotease, slightly decreases the rate of autolysis.

Prior treatment of the yeast for forty-eight hours with Linder's nutrient solution increased the amount of autolysing enzyme (auto-protease). Alteration in the temperature of treatment had very little effect. The treatment has a similar effect on both auto-protease and zymase. The prior treatment with phosphate has no perceptible influence. Prior treatment with sodium fluoride has no marked effect, and certainly does not harm the enzyme.

Yeast fermenting in Linder's nutrient solution in presence of sodium fluoride takes up less nitrogen than in its absence. Both fermentation and nitrogen assimilation are retarded. E. F. A.

**Fermentations with Yeast in the Absence of Sugars. XIV.** Carboxylase. C. NEUBERG and P. ROSENTHAL (*Biochem. Zeitsch.*, 1914, 61, 171—183).—Experiments are described which demonstrate the great stability of the carboxylase of yeast as compared with the zymase. Permanent preparations of the latter could be obtained by precipitation of the yeast juice with alcohol and ether,

or by acetone, even after the juice had been warmed to 50°, under conditions in which the zymase is destroyed. Experiments are described which indicate that an appreciable amount of heat is developed during the carboxylase reaction. Carbon dioxide is evolved from oxalacetic acid in the presence of chloroform. Hydroxypyruvic acid is also acted on by carboxylase, and glycoll-aldehyde formed in the reaction was isolated in the form of its osazone (m. p. 169°). S. B. S.

**Fermentations with Yeast in the Absence of Sugars XV. The Formation of *n*-Propyl Alcohol by Fermentation of  $\alpha$ -Ketobutyric Acid.** C. NEUBERG and JOH. KERB (*Biochem. Zeitsch.*, 1914, **61**, 184—186).—It has been previously shown (A., 1913, i, 231) that  $\alpha$ -ketobutyric acid ferments with yeast, but only small quantities of propaldehyde could be isolated as a result of the action. It is now shown that the aldehyde is reduced in the presence of yeast to the corresponding alcohol, which was isolated mixed with ethyl alcohol. The authors have succeeded, however, in preparing from this mixture propyl naphthylcarbamate, which, after recrystallising from light petroleum, melted at 73°. S. B. S.

**The Union of Poisons with Protoplasm. Disappearance of the Poison from the Solution.** TH. BOKORNY (*Pflüger's Archiv*, 1914, **156**, 443—530).—A detailed account of the concentrations of various poisons which affect yeast cells. The poisons employed were ammonia, soda, mineral and organic acids, metallic salts, formaldehyde, etc. The main point of the paper is expressed in the title; substances which act as poisons diminish in quantity in the fluid used, because they enter into combination with the proteins of the protoplasm. W. D. H.

**Ammonium Nitrate and Free Nitric Acid as Sources of Nitrogen for Moulds.** G. S. RITTER (*Biochem. Zeitsch.*, 1914, **60**, 370—377).—When ammonium nitrate is employed as a source of nitrogen for the growth of *Aspergillus niger*, the culture fluid becomes acid, the acidity being in certain cases due to the free nitric acid, which was directly estimated. When higher concentrations of nitrate are employed, the growth of the mould stops after a certain time, owing to the high acidity. With lower concentrations, however, the growth continues, but the amount of nitric acid diminishes after a certain time, and the high acidity is found to be due partly to oxalic acid. Direct experiment shows that in suitable concentration nitric acid can act as a source of nitrogen for *Aspergillus niger* and other moulds, and even a larger yield of mould can be obtained than when ammonium salts or other nitrates are used as a source of nitrogen supply. S. B. S.

**Relation between Composition and Structure of Organic Compounds and their Antiseptic Properties.** K. V. CHARITSCHKOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 70—76).—The author has investigated the antiseptic properties of a number of organic

compounds; these were introduced in varying quantities into nutrient gelatin, which was then seeded with spores of *Penicillium glaucum*. The cultures obtained were compared with those given by the nutrient gelatin alone, and the antiseptic powers were referred to those of pure phenol as a standard.

The antiseptic power of *p*-nitrophenol is twice that of phenol, but *p*-aminophenol shows diminished power, and picric acid exhibits scarcely any antiseptic property.  $\alpha$ -Naphthol is twice as active as  $\beta$ -naphthol.

Experiments with *Penicillium glaucum*, *Bacillus amylobacter*, and *Merulius lacrimans* show that both naphthenic and polynaphthenic acids, and, to a less degree, the salts of the former acids, show antiseptic properties. On the other hand, cyclohexanebenzoic [*? cyclohexanecarboxylic*] acid is non-antiseptic.

With increase in molecular weight, the antiseptic power generally falls. Acids of high molecular weights and boiling points contain complex radicles, the mass of which often greatly exceeds that of the central cyclic nucleus and paralyses its action. T. H. P.

#### Glycollaldehyde as an Intermediate Product of Assimilation.

HEINRICH FINCKE (*Biochem. Zeitsch.*, 1914, **61**, 157—164).—A theoretical paper, in which the author gives reasons for assuming that glycollaldehyde is an intermediate product in the formation of sugars from carbon dioxide. A scheme is given to explain how this substance can be formed from oxalic acid, which is regarded as the first reduction product of carbonic acid, and is assumed to react with a peroxide,  $R\text{--}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ , to give a product

$R\text{--}\overset{\text{C(OH)}_2}{\underset{\text{C(OH)}_2}{\text{C}}} \text{ (I)}$ , which changes to  $R\text{--}\overset{\text{O--CH}\cdot\text{OH}}{\underset{\text{O--CH}\cdot\text{OH}}{\text{O}}} \text{ (II)}$ . From the latter hypothetical substance,  $R\text{--}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$  and  $\begin{array}{c} \text{CH}\cdot\text{OH} \\ | \\ \text{CH}\cdot\text{OH} \end{array}$  are formed, and

the latter unsaturated alcohol gives rise to glycollaldehyde. II can also condense with glycollaldehyde to give rise to hexoses or inositol.

S. B. S.

#### Toxicity of the Juice Expressed from Germinating Seeds.

S. DEZANI (*Atti R. Accad. Sci. Torino*, 1914, **49**, 425—446).—It is known that the juice expressed from germinating seeds hinders or prevents the germination of other seeds of the same plant. From his experiments on *Zea mais* the author draws the conclusion that the expressed juice does not constitute a protoplasmic poison for the seeds of the plant, and also that the toxicity does not seem to be due to salts absorbed from the juice because salts are apparently not absorbed. The catalases and oxydases of seeds poisoned in this way, however, are less active than those of healthy seeds.

R. V. S.

Action of Isolated Nitrates on the Germinating Period of *Avena sativa*. III. F. PLATE (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 161—164. Compare this vol., i, 367).—This paper describes

the action of solutions of various concentrations of the nitrates of aluminium, tin, lead, cerium, and thorium, taken separately, on the growth of seedlings. The most favourable results are obtained in the case of aluminium; cerium and thorium killed the plants at all concentrations.

R. V. S.

**The Passage of Organic Sulphate from Plant to Medium.** M. X. SULLIVAN (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xliii—xliv).—Wheat seedlings were grown on perforated aluminium disks for ten days, and the water changed every two days. The combined solutions were concentrated, and in them were found creatinine, an aldehyde with a vanillin-like odour, oily matter, and a crystalline substance containing sulphur, and resembling cystine in crystalline form and solubilities. The creatinine and vanillin were also found in the growing plant, and have passed thence to the medium; the cystine-like substance was not found in the plant.

W. D. H.

**Biological Oxidisability and Chemical Constitution.** HERBERT H. BUNZEL (*Proc. Amer. Soc. Biol. Chem.*, 1913; *J. Biol. Chem.*, 17, xxxvi).—The oxydase activities of shoots, leaves, and tubers of healthy and diseased potato plants were increased by the use of catechol, pyrogallol,  $\alpha$ -naphthol, and a number of other reagents. The para-compounds are more easily oxidised than the ortho- or meta-compounds. In some cases the meta-compounds occupy an intermediate position; in others they are the least easily oxidised.

W. D. H.

**The Gaseous Exchanges and the Variation of the Sugars and Glucosides in the Course of the Formation of the Anthocyanic Pigments in the Flowers of *Cobœa scandens*.** EDMOND ROSÉ (*Compt. rend.*, 1914, 158, 955—958).—A study of the above phenomena during the four stages of the flowers of *Cobœa scandens*, namely, (1) flower in bud, (2) green flower expanding, (3) flower at the commencement of pigment forming, (4) flower coloured violet. Experiments were made with varieties yielding respectively coloured and white flowers.

A study of the respiration shows that in the flowers of both varieties the intensity of respiration is at a maximum during the first stage, and decreases steadily as the flower develops. The respiratory quotient remains practically constant. A study of the assimilation shows that the chlorophyll exchanges are more intense than the respiratory exchanges during all the four stages, but the difference decreases progressively to the stage of complete development of the flower, when there is practically an equilibrium between the two exchanges. The intensity of assimilation and the chlorophyll content of the flower diminish from stage one to stage four. During all the stages of development a considerable quantity of oxygen is fixed, the fixation being slightly greater for the coloured than for the white variety.

A study of the variation in the sugar and glucoside content

of the flowers shows that (1) the proportion of sugar in the flower increases from stage one to stage three, and diminishes in stage four; (2) during the first three stages when there is no violet coloration there are no glucosides present. These only appear during the fourth stage during colour formation. The conclusions to be drawn from these results are in agreement with those of Combes (compare A., 1909, ii, 426; 1911, ii, 1125). During the formation of anthocyanic pigments oxygen is retained by the organs in process of reddening, there being an increase in the activity of the oxidation processes in these organs. The formation of the anthocyanin being correlative with the appearance of glucosides in the flower, the total quantity of glucosides which exist in the flower is apparently due to this anthocyanin formation. The phenomenon of coloration is apparently dependent on the luminous intensity, since this coloration does not take place in flowers kept in the dark.

W. G.

**Action of Bleaching Agents on Various Natural Colouring Matters.** R. L. TAYLOR (*J. Soc. Dyers*, 1914, 30, 85—88).—The colouring matters present in cotton, linen, and jute are not destroyed by chlorine, hypochlorous acid, or an hypochlorite when used alone, but are completely eliminated when the fibre is treated with an hypochlorite, together with chlorine or hypochlorous acid. It is probable that the fibres contain two distinct colouring matters, one destroyed by chlorine or hypochlorous acid, whilst the other is destroyed by a hypochlorite. An excess of alkali in the bleaching liquid greatly retards the bleaching action.

W. H. G.

**Plant Chemistry.** P. Q. KEEGAN (*Chem. News*, 1914, 109, 145—146).—Some very mucilaginous leaves and roots fail to give any tannin when extracted with alcohol, and have to be extracted two or three times with boiling water and the solutions evaporated down before tannin can be detected. The bark and leaves of oak, beech, and Spanish chestnut give the vanillin reaction, but do not give the iodine test for gallotannin quite satisfactorily. The varying amounts of gallotannin, or perhaps gallic acid, found in these barks is accounted for by the considerable variations in absorption of oxygen.

Leaves of the Welsh poppy, which are very mucilaginous, yielded extracts, when boiled with water, which gave decisive reactions of caffetannin.

N. H. J. M.

**Oxydases and their Inhibitors in Plant Tissues. III. Localisation of Oxydase and Catalase in Some Marine Algæ.** W. R. G. ATKINS (*Proc. Roy. Dublin Soc.*, 1914, 14, 199—206).—All the species tested were able to decompose hydrogen peroxide. Out of twenty-nine species only one gave an oxydase reaction, and six the peroxydase reaction. The colour reaction of the algæ with benzidine is also produced in boiled specimens, and hence it is not due always to an oxydase.

The change from brown to green when algæ are boiled or steamed is attributed to the reduction of the water-soluble phycophæin

present by some reducing substance liberated from a neighbouring cell.

E. F. A.

**Physico-chemical Properties of Vegetable Saps. II. The Physico-chemical Constants of the Juice of Apples and Pears.** J. ARTHUR HARRIS and ROSS AIKEN GORTNER (*Biochem. Bull.*, 1914, 3, 196—201).—In apples and pears there is a correlation between the size of the fruit and the number of seeds it produces. The size of the fruit is influenced by the number of seeds, rather than conversely. The development of the seeds influences in some way the physico-chemical properties of the sap in the developing fruit.

W. D. H.

**Chemical Constituents of Green Plants. II. Volatile Constituents of Hornbeam Leaves.** THEODOR CURTIUS and HARTWIG FRANZEN (*Annalen*, 1914, 404, 93—130. Compare A., 1912, ii, 797).—Many of the statements in the paper have been already recorded (*loc. cit.*, and A., 1912, ii, 978, 979). Propionic and butyric acids are not present in the volatile acids obtained from hornbeam leaves. The amount of  $\Delta^{\alpha}$ -hexenaldehyde is fifteen to twenty times as great as that of all other aldehydes taken together.

C. S.

**Oxydases and their Inhibitors in Plant Tissues. II. The Flowers and Leaves of Iris.** W. R. G. ATKINS (*Proc. Roy. Dublin Soc.*, 1914, 14, 157—168. Compare A., 1913, i, 1426; Keeble and Armstrong, A., 1912, ii, 673).—The distribution of peroxydase and of an inhibitor of the peroxydase reaction with chromogens in the leaves of *Iris germanica* is not materially effected by prolonged darkness.

The varieties of *Iris* include both dominant and recessive whites and yellows, related varieties having very similar oxydase contents. The general distribution of enzyme and pigment in *Iris* follows that in *Primula sinensis* (Keeble and Armstrong, *loc. cit.*). The forms with a plentiful oxydase supply usually turn a dark brown in drying, whilst those which contain inhibitors remain of a light colour.

E. F. A.

**Phytin. V. Organic Phosphoric Acid of Cottonseed Meal.** R. J. ANDERSON (*J. Biol. Chem.*, 1914, 17, 141—150).—The results obtained in previous experiments (*ibid.*, 1912, 12, 311) are confirmed. The dry acid forms a colourless syrup, and has the composition represented by the formula of inositol hexaphosphate,  $C_6H_{18}O_{24}P_6$ . The tribarium and heptabarium salts form white, crystalline powders, whilst the silver salts are amorphous, and are not readily separated.

N. H. J. M.

**Phytin. VI. Phytin in Oats.** R. J. ANDERSON (*J. Biol. Chem.*, 1914, 17, 151—163).—An organic phosphoric acid, which seems to be identical with the one found in cottonseed meal (preceding abstract), was obtained from oats. The tribarium salt was prepared and analysed. An amorphous barium salt was also obtained, which will be further investigated.

N. H. J. M.



**Phytin. VII. Phytin in Maize.** R. J. ANDERSON (*J. Biol. Chem.*, 1914, 17, 165—170).—The organic phosphorus compound in maize seems to be identical with that prepared from cottonseed meal and from oats (preceding abstract). The barium salt and the free acid were prepared and analysed. N. H. J. M.

**Experiments with Nitrogenous Manures.** E. HASELHOFF (*Landw. Versuchs.-Stat.*, 1914, 84, 1—55).—Pot experiments, in 1907, in which barley, followed by buckwheat, and oats, followed by mustard, were grown in a sandy-loam soil, to which the usual minerals were added, in addition to various forms of nitrogen-sodium nitrate and nitrite, ammonium sulphate, calcium nitrate, and calcium cyanamide. Further experiments were made in 1908—9, in which the plants were grown in loam and in sandy soils. In 1911 the nitrogenous manures included carbamide, carbamide nitrate, galalith (Siegfeld, *Zeitsch. angew. Chem.*, 1904, 17, 1816), hornmeal, etc.; and in 1912—13, guanidine and guanidine nitrate.

Ammonium sulphate, on the whole, gave results equal to those obtained with nitrates, its action being better in loam than in sandy soils. Calcium cyanamide, on the other hand, gave better results with sandy soil than with loam.

Carbamide was found to be at least equal to sodium nitrate, and gave rather better results in loam than in sandy soil. Carbamide nitrate and guanidine nitrate act similarly to carbamide, whilst guanidine was found to have a very slight effect.

Galalith, when applied to loam, gave almost as good results as sodium nitrate, whilst in the case of sandy soil it proved to be less satisfactory.

Sodium nitrite was not utilised by the crop to nearly the same extent as sodium nitrate, especially when applied in the spring.

Carbamide, carbamide nitrate, and guanidine nitrate are utilised to a greater extent when mixed with the soil than when applied as top-dressing. N. H. J. M.

**Manuring Sugar Beet with Magnesia.** F. STROHMER and O FALLADA (*Bied. Zentr.*, 1914, 43, 170—174; from *Oesterr.-ung. Zeits. Zuckerind. Landw.*, 42, 221).—The results of plot experiments showed that application of magnesium sulphate was without effect on the yield of roots and leaves and on the production of sugar. Under the influence of magnesium sulphate, the roots of the plants were found to contain a greater amount of magnesia, whilst the leaves contained less. N. H. J. M.

**A Disease of Ciders called "Verdissement."** WARCOLLIER (*Compt. rend.*, 1914, 158, 973—976).—This disease is due to the formation of an olive-green ferrous tannate, and appears generally at the commencement of the fermentation of ciders, poor in malic acid, tannin, and nitrogenous material, and rather rich in mineral matter and particularly in lime. The fermentation completely stops, although the yeast forms an abundant deposit. Such diseased ciders invariably contain nitrites, and their coloration

is due to the combination of the partly oxidised tannin with ferrous salts. The origin of these nitrites has been discovered in two cases. In the one it was introduced as nitrate in the water used to dilute the juice from the first pressing. In the other case it was found that the fresh pulp of certain varieties of cider apples exposed to the air for a few minutes after pulping contained appreciable quantities of nitrites, which were shown to be absent from the original apples. To avoid the onset of the disease it is desirable to avoid the use of water rich in nitrates, in the manufacture, and the exposure of the pulp to the air and the contact of the apparatus or iron material with the pulp or the juice. W. G.

**Adsorption Phenomena in Soils and Kaolin.** J. E. HARRIS (*J. Physical Chem.*, 1914, 18, 355—372).—It has been found that acid soils of the sandy-loam type liberate different quantities of acid when shaken up with 1*N*-solutions of different salts. The quantity increases in the order sodium chloride, potassium nitrate, sodium acetate. The quantities liberated in successive "extractions" with the different salt solutions show no tendency to approach the same limiting value, the relative differences increasing with each successive application of the solutions. These results show that the liberation of the acid is not due to double decomposition in which insoluble humic acids are involved, but to the adsorption of the base of the salt.

If the soil is treated with dilute acid, and then washed until the soluble acid is removed, its power of liberating acids from salt solutions is greatly increased. This is supposed to be due to the neutralisation of basic substances in the soil, whereby it becomes capable of removing larger quantities of base from the neutral salt solutions. When kaolin is treated in the same manner, it behaves quite similarly, and the quantities of acid set free from solutions of sodium acetate, potassium nitrate, and sodium chloride stand in the same order as they do when these solutions are subjected to the action of soil. The concentration of the acid solution used in the preliminary treatment of the soil has no appreciable influence on the subsequent acid-liberating capacity of soil, but in the case of kaolin the effect decreases with decrease in the concentration of the acid.

That the acid is not adsorbed by the soil and kaolin, and liberated again when treated with a salt solution, has been shown by experiments in which the soil and kaolin were treated with sulphuric acid, washed, and then subjected to the action of a solution of potassium nitrate. There was no evidence of the presence of sulphate in the salt solution.

To show that the base of the salt is actually adsorbed by the soil and kaolin, samples of these were treated with hydrochloric acid, and afterwards with barium chloride. After washing, the soil and kaolin were again treated with hydrochloric acid, and the barium recovered by this process was found to correspond with 95% of the acid liberated from the barium chloride by the soil, and with 89% of the acid set free by the kaolin.

A sample of soil which had been boiled for six to seven hours with concentrated sulphuric acid and then washed, was found to liberate the same quantity of acid from salt solutions as a second sample which had been treated with  $N/20$ - or  $N/40$ -acid. This would seem to show that acid soils of the sandy-loam type owe their acidity, not to organic matter, but to inorganic substances (probably hydrated silicates).  
H. M. D.

**Plant Growth in Heated Soil.** GUY WEST WILSON (*Biochem. Bull.*, 1914, 3, 202—209).—All the plants used increased in growth and vigour on soil which had been heated to  $95^{\circ}$ . These were retarded if the soil had been heated to  $135$ — $175^{\circ}$ ; such plants, moreover, were more susceptible to attack by parasitic fungi. Soil fungi grew more abundantly on soils subjected to high temperatures.  
W. D. H.

**Catalytic Power of Arable Soils.** H. KAPPEN (*Bied. Zentr.*, 1914, 43, 145—148; from *Füh'ing's Landw. Zeit.*, 1913, 377—392).—When soil is added to a solution of hydrogen peroxide the action is at first more vigorous than afterwards, when the rate of the reaction is generally in proportion to the amount of soil. In the case of soil which has been heated to  $100^{\circ}$  the rate of the action is greatly reduced, and heating to  $250^{\circ}$  results in a still greater reduction in the catalytic power of the soil. Treatment with mercuric chloride, phenol, and formalin was found to be without effect on the catalytic properties of soils, except that mercuric chloride, which is very difficult to remove completely, caused a slight diminution. The conclusion is drawn that the catalytic properties of soils are not essentially due to enzymes and micro-organisms, but rather to colloids.  
N. H. J. M.

**Action of Calcium and Magnesium Carbonates on Some Biological Changes of Nitrogen in Soils.** W. P. KELLEY (*Bied. Zentr.*, 1914, 43, 149—153; from *Univ. Cal. Publ. Agric. Sci.*, 1912, 1, 39—49).—Addition of 4—6% of calcium carbonate to soil increased the production of ammonia from blood-meal; with larger amounts, 8—12%, there was a smaller increase in the amount of ammonia produced. Magnesium carbonate greatly diminished the production of ammonia when only 1% was added, and even 0.1% had a very distinct effect; 4% of magnesium carbonate caused a slightly increased reduction as compared with 1%. The addition of calcium carbonate, in conjunction with magnesium carbonate, had no effect on the injurious action of the latter.

Nitrification was found to be increased by 1% of calcium carbonate, larger amounts being somewhat less beneficial. Magnesium carbonate alone, and with calcium carbonate, completely checked the production of nitrates, even when only 0.1% was present.

The conclusion is drawn that large amounts of magnesium carbonate are injurious both to nitrifying and denitrifying organisms; whilst small amounts are only toxic to nitrifying organisms.

N. H. J. M.

## Organic Chemistry.

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**Catalytic Hydrogenation of Liquids, under the Influence of the Common Metals, at Moderate Temperature and Pressure.** ANDRÉ BROCHET (*Compt. rend.*, 1914, 158, 1351—1353).—Nickel can be used as a catalyst in the hydrogenation of liquids at the ordinary temperature and pressure, or with each of these slightly increased, provided that the mixture is well agitated in the presence of hydrogen. Under ordinary pressure the operation can be carried out in glass vessels, and under pressure of a few kilograms per sq. cm. in metallic vessels, the course of the reaction being followed by manometric readings. The process is applicable to the hydrogenation of substances containing an acetylenoid or an ethenoid linking, of phenols, the nucleus combining with hydrogen, and of aldehydes and ketones; also to the reduction of nitro-, azoxy-, azo-, and hydrazo-derivatives  
W. G.

**Applications of Petroleum in the Early Middle Ages.** EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1914, 38, 473—474).—References to the use of petroleum in the early middle ages have been collected by the author, showing that it was used for heating, for incendiary purposes in military and naval warfare, and in medicine. Its application as a burning oil in lamps dates back to the ninth century. The "Greek fire" used by the Arabian merchantmen as a protection against attack by pirates consisted of a mixture of petroleum or petroleum solutions and burnt lime.  
H. M. D.

**The Presence of Cholesterol in Mineral Oils.** WILHELM STEINKOPF and HANS WINTERNITZ (*Chem. Zeit.*, 1914, 38, 613—615).—The authors have tested two Java mineral oils for cholesterol by means of the sensitive digitonin reaction and find that it is not present therein. This fact does not negative the assumption, however, that the optical activity of mineral oils may be due to decomposition products of cholesterol.  
T. S. P.

**Thermal Reactions in Carburetting Water Gas. I. Theoretical.** M. C. WHITAKER and W. F. RITTMAN (*J. Ind. Eng. Chem.*, 1914, 6, 383—392).—A theoretical paper, the subject being treated from the point of view of mass action and thermodynamics. It is shown: (1) that it is possible to arrange so that the oil cracking process can be carried out at a higher temperature than is now used in oil gas processes, and thereby greatly increase the yield of valuable hydrocarbons; (2) that it is possible to crack oil without depositing carbon and without the formation of water vapour and carbon dioxide; (3) that it is possible to control partly the quantity and composition of tar produced in gas manufacture; (4) that it is impossible to preserve hydrocarbons and at the same time avoid carbon dioxide,

water vapour, and deposited carbon, when oil is cracked as in the present carburetted water gas process.

Experimental results are to be given in later papers. T. S. P.

**New Processes for the Preparation of  $\Delta^{\alpha\gamma}$ -Butadiene Hydrocarbons. II. Pyrogenetic Decomposition of Hydroxy-compounds.** L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1914, **36**, 980—987).—Experiments are described which show that glycols and unsaturated alcohols can be dehydrated to divinyl hydrocarbons. The best results are obtained by carrying out the pyrogenetic decomposition under reduced pressure at temperatures above 350°.

When  $\beta$ -butylene glycol (butane- $\alpha\gamma$ -diol) is dropped into a tube containing kaolin at 380—400° or aluminium phosphate at 450°, divinyl ( $\Delta^{\alpha\gamma}$ -butadiene) is produced. Under similar conditions,  $\beta$ -methylbutane- $\alpha\gamma$ -diol yields isoprene, and pentane- $\beta\delta$ -diol gives piperylene. When pinacone is distilled slowly over finely divided copper at 430—500°,  $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene is produced. By the dehydration of  $\Delta^{\beta}$ -buten- $\alpha$ -ol at 400—450°, divinyl is readily obtained.  $\Delta^{\beta}$ -Penten- $\delta$ -ol similarly yields piperylene, and  $\Delta^{\beta}$ -hexen- $\delta$ -ol gives hexa- $\Delta^{\beta\delta}$ -diene. E. G.

**New Processes for the Preparation of  $\Delta^{\gamma}$ -Butadiene Hydrocarbons. III. Catalytic Dehydration of Hydroxy Compounds.** L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1914, **36**, 987—1005).—The preparation of  $\Delta^{\alpha\gamma}$ -butadiene hydrocarbons by catalytic, methods in the wet way is preferable to that depending on pyrogenetic decompositions (preceding abstract) as it can be carried out with simple apparatus, and the resulting hydrocarbons can be easily purified. The pyrogenetic method is, however, of more general applicability.

When pinacone is heated in presence of a little hydrobromic acid,  $\gamma\delta$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene can be obtained in a yield exceeding 70% of the theoretical. Hydriodic acid acts as well as hydrobromic acid as catalyst, but hydrochloric acid is not so satisfactory. By the use of trichloroacetic acid, a 50% yield of the hydrocarbon was obtained. Aniline hydrobromide gave a 70% yield, ferric chloride a 35% yield, and trimethylethylene dibromide a 35% yield of the dimethylbutadiene. Aluminium bromide is approximately equal to hydrobromic acid as a catalyst in this reaction.

By the catalysis of  $\beta$ -methylpentane- $\beta\delta$ -diol with aniline hydrobromide,  $\beta$ -methyl- $\Delta^{\beta\delta}$ -pentadiene,  $\text{CMe}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}_2$ , b. p. 75·5—76·5°, is produced; when this hydrocarbon is treated with sodium it is converted into a substance with properties like those of caoutchouc.

When pentane- $\beta\delta$ -diol is heated with hydrobromic acid, piperylene is obtained in a yield of at least 50%.

If  $\beta$ -methyl- $\Delta^{\beta}$ -penten- $\delta$ -ol,  $\text{CMe}_2\text{:CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , b. p. 130°, is catalysed with hydrobromic acid or aniline hydrobromide,  $\beta$ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene,  $\text{CH}_2\text{:CMe}\cdot\text{CH}\cdot\text{CHMe}$ , b. p. 76—77°, is produced. Under similar conditions,  $\gamma$ -methyl- $\Delta^{\alpha}$ -butan- $\gamma$ -ol yields isoprene.

When dimethylethylcarbinol is heated with a little hydriodic acid or with aniline hydrobromide and hydrobromic acid, it is converted into trimethylethylene. E. G.

**Preparation from Oil of Turpentine or Crude Turpentine of Hydrocarbons of Low Boiling Point.** ARTHUR HEINEMANN (D.R.-P. 270485).—A yield of 30% of hydrocarbons boiling below 100°, of which about two-thirds is isoprene, is obtained by passing turpentine vapour carried by means of superheated steam over a surface heated preferably to 750°. J. C. C.

**Preparation of Isoprene.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (Austrian Patent, 63501).—Isoprene is obtained by passing nopinene through an iron tube heated at 500–520°, or by passing the vapour of nopinene over an electrically-heated wire gauze. J. C. C.

**Preparation of Additive Compounds of Acetylene and Halogen Hydrides.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (Fr. Patent, 462711).—Additive compounds of acetylene and halogen hydrides can be easily prepared in good yield if the gases are allowed to interact in the presence of a catalyst, preferably a compound of mercury. If a mixture of acetylene and hydrogen bromide is passed over coke impregnated with mercury bromide at 200°, a mixture of vinyl bromide and *as*-dibromoethane is obtained, and vinyl chloride is produced by passing acetylene into aqueous hydrochloric acid containing mercury chloride. J. C. C.

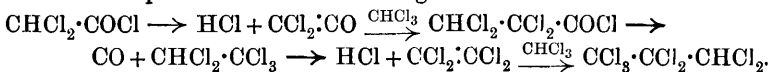
**The Preparation of Pure Butinene.** M. PICON (*Compt. rend.*, 1914, 158, 1184–1187).— $\Delta^a$ -Butinene is readily obtained in a pure state by the action of ethyl iodide on monosodioacetylene in liquid ammonia at  $-40^\circ$ . When the reaction is over the temperature is allowed to rise, the gases are passed through water and dilute sulphuric acid and then dried over calcium chloride and finally cooled to  $-80^\circ$ . Any trace of acetylene is then pumped off and pure butinene is left. Ethyl bromide can replace the ethyl iodide, but only acts slowly at  $-40^\circ$ , whilst ethyl chloride only acts at the ordinary temperature (compare Lebeau and Picon, A., 1913, i, 438). The gas so obtained is colourless and has a sweet taste. On cooling it solidifies to a crystalline mass and has m. p.  $-137^\circ$ ; b. p.  $8.3^\circ$  (compare Dupont, A., 1909, i, 545). Its density between  $11^\circ$  and  $13^\circ$  is  $2.47 \pm 0.01$  (referred to  $0^\circ$  and 760 mm.). It behaves as a true acetylenic hydrocarbon towards the usual reagents. W. G.

**Preparation of Normal Pentinene. Remarks on the Melting Points and Boiling Points of the First Terms of the True Normal Acetylenic Hydrocarbons.** M. PICON (*Compt. rend.*, 1914, 158, 1346–1349).—Normal pentinene has been prepared by the method already described (compare A., 1913, i, 438; preceding abstract), and isolated in the manner described for butinene (*loc. cit.*). The starting material is propyl iodide, and the reaction is carried out under a pressure of one atmosphere. Pentinene, so prepared, has b. p.  $40^\circ$ ;  $D_4^{20}$  0.7221, and solidifies in liquid air to a crystalline mass, m. p.  $-95^\circ$ . Starting with the second member of the series and passing up to the sixth, the normal acetylenes show a rise of  $31.5^\circ$ – $32^\circ$  in boiling point

in passing from one homologue to the next higher. No such regular gradation is to be found in the melting points of the acetylenes except for the first three members of the series.

W. G.

**Catalytic Action. Synthesis of Some Chloropropanes and their Derivatives.** H. J. PRINS (*J. pr. Chem.*, 1914, [ii], 89, 414—424, 425—451).—It has been shown by Böeseken (A., 1910, i, 152) that dichloroacetyl chloride is decomposed by aluminium chloride with the formation of carbon monoxide, hydrogen chloride, chloroform, and a substance which was considered to have the formula  $C_5H_{10}$ . The latter substance is produced in considerable yield when the decomposition of the acid chloride is carried out in chloroform solution. It has the composition  $C_5H_7Cl_7$ , and is identical with *as*-heptachloropropane (Fritsch, A., 1898, i, 63). It is also obtained by the condensation of pentachloroethane and chloroform, or by the direct union of tetrachloroethylene and chloroform in the presence of aluminium chloride. The formation of heptachloropropane from dichloroacetyl chloride is represented in the following scheme:



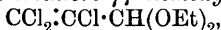
The formation of chloropropanes by the direct combination of carbon tetrachloride and chloroform with mono-, di- and tri-chloroethylene under the influence of aluminium chloride is also described.

*as*-Heptachloropropane has b. p.  $247^\circ$  under ordinary pressure,  $164^\circ/9$  mm., m. p.  $29.4^\circ$ ;  $D_4^{25}$  1.8048, and is converted by strong sulphuric acid at  $110$ — $120^\circ$  into trichloroacrylic acid. On treatment with alcoholic potassium hydroxide it yields *hexachloropropylene*, which has b. p.  $210^\circ$ , or  $99^\circ/15$  mm., and forms a crystalline additive compound with aluminium chloride.

Octachloropropane, prepared from hexachloropropylene and chlorine in sunlight, sublimes in large, flexible plates, and is quantitatively decomposed by aluminium chloride into tetrachloroethylene and carbon tetrachloride.

*s*-Heptachloropropane,  $CCl_3 \cdot CHCl \cdot CCl_3$ , is obtained by the action of aluminium chloride on carbon tetrachloride and trichloroethylene. It has b. p.  $165^\circ/9$  cm. or  $249^\circ$  at ordinary pressure, m. p.  $11$ — $11.5^\circ$ ,  $D_4^{25}$  1.7921,  $n_D^{25}$  1.5427.

*as*-Hexachloropropene,  $CCl_3 \cdot CHCl \cdot CHCl_2$ , prepared from (1) chloroform and trichloroethylene or (2) carbon tetrachloride and *s*-dichloroethylene in the presence of aluminium chloride at a low temperature has b. p.  $216^\circ$  or  $145^\circ/9$  cm.,  $n_D^{17}$  1.5250,  $D_4^{25}$  1.6980. On treatment with alcoholic potassium hydroxide, it yields *aaβγγ-pentachloro-Δ<sup>α</sup>-propylene*,  $CCl_2 \cdot CCl \cdot CHCl_2$ , which has b. p.  $183^\circ$  or  $116^\circ/9$  cm.,  $D_4^{25}$  1.6317,  $n_D^{20}$  1.5313, and is converted by sodium ethoxide in ethyl alcoholic solution into *aaβ-trichloro-γγ-diethoxypropylene*,

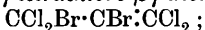


b. p.  $136^\circ/9$  cm. The latter compound is hydrolysed by hydrochloric acid to *αββ-trichloroacetaldehyde*, which forms a pungent oil, b. p.  $164^\circ$ , m. p.  $10^\circ$ ,  $n_D^{19}$  1.5364, and is also produced by warming the pentachloropropylene with concentrated sulphuric acid at  $30^\circ$

Trichloroacetaldehyde loses hydrogen chloride on exposure to moist air, and is instantly hydrolysed by potassium hydroxide to trichloroethylene and potassium formate. The *phenylhydrazones* forms yellowish-brown needles, m. p. 97—98°; the *oxime* crystallises in white needles, m. p. 101°, and is simultaneously transformed into an *isomeride* having m. p. 132°.

When warmed with sulphuric acid at 40—50°, pentachloropropylene is converted into  $\alpha\beta$ -dichloroacrylic acid,  $\text{CHCl}:\text{CCl}\cdot\text{CO}_2\text{H}$ , m. p. 86°, which yields a *chloride*, b. p. 145—146°,  $n_D^{17}$  1.5288, *amide*, m. p. 134°, and combines with chlorine in sunlight to form  $\alpha\alpha\beta\beta$ -tetrachloropropionic acid. The chloride of the last named acid is decomposed by warming with aluminium chloride into carbon monoxide, hydrogen chloride, tetrachloroethylene, and carbonyl chloride.

$\alpha\alpha\beta\gamma\gamma$ -Pentachloropropylene combines slowly with bromine, yielding  $\alpha\alpha\beta\gamma\gamma$ -pentachloro- $\alpha\beta$ -dibromopropene, which on treatment with alcoholic potassium hydroxide gives rise to  $\alpha\alpha\beta\gamma\gamma$ -pentachloro- $\gamma$ -bromo- $\Delta^a$ -propylene,  $\text{CCl}_2\text{Br}\cdot\text{CCl}:\text{CCl}_2$ , and  $\alpha\alpha\beta\gamma\gamma$ -tetrachloro- $\beta\gamma$ -dibromo- $\Delta^a$ -propylene,



when heated with strong sulphuric acid the latter two substances are transformed into  $\alpha\beta\beta$ -trichloroacrylic acid and  $\beta\beta$ -dichloro- $\alpha$ -bromoacrylic acid,  $\text{CCl}_2\cdot\text{CBr}\cdot\text{CO}_2\text{H}$ , respectively. The pentachloropropylene combines with chlorine in sunlight yielding *as*-heptachloropropene, and when heated with potassium hydroxide in toluene solution gives rise to a *compound*,  $\text{C}_6\text{Cl}_8$ , which crystallises in colourless needles, m. p. 93—94°, and is extraordinarily stable, being attacked by a mixture of sulphuric and nitric acid only at the b. p.

If the action of aluminium chloride on a mixture of chloroform and tetrachloroethylene is conducted at 50—60° only a small amount of *as*-hexachloropropene is produced; from the fraction of the product boiling about 200°/2 mm., two *substances*,  $\text{C}_6\text{Cl}_{10}\text{H}_2$  (?), m. p. 107—108° and 94—96°, were isolated by fractional crystallisation from alcohol. The more fusible substance is converted by alcoholic potassium hydroxide into a compound  $\text{C}_6\text{Cl}_8$ , identical with that obtained by the action of copper bronze on hexachloroethane (see below).

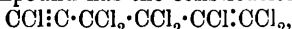
*s*-Pentachloropropene,  $\text{CHCl}_2\cdot\text{CHCl}\cdot\text{CHCl}_2$ , prepared from chloroform and *s*-dichloroethylene in the presence of aluminium chloride, has b. p. 198°, or 126°/9 mm.,  $n_D^{16.5}$  1.5131,  $D_4^{25}$  1.6086, and on treatment with alcoholic potassium hydroxide (1 mol.) gives rise to  $\alpha\beta\gamma\gamma$ -tetrachloro- $\Delta^a$ -propylene,  $\text{CHCl}:\text{CCl}\cdot\text{CHCl}_2$ , b. p. 165°,  $n_D^{18}$  1.5272,  $D_4^{25}$  1.5274, which with sulphuric acid at 30—40° yields  $\alpha$ -chloro- $\beta$ -hydroxyacetaldehyde, and combines with chlorine to form *s*-hexachloropropene,  $\text{CHCl}_2\cdot\text{CCl}_2\cdot\text{CHCl}_2$ , b. p. 218.5°,  $D_4^{25}$  1.7137,  $n_D^{18}$  1.5262.  $\alpha\beta\gamma\gamma$ -Tetrachloro- $\alpha\beta$ -dibromopropene,  $\text{CHClBr}\cdot\text{CClBr}\cdot\text{CHCl}_2$ , prepared by the addition of bromine to the preceding tetrachloropropylene, has b. p. 142°/28 mm.,  $n_D^{10.5}$  1.5804, and on treatment with alcoholic potassium hydroxide yields  $\alpha\alpha\beta\gamma$ -tetrachloro- $\gamma$ -bromopropylene,  $\text{CCl}_2:\text{CCl}\cdot\text{CHClBr}$ , which is converted by sulphuric acid into  $\alpha\beta\beta$ -trichloroacetaldehyde.

Hexachloroethane yields coloured condensation products with phenols and amines, and when heated with copper bronze in methyl-alcoholic solution is transformed into a *substance*,  $\text{C}_6\text{Cl}_8$ , m. p. 183°, from which a *ketone*,  $\text{C}_6\text{Cl}_4\text{O}_2$ , is produced by the action of sulphuric acid at



70°. The ketone sublimes at about 215°, and is decomposed by aqueous alkalis at the ordinary temperature with the formation of monochloroacetylene.

From these reactions the author draws the conclusion that the original octachloro-compound has the constitution



whilst the ketone is probably represented by the following formula:  $\text{CCl:C}\cdot\text{CO}\cdot\text{CO}\cdot\text{CCl:CCl}_2$ . It is particularly noteworthy that the octachloride does not combine with chlorine even in sunlight.

The second part of the paper deals with the mechanism of catalytic action. The author suggests that the action of the catalyst consists in the activation of the linkings in the molecules of the reacting substances, and discusses at length the catalytic action of aluminium chloride from this point of view.

F. B.

**Preparation of Allyl Iodide.** RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1914, 36, 1005—1007).—An improved method of preparing allyl iodide from glycerol, iodine, and phosphorus is described, which obviates the use of carbon dioxide as recommended by Saytzev and Kanonnikov (*A.*, 1877, ii, 730). The iodine is mixed with the glycerol, the mixture is heated on the water-bath, and yellow phosphorus is added gradually.

E. G.

**Reduction by means of Aluminium and Alkali Hydroxides. Formation of *iso*Propyl Alcohol from Acetone.** F. LAVILLA LLORENS (*Anal. Fis. Quim.*, 1914, 12, 236—239).—The reduction of acetone by aluminium and sodium hydroxide (15%) in the cold gave 45 to 50% yields of *isopropyl* alcohol without formation of pinacone.

G. D. L.

**Some Derivations of  $\Delta^8$ . Octadi-inene- $\alpha\theta$ -diol.** LESPIEAU (*Compt. rend.*, 1914, 158, 1187—1188. Compare this vol., i, 134).— $\Delta^8$ . Octadi-inene- $\alpha\theta$  diol yields a *diacetin*, m. p. 59—60°, on heating at 100° for a few hours with acetic anhydride. It unites with four atoms of bromine or iodine, giving  $\beta\gamma\zeta\eta$ -tetrabromo-octadiene- $\alpha\theta$ -diol, m. p. 116° (compare *loc. cit.*), and  $\beta\gamma\zeta\eta$ -tetraiodo-octadiene- $\alpha\theta$ -diol,  $\text{C}_8\text{H}_{10}\text{O}_2\text{I}_4$ , m. p. 147.5—148.5°. It readily combines with eight atoms of hydrogen in the presence of platinum black, and if the hydrogenation is carried out in alcoholic solution one hydroxyl group is reduced, giving octan- $\alpha$ -ol, b. p. 193°/750 mm., together with some octane- $\alpha\theta$ -diol.

W. G.

**The Fission of Ethers and the Replacement of Alkoxy by Alkyl by means of Organo-magnesium Haloids.** ERNST SPÄTH (*Monatsh.*, 1914, 35, 319—332).—A condensed discussion of the results of this investigation has already been published (Späth, this vol., i, 1).

Various ethers have been examined as to their behaviour towards organo-magnesium compounds. The experimental method was to add the ether under investigation to the Grignard reagent, from which the ethyl ether used in its preparation had been previously removed at 110—130°. The mixture was then heated, when any residual ethyl

ether was first expelled, and the remaining compound of Grignard reagent and the new ether was subsequently decomposed under reflux at a higher temperature. The reaction product was then cooled, acidified, and examined.

*iso*Amyl ether,  $\epsilon$ -ethoxy- $\beta$ -methylhexane, anisole, anethole, veratrole, guaiacol, 1:2-methylenedioxy-4-ethylbenzene, phenyl ether, benzyl ethyl ether, benzyl methyl ether, benzyl ether, phenyl benzyl ether, methylal, ethylal, acetal, ethoxyacetal, and acetophenone diethylacetal were applied to the reaction, the organomagnesium reagents being derived from methyl iodide, ethyl iodide, propyl bromide, *iso*amyl bromide, *p*-anisyl iodide, bromobenzene, and 4-iodo-*m*-xylene.

Of the products obtained the following appear to be described for the first time: a *heptene*, possibly  $\epsilon$ -methyl- $\Delta^8$ -hexene; *dibromide*, b. p.  $85^\circ/12$  mm.; 1:2- or 2:1-*hydroxyethoxy-4-ethylbenzene*, b. p.  $123$ — $126^\circ/10$  mm.; 3:4-*dimethylbenzyl ethyl ether*, b. p.  $98$ — $100^\circ/10$  mm.; *anisyl ethyl ether*, b. p.  $111$ — $113^\circ/11$  mm.;  $\epsilon$ -ethoxy- $\beta$ -methylhexane, b. p.  $138$ — $142^\circ/740$  mm.;  $\alpha$ -ethoxy- $\alpha$ -phenylethane, b. p.  $67$ — $69^\circ/11$  mm.;  $\alpha\beta$ -diethoxy- $\alpha$ -phenylethane, b. p.  $105$ — $106^\circ/10$  mm.; the *ethyl ether* of phenylmethylpropylcarbinol, b. p.  $92$ — $93^\circ/12$  mm.

D. F. T.

**Action of Acidified Water on Esters of Phosphorous Acid.** A. E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 291—294. Compare A., 1913, i, 1051, 1052).—It has been found previously that, at the ordinary temperature, water energetically attacks trimethyl phosphite, with formation of methyl alcohol and dimethylphosphorous acid:  $P(OMe)_3 + H_2O = Me \cdot OH + OH \cdot P(OMe)_2$ , whereas the tri-ethyl, tri-propyl, and tri-*isopropyl* esters are so stable that they are not appreciably affected when heated with water in a sealed tube at  $110^\circ$ , or even a higher temperature (A., 1907, i, 275).

Further experiments indicate that the action of water on trimethyl phosphite is determined by the presence in the water of traces of acid derived from the atmosphere of the laboratory. Similar actions are found to occur with triethyl, tripropyl, and tri-*isobutyl* phosphites if the water is previously rendered acid with hydrochloric acid. In aqueous alcoholic solutions, these reactions proceed rapidly even with a minimal quantity of the acid catalyst and are irreversible and proceed practically to an end, without formation of secondary products. They are hence eminently suitable for calorimetric investigation, which is now being undertaken.

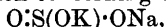
T. H. P.

**Double Salts of the Alkali Metals with Sulphurous Acid.** A. E. ARBUZOV and A. V. KARTASCHEV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 284—291).—In view of the divergent views which have been expressed concerning the existence of isomeric sodium potassium sulphites (compare Röhrig, A., 1888, 649; Schwicker, A., 1889, 942; Barth, A., 1892, 564; Fraps, A., 1900, ii, 276; Godby, P., 1907, 241; Arbuzov, A., 1900, ii, 573), the author has investigated the action of methyl iodide on a number of pairs of carbonates and hydrogen sulphites in order to ascertain which methanesulphonate is formed in each case.

Rubidium carbonate and potassium hydrogen sulphite give rubidium

methanesulphonate; caesium carbonate and potassium hydrogen sulphite, caesium methanesulphonate; lithium carbonate and potassium hydrogen sulphite, potassium methanesulphonate; sodium carbonate and ammonium hydrogen sulphite, sodium methanesulphonate; lithium carbonate and ammonium hydrogen sulphite, ammonium methanesulphonate and a small proportion of a halogen-free salt containing both lithium and ammonium; ammonium hydroxide and potassium hydrogen sulphite, potassium methanesulphonate; lithium sulphite, lithium methanesulphonate; and ammonium sulphite, ammonium methanesulphonate.

Hence, in the decomposition of double salts of sulphurous acid by means of methyl iodide, the methanesulphonate finally resulting is that of the metal with the higher atomic weight, independently of the method by which the double salt was prepared. The results do not, however, permit of a decision concerning the symmetrical,



or unsymmetrical structure,  $\text{O:SO(K)·ONa}$ , of the double sulphites.

The solubilities, in grams per 100 c.c. of solution, have been determined at the ordinary temperature for the methanesulphonates and iodides of the alkali metals in 95% and in 85% alcohol. In each series, the solubility diminishes with increase of the atomic weight of the metal, the diminution being especially marked in the earlier members of the series; the methanesulphonates are considerably less soluble than the corresponding iodides. In the reaction between a double sulphite and methyl iodide, the most soluble methanesulphonate and the least soluble iodide are always formed. The influence of solubility on the result is indicated by the ease with which interaction of methanesulphonates of metals with low atomic weights and iodides of metals with high atomic weight takes place.

Owing to the fact that the sodium, potassium, rubidium, and caesium salts of methanesulphonic acid crystallise from alcohol in a mass which resembles cotton-wool, and permeates the whole of the solvent, the above reaction may serve as a test for these metals. Further experiments are being made in this direction.

T. H. P.

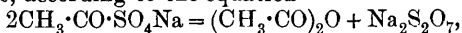
**The Formation of Strontium Formate by Decomposition of "Schleudersalz."** K. URBAN (*Zeitsch. Zuckerind. Böhm.*, 1914, **38**, 358—363).—The di-strontium saccharate first formed in the process of removal of sugar from molasses decomposes on cooling into mono- and sesqui-saccharate which remain in solution whilst strontium hydroxide ("Schleudersalz") separates, and is separated from the solution by centrifugal treatment. If this material is kept in heaps exposed to the air, its temperature gradually rises as high as 85°, due to atmospheric oxidation of the sugar still retained; no indications that this oxidation was effected through micro-organisms were observed. Examination showed that the oxidised mass contained a considerable quantity of strontium formate and strontium carbonate which represent successive oxidation products of the sugar or calcium saccharate.

That sugar can undergo atmospheric oxidation in the presence of alkalis was confirmed by experiments with sugar solutions to which various alkalis had been added.

D. F. T.

**A New Method of Preparing Carboxylic Anhydrides.** A. J. VAN PESKI (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 969—970).—The suggestion of Franchimont (A., 1881, 716) that the formation of sulphoacetic acid by the action of sulphur trioxide or fuming sulphuric acid on acetic acid is due to the intermediate production of acetylsulphuric acid is confirmed by the isolation of this acid.

When acetic acid and sulphur trioxide are allowed to react below  $0^{\circ}$ , acetylsulphuric acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{SO}_4\text{H}$ , is obtained identical with the product of reaction of acetic anhydride and sulphuric acid below  $0^{\circ}$ . The *sodium* salt, obtained by the addition of sodium acetate to the acid below  $0^{\circ}$ , decomposes when heated, either alone or suspended in acetic acid or toluene, according to the equation



whilst the decomposition in the presence of sodium acetate and acetic acid follows the course  $\text{CH}_3\cdot\text{CO}\cdot\text{SO}_4\text{Na} + \text{CH}_3\cdot\text{CO}_2\text{Na} = \text{Ac}_2\text{O} + \text{Na}_2\text{SO}_4$ . On distillation of the product of the former action, the residual sodium pyrosulphate is very bulky and when distilled with sodium acetate and acetic acid produces more acetic anhydride. If, however, the pyrosulphate is previously fused, it loses this power. The action of sodium chloride on acetylsulphuric acid yields acetyl chloride.

Butyrylsulphuric acid and benzoylsulphuric acid, obtained in a manner analogous to the preceding, were similarly convertible into butyric and benzoic anhydrides. D. F. T.

**Action of Halogen-substituted Esters of Aliphatic Acids on Esters of Phosphorous Acids.** I. A. E. ARBUZOV and A. A. DUNIN (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 295—302).—The action of alkyl haloids on phosphorous esters proceeds according to the equations:  $\text{P(OR)}_3 + \text{R}'\text{X} = \text{PR}'\text{X(OR)}_3$ , and the latter

$$= \text{RX} + \text{O}\cdot\text{PR}'\text{(OR)}_2,$$

where X = halogen (see A., 1907, i, 275). Similar reactions occur with halogen derivatives of aliphatic esters, the two stages being represented by:

$$\text{R}'\text{X}\cdot\text{CO}_2\text{R}'' + \text{P(OR)}_3 = \text{CO}_2\text{R}''\cdot\text{R}'\cdot\text{PX(OR)}_3 = \text{RX} + \text{CO}_2\text{R}''\cdot\text{R}'\cdot\text{PO(OR)}_2.$$

The esters thus obtained from triethyl phosphite and the following halogenated aliphatic esters were prepared.

Ethyl chlorocarbonate gives the *ester*,  $\text{C}_7\text{H}_{15}\text{O}_5\text{P}$ , which is a mobile, pleasant-smelling liquid, b. p.  $138\cdot25^{\circ}/12\cdot5$  mm.,  $\text{D}_0^{\circ} 1\cdot1422$ . Ethyl bromoacetate yields the *ester*,  $\text{C}_8\text{H}_{17}\text{O}_5\text{P}$ , as a colourless liquid, b. p.  $149\text{—}150^{\circ}/12$  mm.,  $\text{D}_0^{\circ} 1\cdot1392$ . Ethyl  $\alpha$ -bromopropionate gives the *ester*,  $\text{C}_9\text{H}_{19}\text{O}_5\text{P}$ , which is a colourless liquid, b. p.  $138\cdot5\text{—}138\cdot75^{\circ}/10$  mm.,  $\text{D}_0^{\circ} 1\cdot111$ ; the isomeric *ester* from ethyl  $\beta$ -bromopropionate is a colourless liquid, b. p.  $167^{\circ}/12$  mm.,  $\text{D}_0^{\circ} 1\cdot1177$ . Ethyl  $\alpha$ -bromobutyrate gives the *ester*,  $\text{C}_{10}\text{H}_{21}\text{O}_5\text{P}$ , which is a colourless liquid with a faint, aromatic odour, b. p.  $147\cdot5\text{—}148^{\circ}/10\cdot5$  mm.,  $\text{D}_0^{\circ} 1\cdot0919$ . T. H. P.

**Stearates and Palmitates of the Heavy Metals with Remarks Concerning Instantaneous Precipitations in Insulating Solutions.** ALFRED E. KOENIG (*J. Amer. Chem. Soc.*, 1914, **36**, 951—961).—Kahlenberg (A., 1902, ii, 301) has found that double decompositions take place in non-conducting solvents. In the present paper an account is given of the preparation and properties of the

copper, cobalt, nickel, ferric, manganese, chromium, and lead stearates, and copper, cobalt, and nickel palmitates. The solubility of these salts in various organic solvents has been determined. Several instantaneous double decompositions with the stearates and palmitates in insulating solutions were observed. For example, on mixing benzene solutions of cupric stearate and stannic chloride, cupric chloride is immediately precipitated and a solution of stannic stearate obtained. The fact that these reactions take place with saturated compounds, such as the stearates and palmitates, refutes Cady and Lichtenwalter's view (A., 1913, ii, 916) that similar precipitations in the case of the oleates are due to the unsaturated condition of these salts. Copper, cobalt, and nickel stearates, and copper and cobalt palmitates yield additive compounds with pyridine; the copper compounds have the composition  $\text{Cu}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2, \text{C}_5\text{H}_5\text{N}$  and  $\text{Cu}(\text{C}_{16}\text{H}_{31}\text{O}_2)_2, \text{C}_5\text{H}_5\text{N}$ ;

the cobalt and nickel compounds contain 2 mols. of pyridine to 1 mol. of the stearate or palmitate.

Solutions of cobalt stearate and palmitate in certain organic solvents change from pink to blue when heated. This indicates that the change is not due to hydration or to the presence of ions, but is probably caused by an intramolecular alteration. The absorption spectra have been photographed of solutions of cobalt, copper, and nickel chlorides in water, and of the stearates of these metals in pyridine and in carbon tetrachloride. The absorption spectra of the aqueous and non-aqueous solutions do not exhibit any fundamental difference.

E. G.

**The Fats. I. Refractive Indices of Mixtures of Olein, Palmitin, and Stearin.** P. PASCAL (*Bull. Soc. chim.*, 1914, [iv], 15, 360—367).—The author has determined the index of refraction of binary and ternary mixtures derived from olein, palmitin, and stearin for sodium light at temperatures in the neighbourhood of 70°, and has calculated the coefficient of thermal variation of the index according to the formula  $n_D^t = n_D^{70} - \alpha(t - 70^\circ)$ .

Mixtures of palmitin and olein and of stearin and olein behave normally. With mixtures of stearin and palmitin, on the other hand, the coefficient of thermal variation attains a maximum when about 55% of stearin is present, that is, when the mixture has a composition corresponding with that of margarin. Palmitin and stearin have  $n_D^{20}$  1.4377 and 1.4385 respectively, whereas Schey (A., 1899, i, 669) gives 1.4380 and 1.4393.

The experiments with ternary mixtures have been mainly effected with specimens prepared by the gradual addition of olein to a mixture of equal weights of stearin and palmitin, whilst some data for mixtures containing 25 and 75% of stearin are also given. The application of the results, taken in conjunction with determinations of the iodine value, to the analysis of butter is discussed.

H. W.

**The Fats. II. Refractive Indices of Mixtures of Palmitic, Stearic, and Oleic Acids.** PAUL PASCAL (*Bull. Soc. chim.*, 1914, [iv], 15, 397—401. Compare preceding abstract).—The author has

determined the refractive indices of mixtures of oleic and palmitic acids, oleic and stearic acids, and palmitic and stearic acids in varying proportions, and of mixtures of equal proportions of palmitic and stearic acid with varying amounts of oleic acids, at 60°, 70°, and 80°, and from his results has plotted diagrams by means of which it is possible to determine the amounts of each of these three acids, in mixtures of which the refractive index and the iodine number is known.

W. G.

**Transformation of Unsaturated Fatty Acids and their Esters into Saturated Compounds.** DE NORDISKE FABRIKER DE-NO-FA (Fr. Patent, 462905).—Hydrogenation of unsaturated fatty acids and their esters is effected at 100—180° by the action of hydrogen in the presence of a basic salt of a heavy metal (copper, nickel, etc.) with a fatty acid of high molecular weight.

J. C. C.

**Hydrogenation of Fats by means of Nickel Oxides or Reduced Nickel.** VL. IPATIEV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 302—311).—With hydrogenation by the author's method, in which reduced nickel or an oxide of nickel is employed in presence of hydrogen under pressure, purity of the nickel is not so essential as when the catalysis is carried out at the ordinary pressure. Thus, the most resistant aromatic nucleus may be hydrogenated in presence of nickel prepared by reducing commercial nickel oxide by means of hydrogen from commercial zinc and hydrochloric acid.

Certain of Bedford and Erdmann's conclusions (A., 1913, i, 701) are criticised. Thus, hydrogenation of a double linking proceeds considerably more easily than that of an aromatic nucleus (compare this vol., i, 38). Further, the statement that the author's method is inapplicable to the hydrogenation of fats, which would readily decompose at the high pressures employed, is controverted; 50 grams of cottonseed oil heated for four hours at 220—230°, with 3 grams of nickel oxide in hydrogen at 60 atmos. pressure yielded a solid fat with the iodine number 11. When a constant current of hydrogen at ordinary pressure is passed through the same mixture and the latter is kept well mixed, good results are obtained only if the temperature is at least 255°.

Similar results are obtainable with other oils, which should be continually stirred with the catalyst, but need not be purified beforehand; the pressure in the reaction vessel falls from 12—20 to 7—8 atmospheres. The acid and iodine numbers of the final fat may be varied by regulating the time of the action. High velocities of hydrogenation may be attained, and the same catalyst may be used in several successive reductions.

T. H. P.

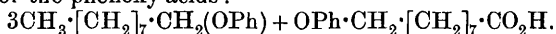
**Some Transformations of Ricinoleic and Oleic Acids.** II. **Action of Monopotassium Anilide and Potassium Phenoxide on Dibromohydroxystearic and Dibromostearic Acids.** B. R. HONOVSKI (CHONOWSKY) (*J. Amer. Chem. Soc.*, 1914, 36, 1028—1035).—In an earlier paper (A., 1909, i, 760), experiments were described which support the view that the constitution of ricinoleic acid is represented by the formula  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$ .

In order to obtain further evidence on this point, the work described in the present paper was undertaken.

By the action of potassium anilide on dibromohydroxystearic acid, *κ-hydroxy-θ-phenyliminoundecoic acid*,  $\text{NPh} \begin{array}{c} \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ | \\ \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \end{array}$ , m. p. 57—58°, is obtained which crystallises in lustrous leaflets; the *barium* and *silver* salts were prepared. The *acetyl* derivative is a colourless, viscous liquid. The acid gradually changes to the *lactone* when left, and the same change takes place rapidly when the acid is warmed with dilute sulphuric acid. The *dibromo*-derivative of the acid was obtained as a yellow, viscous liquid.

*θ-Phenyliminodecoic acid*,  $\text{NPh} \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \end{array}$ , m. p. 54—55°, obtained by the action of potassium anilide on dibromostearic acid, is a white, amorphous powder, and does not unite with bromine; its *barium* and *silver* salts were prepared.

By the action of phenol on dibromostearic acid in presence of potassium carbonate at 105—108°, phenoxy-derivatives of oleic acid were produced and were precipitated as the *barium* salts. On decomposing this precipitate with boiling, dilute hydrochloric acid, *θ-phenoxy-nononic acid*,  $\text{OPh} \cdot \text{CH}_2 \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$ , m. p. 58—59°, was produced which forms a white, crystalline powder; its *barium* and *silver* salts and *bromo*-derivative were prepared. Another compound,  $\text{C}_{60}\text{H}_{94}\text{O}_6$ , m. p. 96—97°, was also formed in this reaction as a white, crystalline powder, which is probably a condensation product of the decomposition products of the phenoxy-acids:



In another experiment, carried out at 140°, an *acid*, m. p. 54—55°, was obtained of the same composition as the *θ-phenoxy*nononic acid, but apparently twice the molecular weight; it gives a white, crystalline *bromo*-derivative. E. G.

**Action of Oxalic Acid and of Phosphorus Pentoxide on Ricinoleic and Hydroxystearic Acids.** S. FOKIN (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 224—226).—Treatment of the hydroxystearic acid prepared from ricinoleic acid with oxalic acid, either in the anhydrous form or in concentrated aqueous solution in a sealed tube, yields a mixture of the oxalic ethers of hydroxystearic acid and of an oleic acid, m. p. 33—35°, consisting principally of the isomeride with the double linking in the  $\lambda\mu$ -position. In order to avoid the formation of anhydrides of the hydroxystearic and oleic acids and to render easier the separation of the resulting oxalic ethers, use may be made of the triglyceride of hydroxystearic acid, obtained by reduction of castor oil.

Powdered hydroxystearic acid and phosphoric oxide react in the cold with development of heat, yielding: (1) A resinous mass which contains phosphorus and seems to be analogous in structure to sulphostearic acid. (2) An oleic acid, which solidifies at 14—15°, forms crystals distinct from those of the oleic acid yielded by oxalic acid, and has the iodine number 82, the value for  $\text{C}_{18}\text{H}_{34}\text{O}_2$  being 90.

The action of phosphoric oxide on castor oil gives a product of

increased unsaturation, the iodine number of the glyceride being 149.3 and that of the corresponding acid, 148.2. Since the theoretical value for linoleic acid is 182, the product contains some 70% of linoleic acid. The latter is regarded as a mixture of the two isomerides,

$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$ ,  
and  $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$ , of which the former constitutes a resinous mass insoluble in light petroleum. From the latter isomeride, which dissolves in light petroleum, the corresponding glyceride was prepared and was found to undergo ready oxidation in air in presence of a drying agent; when treated with bromine, the acid did not yield a crystalline tetrabromo-derivative but remained liquid. This linoleic acid and the oleic acid obtained from hydroxystearic acid and phosphoric oxide appear to be stereoisomerides of the acids occurring in vegetable oils.

T. H. P.

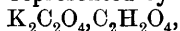
**The Preparation of Valerolactone.** M. S. LOSANITSCH (*Monatsh.*, 1914, 35, 301—306).—The author finds that lævulic acid can be conveniently reduced to valerolactone by sodium and alcohol (compare Tafel and Emmert, A., 1911, i, 746; Sabatier and Mailhe, A., 1909, i, 131; Neugebauer, A., 1885, 651; Fittig and Wolff, A., 1882, 35). The reduction is effected in a reflux apparatus and occupies about a half-hour; after adding water and distilling off the alcohol, the residue is acidified and the lactone extracted with ether.

The product, which was obtained in a yield exceeding 80%, had b. p. 206—206.3° (corr.)/749 mm., 91° (corr.)/16 mm.

A modification of the usual apparatus for the continuous extraction of a liquid by ether is described. This was applied to the extraction of the lævulic acid obtained by the action of hydrochloric acid on sucrose.

D. F. T.

**The Acid Salts of Dibasic Acids. III. Oxalates.** E. JUNGFLIECH and PH. LANDRIEU (*Compt. rend.*, 1914, 158, 1306—1311).—In view of the results obtained in the study of the normal and acid camphorates (compare this vol., i, 416), the authors have studied the similar salts of another dibasic acid, oxalic acid. They have obtained in the crystalline state the salts  $\text{C}_2\text{O}_4\text{HK} \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{C}_2\text{O}_4\text{HK} \cdot \text{H}_2\text{O}$ , and  $\text{C}_2\text{O}_4\text{K}_2 \cdot \text{H}_2\text{O}$ . They show from their results that potassium hydrogen oxalate should be represented by the formula



and not by the usual one as given above.

W. G.

**Glucinum Oxalate and Acetate.** F. WIRTH (*Zeitsch. anorg. Chem.*, 1914, 87, 7—8).—Glucinum oxalate,  $\text{Gl}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ , dissolves to the extent of 63.2 grams in 100 c.c. of water at 25°, and more readily in oxalic acid solution. The basic acetate,  $\text{Gl}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ , is scarcely wetted by water, but on long shaking at 40° considerable quantities dissolve, leaving a gummy mass on evaporation. It dissolves readily in, and may be crystallised from, organic solvents.

C. H. D.

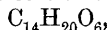
**Cholic Acid and its Origin.** I. LIFSCHÜTZ (*Ber.*, 1914, 47, 1459—1460).—When cholic acid is oxidised with benzoyl peroxide in



acetic acid and the solution is treated successively with sulphuric acid, ferric chloride and chromic acid, the colour changes and spectra observed are identical with those of oxycholesterol (A., 1913, ii, 350). Cholic acid is therefore derived from cholesterol, but whether directly or by way of oxycholesterol is still the subject of investigation.

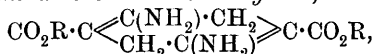
J. C. W.

**Esters of Succinylsuccinic Acid and their Reactions with Ammonia and Primary Amines.** HANS LIEBERMANN (*Annalen*, 1914, 404, 272—321).—The disodio-derivatives of alkyl succinylsuccinates can be prepared in a few hours by heating at 90—105° a mixture of sodium, an alkyl succinate, and not too small a quantity of the corresponding alkyl acetate. *Propyl succinylsuccinate*,

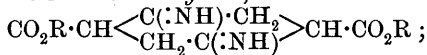


m. p. 91°, colourless needles, the *isobutyl* ester, m. p. 100°, and *allyl* ester, m. p. 115°, have thus been prepared; by-products of the first two reactions are the *propyl hydrogen* ester, m. p. 115° (decomp.), yellowish-white needles, and the *isobutyl hydrogen* ester, m. p. 126° (decomp.), respectively. The new normal esters resemble methyl and ethyl succinylsuccinates in solubility, colour reactions, and other properties; their solubility in cold, dilute aqueous ammonia diminishes as the alkyl groups become more complex. The hydrogen esters are soluble in aqueous sodium carbonate, develop violet-blue colorations with alcoholic ferric chloride, and form solutions with a faint green fluorescence.

As Baeyer has shown in the case of the ethyl ester, alkyl succinylsuccinates react with fused ammonium acetate to form *alkyl 2:5-diamino-Δ<sup>1:4</sup>-cyclohexadiene-1:4-dicarboxylates*,



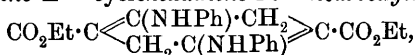
the intense colour of which the author explains by Kauffmann's theory (A., 1906, i, 841). *Propyl 2:5-diamino-Δ<sup>1:4</sup>-cyclohexadiene-1:4-dicarboxylate*, m. p. 173°, orange-yellow needles, the *isobutyl* ester, m. p. 165°, greenish-yellow prisms, and *allyl* ester, m. p. 154°, orange-yellow needles, have been prepared. By boiling with alcohol and *N*-potassium hydroxide (2 mols.), these esters are not hydrolysed, but are changed to colourless isomerides which are regarded as *alkyl 2:5-di-iminocyclohexane-1:4-dicarboxylates*,



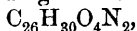
the *ethyl* ester, m. p. 178°, and *propyl* ester, m. p. 173°, have thus been obtained in colourless needles, and the *isobutyl* ester, m. p. 165°, in colourless prisms. The colourless esters are stable in the solid state and in solution in darkness, but are changed to the coloured isomerides by heating above the m. p. or by exposing their solutions to sunlight. By heating with 10% alcoholic ammonia at 100°, methyl succinylsuccinate is converted directly (without the formation of the coloured isomeride) into *methyl 2:5-di-iminocyclohexane-1:4-dicarboxylate*, m. p. 212° (to an orange oil), colourless needles. The coloured and the colourless esters are reconverted into alkyl succinylsuccinates by concentrated hydrochloric acid at 30—40°, or by boiling glacial acetic

acid. By prolonged heating in air, alkyl 2:5-diamino- $\Delta^{1:4}$ -cyclohexadiene-1:4-dicarboxylates lose two atoms of hydrogen, and are converted into alkyl diaminoterephthalates.

Succinylsuccinic esters react with substances containing an amino-group just as they do with ammonia, and yield coloured substances analogous to the diaminocyclohexadienedicarboxylates, in which the iminic hydrogen can be detected by Zerevitinov's method and by benzoylation. The condensation with aromatic primary amines is effected in boiling glacial acetic acid and a little alcohol; with aliphatic primary amines, the best results are obtained in boiling alcohol. *Ethyl 2:5-dianilino- $\Delta^{1:4}$ -cyclohexadiene-1:4-dicarboxylate*,



m. p. 163°, orange needles (*dibenzoyl* derivative, colourless), has been prepared, also the corresponding *di-o-toluidino*-derivative,



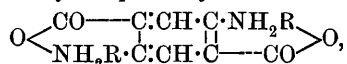
m. p. 181°, rose needles, *di-p-toluidino*-derivative, m. p. 214°, rose needles (changing at about 140° to orange needles), *di-a-naphthylamino*-derivative, m. p. 230°, pale violet needles (becoming orange at about 140°), *di- $\beta$ -naphthylamino*-derivative, m. p. 228°, rose needles and orange-yellow needles (*dibenzoyl* derivative, m. p. about 110°, colourless), *di-o-anisidino*-derivative, m. p. 159°, orange-yellow prisms, *di-p-anisidino*-derivative, m. p. 191°, pale violet needles, and *di-o-aminoanilino*-derivative, m. p. 243°, violet-red needles. *Methyl 2:5-dianilino- $\Delta^{1:4}$ -cyclohexadiene-1:4-dicarboxylate*, m. p. 235°, crystallises in orange-yellow needles. *Ethyl 2:5-diethylamino- $\Delta^{1:4}$ -cyclohexadiene-1:4-dicarboxylate*, m. p. 169°, orange prisms, is obtained accompanied by colourless prisms. The corresponding *dimethylamino*-derivative,  $\text{C}_{14}\text{H}_{22}\text{O}_4\text{N}_2$ , m. p. 150°, violet-red needles, is converted by boiling alcoholic potassium hydroxide (2 mols.) into a colourless *isomeride*, m. p. 150°, changes to the coloured form at its m. p., and is probably *ethyl 2:5-dimethylimino-cyclohexane-1:4-dicarboxylate*.

In some cases the condensation of alkyl succinylsuccinates and aromatic amines in boiling glacial acetic acid and an excess of alcohol yields alkyl 2:5-diarylamino-terephthalates, provided a sufficiency of air is admitted; thus ethyl succinylsuccinate and aniline under these conditions yield *ethyl 2:5-dianilino-terephthalate*, m. p. 143°, red needles or orange-yellow needles, but the corresponding methyl ester cannot be similarly prepared. In all cases, however, alkyl 2:5-diarylamino- or alkylamino-terephthalates can be prepared by oxidising alkyl 2:5-diarylamino- or alkylamino- $\Delta^{1:4}$ -cyclohexadiene-1:4-dicarboxylates with iodine in ethyl alcohol, amyl alcohol, or acetone. Some of the alkyl diarylamino- or dialkylamino-terephthalates can be obtained at will in two modifications. These two modifications are unimolecular and have the same colour in solution; in the solid state, each is stable at the ordinary temperature, but by heating the stable form is that the colour of which is nearer the red end of the spectrum. The author accounts for the existence of the two modifications by Hantzsch's theory of chromoisomerism. The following esters have been prepared: *Ethyl 2:5-di-o-toluidino-terephthalate*, m. p. 181°, red needles, and the *di-p-toluidino*-analogue, m. p. 187°, *ethyl*

2:5-*di-α-naphthylaminoterephthalate*, m. p. 230°, orange-red needles and a violet modification, and the *di-β-naphthylamino*-analogue, m. p. 182°, orange-red and yellow needles (*dibenzoyl* derivative, m. p. 275°, yellow prisms), *ethyl 2:5-di-o-anisidinoterephthalate*, m. p. 170°, orange-brown needles, and the *di-p-anisidino*-analogue, m. p. 171°, orange-red needles, *ethyl 2:5-di-o-aminoanilinoterephthalate*, m. p. 232°, reddish-violet and orange-yellow needles, *ethyl 2:5-diethylaminoterephthalate*, m. p. 142°, orange-red needles, and the *dimethylamino*-analogue, m. p. 117°, orange-red needles.

By hydrolysis with *N*-alkali hydroxide in boiling alcoholic solution or suspension, the preceding esters containing arylamino-groups yield the alkali salts (which are yellow or green) of the corresponding acids. The acids are blue or reddish-violet, contain two NH-groups, form yellow solutions in ordinary solvents, and dissolve to a colourless solution in concentrated sulphuric acid, probably because the nitrogen atoms become quinquevalent. The following are described: 2:5-*dianilinoterephthalic acid*, m. p. above 300°, violet crystals (*dibenzoyl* derivative, yellow crystals; *dinitroso*-derivative, decomp. 100—200°, almost colourless), 2:5-*di-α-naphthylaminoterephthalic acid*, blue crystals, and the *di-β-naphthylamino*-analogue, bluish-violet needles. 2:5-*Di-o-aminoanilinoterephthalic acid* is a yellow or olive-brown powder, which forms in concentrated sulphuric acid a blue solution with a red fluorescence.

The acids obtained by the hydrolysis of alkyl 2:5-diethylamino- or dimethylamino-terephthalates are colourless or nearly so in the solid state, and therefore must have a different constitution from their coloured esters and from the highly coloured 2:5-diarylamino-terephthalic acids. They are probably betaine salts,



containing quinquevalent nitrogen; the metallic salts are coloured, because the betaine rings are ruptured and the salts have the same constitution as the esters. 2:5-*Diethylaminoterephthalic acid* (R = Et), almost colourless crystals (green *barium* salt, C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>N<sub>2</sub>Ba), and 2:5-*dimethylaminoterephthalic acid*, m. p. 295°, almost colourless needles, are described; they form orange-yellow solutions in alcohol. By hydrolysis with potassium hydroxide (1 mol.) and subsequent acidification, three of the preceding ethyl 2:5-diarylamino- or dialkylamino-terephthalates yield ethyl hydrogen esters, namely, *ethyl hydrogen 2:5-dianilinoterephthalate*, m. p. 258°, red needles (*barium* salt, [C<sub>22</sub>H<sub>19</sub>O<sub>4</sub>N<sub>2</sub>]<sub>2</sub>Ba, 5H<sub>2</sub>O, golden-yellow needles), *ethyl hydrogen 2:5-diethylaminoterephthalate*, m. p. 179°, red needles, and *ethyl hydrogen 2:5-dimethylaminoterephthalate*.

By boiling ethyl succinylsuccinate (1 mol.), iodine (1 mol.), and an aromatic primary amine (3—4 mols.) in a mixture of glacial acetic acid and alcohol, in many cases there are formed, in addition to the ethyl 2:5-diarylamino-terephthalates, *ethyl 2-arylamino-5-hydroxyterephthalates*, which form *dibenzoyl* derivatives, are insoluble in cold alkalis, and form coloured solutions in concentrated sulphuric acid. *Ethyl 2-anilino-5-hydroxyterephthalate*, m. p. 83—84°, brick-red prisms,

*ethyl 2-p-iodoanilino-5-hydroxyterephthalate*, m. p. 119°, orange-red needles, and *ethyl 2-β-naphthylamino-5-hydroxyterephthalate*, m. p. 125°, orange needles, are described. The corresponding acids, *2-anilino-5-hydroxyterephthalic acid*, brownish-red needles, *2-p-iodoanilinoterephthalic acid*, orange-red needles, and *2-β-naphthylamino-5-hydroxyterephthalic acid*, violet-red prisms, are strong dibasic acids which form colourless solutions in concentrated sulphuric acid and yellow or orange solutions in ordinary solvents and yield green and yellow alkali and alkaline earthy salts. *Ethyl hydrogen 2-β-naphthylamino-5-hydroxyterephthalate*, m. p. 253°, crystallises in orange needles and forms highly coloured salts.

*s*-Diphenylcarbamide is produced by heating ethyl succinylsuccinate with aniline alone at 180°. C. S.

**Salts of Formaldehyde.** HARTWIG FRANZEN (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), 2, 277—279).—By the action of calcium, barium, strontium, magnesium and lead hydroxides on formaldehyde solution, compounds can be obtained. For the preparation of the corresponding compounds of the heavier metals, for example, of copper, zinc and cadmium, the necessary quantity of a suitable salt was added to an aqueous solution of formaldehyde and sodium hydroxide.

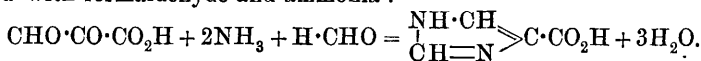
With the exception of the copper compound, the substances were colourless solids completely soluble in water, and had an odour of formaldehyde. The ratio between the number of atomic weights of the metal and molecular weights of formaldehyde present ranged from 2:1 to 1:2. Structural formulæ of the chain type are suggested, as, for example,  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{Ca}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$  for the calcium compound. In the case of the lead compound with a ratio 6:5, the chain is much longer, and such compounds as these are regarded as intermediate steps in the polymerisation of formaldehyde to sugar.

In addition to the components, metallic hydroxide and formaldehyde, there is also generally present a certain amount of water of crystallisation. D. F. T.

**Preparation of Aldol from Acetaldehyde.** CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 269996).—Aldol is readily obtained from acetaldehyde by treating it with a small amount (not more than 5%) of an alkali or alkaline earth metal, their amalgams or alloys, or the products of the interaction of these materials and acetaldehyde or compounds of these metals such as the alcoholates, cyanides, etc., which dissolve in acetaldehyde. The aldol formed can be isolated by distillation in a vacuum. For example, 1000 parts of acetaldehyde are treated (1) with 70 parts of a 2% calcium amalgam or (2) with one part of dry powdered potassium cyanide. J. C. C.

**Combination of Boric Acid with Mannitol.** G. MAGNANINI (*Gazzetta*, 1914, 44, i, 396—398).—The author replies to Ageno and Valla's criticisms (*A.*, 1913, i, 1052) of his conclusions (*A.*, 1912, ii, 142). T. H. P.

**Action of Ammoniacal Copper Hydroxide on Dextrose.** ADOLF WINDAUS and ARTHUR ULLRICH (*Zeitsch. physiol. Chem.*, 1914, **90**, 366—368).—Investigations of Windaus and Knoop (A., 1905, i, 381) have shown that dextrose is converted into 4-methylglyoxaline by the action of ammoniacal zinc or cadmium hydroxide. Ammoniacal copper hydroxide is now shown to oxidise it to oxalic acid and glyoxaline-4-carboxylic acid (Knoop, A., 1907, i, 788). The latter is probably formed by the condensation of the semialdehyde of mesoxalic acid with formaldehyde and ammonia :



Dextrose is allowed to remain in contact with an ammoniacal solution of copper hydroxide for three years. The solution is evaporated to dryness, the residue dissolved in dilute sulphuric acid, and, after removal of copper, oxalic acid is extracted with ether. Glyoxaline-4-carboxylic acid is isolated from the aqueous solution by successive treatment of the latter with barium hydroxide and phosphotungstic acid, and further identified by converting it into glyoxaline, m. p. 89° (compare Knoop, *loc. cit.*), and glyoxaline picrate, m. p. 206°.

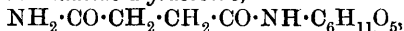
H. W.

**Biochemical Synthesis, by means of  $\alpha$ -Glucosidase, of  $\alpha$ -Glycol Monoglucoside.** EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1914, **158**, 1219—1222; *J. Pharm. Chim.*, 1914, [vii], **9**, 514—519. Compare A., 1913, i, 1080; this vol., i, 72).—The authors have isolated, in a crystalline form, the glucoside formed by the action of  $\alpha$ -glucosidase on a solution of dextrose in 50% aqueous glycol.  *$\alpha$ -Glycol monoglucoside* crystallises in colourless needles,  $[\alpha]_D^{25} + 135.48^\circ$ , having a slightly sweet taste. It is very soluble in alcohol and water, and almost insoluble in ether and ethyl acetate. It does not reduce Fehling's solution. It is readily hydrolysed in aqueous solution by  $\alpha$ -glucosidase, or by heating with 3% sulphuric acid in a sealed tube for two hours at 110°.

W. G.

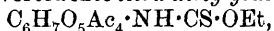
**Synthesis of New Glucosides.** EMIL FISCHER (*Ber.*, 1914, **47**, 1377—1393).—The method used for the preparation of glucosides of the purines by interaction of the silver salts of the latter with acetobromoglucose in anhydrous solvents (Fischer and Helferich, this vol., i, 333) is found to be of wide applicability.

Acetobromoglucose in warm xylene solution rapidly reacts with a slight excess of silver succinimide, giving *tetra-acetylsuccinimide-d-glucoside*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CO} \end{array} > \text{N} \cdot \text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$ , colourless needles, or triangular platelets, m. p. 203—204° (corr.),  $[\alpha]_D^{25} + 12.8^\circ$  (in *s*-tetrachloroethane), which on treatment in methyl-alcoholic solution with dry ammonia yields *succinamide-d-glucoside*,



microscopic prisms (with  $2\text{H}_2\text{O}$ ), m. p.  $88-90^\circ$ ; the anhydrous substance melts if introduced into a bath at  $153^\circ$ , but may again resolidify and then melt again near  $192^\circ$  (decomp.), this being the only m. p. observed when the anhydrous substance is slowly heated.

Interaction of silver thiocyanate and acetobromoglucose in xylene solution at water-bath temperature produced *acetothiocarbimidoglucose*,  $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{NCS}$ , tetragonal plates; the physical properties varied according to the method of purification, rapid recrystallisation from alcohol giving a product, m. p.  $114^\circ$ ,  $[\alpha]_D^{17} + 6.0^\circ$  (in *s*-tetrachloroethane), whilst repeated separation from chloroform by the addition of light petroleum gave a product, m. p. near  $100^\circ$ ,  $[\alpha]_D^{20} - 8.5^\circ$ . Treatment of the last substance in methyl-alcoholic solution with gaseous ammonia gave *glucosethiocarbamide*,  $\text{C}_6\text{H}_{11}\text{O}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , a crystalline solid,  $[\alpha]_D^{20} - 35.73^\circ$  (in water), m. p.  $215-216^\circ$  (corr., decomp.) (compare Schoorl, A., 1902, i, 83). This thiocarbamide derivative can be desulphurised by treating with mercuric oxide in aqueous solution, the product being probably *glucose-cyanamide*, an amorphous solid difficult to purify. When boiled for an hour with alcohol, acetothiocarbimidoglucose is converted into *tetra-acetylglucosethiourethane*,



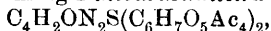
a crystalline solid, m. p.  $159-160^\circ$  (corr.),  $[\alpha]_D^{21} + 11.5^\circ$  (in *s*-tetrachloroethane).

The action of silver cyanate on acetobromoglucose gave *tetraacetylglucosecarbimide*,  $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{NCO}$ , needles, m. p.  $117-118^\circ$  (corr.)  $[\alpha]_D^{18} - 7.54^\circ$  (in *s*-tetrachloroethane), but there was also produced a less soluble, amorphous solid of approximately the same composition, m. p.  $115-120^\circ$ ,  $[\alpha]_D^{16} + 15.86^\circ$  (in *s*-tetrachloroethane), the nature of which was uncertain and which gave another amorphous product,  $\text{C}_7\text{H}_{14}\text{O}_6\text{N}_2$ , m. p.  $195^\circ$  (decomp.),  $[\alpha]_D^{17} - 35.3^\circ$ , on shaking with aqueous ammonia. Tetra-acetylglucosecarbimide itself reacted with aqueous ammonia, producing glucosecarbimide (Schoorl, *loc. cit.*), m. p. near  $207^\circ$  (decomp.),  $[\alpha]_D^{19} - 23.41^\circ$  (in water), whilst treatment with boiling alcohol converted it into *tetra-acetylglucoseurethane*,  $\text{C}_{17}\text{H}_{25}\text{O}_{11}\text{N}$ , which was not obtained pure.

The preparation of the glucosides of the uracils gave considerable difficulty (compare Fischer and Helferich, *loc. cit.*).

Acetobromoglucose in xylene solution reacted with the silver derivative of cytosine, giving an uncrystallisable substance which was very unstable and even in cold alcoholic solution to which picric acid had been added gradually gave a precipitate of cytosine picrate. Uracil gave a product similar to cytosine.

The silver salt of 2-thiouracil reacted with acetobromoglucose under the usual conditions, forming *2-thiouracilditetra-acetylglucoside*,



needles, m. p.  $230^\circ$  (corr.),  $[\alpha]_D^{19} + 12.44^\circ$  (in *s*-tetrachloroethane).

In a similar manner the silver salt of 2-ethylthiouracil gave *2-ethylthiouracilditetra-acetylglucoside*,  $\text{C}_6\text{H}_7\text{ON}_2\text{S}\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$ , m. p.  $108^\circ$  (corr.),  $[\alpha]_D^{19} + 3.14^\circ$  (in *s*-tetrachloroethane). These acetyl derivatives underwent hydrolysis on treatment with ammonia, but it was not found possible to obtain the products in a pure condition.

D. F. T.

**Resolution of Racemic Sugars by means of Optically Active Amyl Mercaptan and Certain Mercaptals.** E. Voroček and V. VESELY (*Ber.*, 1914, 47, 1515—1519. Compare Neuberg and Federer, A., 1905, i, 299).—The authors have investigated the applicability of *d*-amyl mercaptan to the resolution of racemic sugars and have thus been able to resolve *dl*-arabinose. They have further prepared a series of mercaptals of various aldoses, since the data given in the literature are frequently inaccurate owing to the use of the impure, commercial amyl mercaptan.

*d*-Amyl alcohol,  $\alpha_D - 9.6^\circ$  ( $l = 2$ ), is prepared by Marckwald's method and purified by means of 3-nitrophthalic acid. The ester has m. p. 114.8—115.2°, whereas Marckwald gives 113.5—114.5° and Sautter 111—112°.

*d*-Amyl mercaptan,  $D^{25} 0.8415$ ,  $[\alpha]_D^{25} + 3.21^\circ$ , is prepared by converting the alcohol into potassium *d*-amyl sulphate and distillation of the latter with potassium hydrosulphide solution in a slow stream of hydrogen sulphide. It has b. p. 119—121° (uncorr.).

*l*-Arabinose-*d*-amylmercaptal, long needles, m. p. 114—116°, is obtained by warming a solution of *l*-arabinose in fuming hydrochloric acid with *d*-amyl mercaptan at 30—35° until the emulsion first formed is replaced by a clear solution. The similarly prepared *d*-arabinose-*d*-amylmercaptal, pearly scales, m. p. 118—120°, differs sharply from the isomeride in crystalline form and also in solubility in alcohol. The resolution of *dl*-arabinose is therefore effected by conversion into the *d*-amylmercaptal and fractional crystallisation of the crude product from alcohol, whereby *d*-arabinose-*d*-amylmercaptal is readily obtained in a state of purity; the isolation of the *l*-form from the mixture has not been successfully accomplished, owing to the small amount of substance available.

Preliminary experiments on the resolution of rhodose and fucose by means of *d*-amyl mercaptan are also described. It is found, however, that the *d*-amyl mercaptals prepared from the respective pure *d*- and *l*-forms show but little difference in m. p. or solubility in the usual media. Since further, dissimilarity in crystalline form can only be detected under the microscope, whilst, also, polarimetric measurements are rendered difficult by the small solubility and slight optical activity of the products, the prospects of a successful resolution are not considered sufficiently promising for a continuation of the work at present for these two substances.

The following mercaptals have been prepared according to the method of Fischer (A., 1894, i, 269): *l*-Arabinose-*iso*amylmercaptal, m. p. 121—124°; *d*-arabinose-*iso*amylmercaptal, m. p. 121—124°; *dl*-arabinose-*iso*amylmercaptal, m. p. 113—115°; *rhodose*-*iso*amylmercaptal, m. p. 151—152.5°; *rhodose*-*d*-amylmercaptal, m. p. 136—138.5°; *fucose*-*d*-amylmercaptal, m. p. 140—142°; *fucose*-*iso*amylmercaptal, m. p. 151—152.5°; *dl*-fucose(*dl*-rhodose)-*iso*amylmercaptal, m. p. 160—162°; *rhamnose*-*iso*amylmercaptal, m. p. 108—110.5°; *d*-glucose-*d*-amylmercaptal, m. p. 138—139°; *d*-glucose-*iso*amylmercaptal, m. p. 142—144°; *d*-galactose-*d*-amylmercaptal, m. p. 123—124°; *d*-galactose-*iso*amylmercaptal, m. p. 122—123°; *rhodose*-ethylmercaptal, m. p. 167—168.5°; *fucose*-ethylmercaptal, m. p. 167—168.5°; *rhodose*-

*ethylenemercaptal*, m. p. 191—191·5°; *fucose-ethylenemercaptal*, m. p. 191—191·5°. H. W.

**The Plurality of Starches.** CHARLES TANRET (*Compt. rend*, 1914, 158, 1353—1356).—To solve the question as to whether there is only one or several starches, the author has estimated the amounts of amylopectin and amylose present in starches from different plants. The proportions of these two substances, which are always present, differ with the origin of the starch, and the starches can be further distinguished among themselves by the sensitiveness of the amylopectin to water, and the differing solubility of the amylose on warming. The author finds that cellulose in the shape of well-washed cotton can be used to fix amylose and remove it from a solution, thus leaving the way clear to test for amylopectin. W. G.

**Reductions by Aluminium. Preparation of Ethylamine.** J. FERRER (*Anal. Fis. Quim.*, 1914, 12, 239—240). The reduction of acetonitrile by aluminium and cold sodium hydroxide (15%) gave a 75% yield of ethylamine. Potassium cyanide gave a 10% yield of methylamine, and benzonitrile a 17% yield of benzylamine. G. D. L.

**Preparation of Trimethylamine.** KARL HEINRICH SCHMITZ (D.R.-P. 270260).—A mixture of ammonium chloride (1 part) and trioxymethylene (2·65 parts) is heated under reflux for one to two hours at 120—170°. On cooling, part of the trimethylamine hydrochloride crystallises out; alkali is added, and the base condensed in water, alcohol or hydrochloric acid. Other ammonium salts may also be used. J. C. C.

**Constitution of Pseudomuscarine ("Synthetic Muscarine").** ARTHUR JAMES EWINS (*Biochem. J.*, 1914, 8, 209—215).—"Pseudomuscarine," obtained by the action of concentrated nitric acid on choline is shown to be choline nitrite,  $\text{NO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$ .

It seems doubtful whether the formula assigned to muscarine is correct. N. H. J. M.

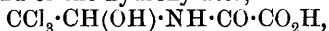
**The Preparation of Creatine, Creatinine, and Standard Creatinine Solutions.** OTTO FOLIN (*J. Biol. Chem.*, 1914, 17, 463—468).—The dichromate standard hitherto used should be replaced in accurate colorimetric work by standard solutions of creatinine itself. Directions are given for the preparation of the latter substance as a picrate, from which creatinine zincchloride is prepared; this is decomposed with lead hydroxide. The further treatment of the creatine-creatinine solution depends on whether creatinine or creatine is desired; it is evaporated on the water-bath, and the residue dissolved in boiling water, and then twice as much alcohol (95%), this precipitates most of the creatine and no creatinine; the creatine is obtained pure by repeating the process, but this involves a 30% loss. Creatinine is obtained by heating the mixture at 135—140° for three hours. Full details of the process, and the method of preparing standard creatinine solutions are given. W. D. H.



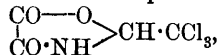
# The Condensation Products of Chloral with Acid Amides.

II. FRANZ FEIST [with FREDERICK NISSEN and GEORG STADLER] (*Ber.*, 1914, **47**, 1173—1193. Compare Feist, A., 1912, i, 420).—A closer examination of some of the products described earlier, together with an investigation of the behaviour of other products of the same type.

Chloral oxamethane,  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , can be prepared by merely warming a mixture of chloral and oxamethane on the water-bath for three hours (compare Moscheles, A., 1891, 1003); it has m. p.  $121^\circ$ , b. p.  $182^\circ/23$  mm. (partial decomp.). It is very sensitive towards alkalis, passing readily into the sparingly soluble sodium salt of the unstable *chloraloxamic acid*,  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ . By treating the aqueous solution of the sodium salt with solutions of various metallic salts, the *lead*, *mercurous*, *silver*, and *copper* salts were obtained as precipitates. On shaking for twelve hours with a 16% solution of sodium carbonate, chloraloxamethane passes into an acid,  $[\text{C}_5\text{H}_6\text{O}_4\text{NCl}_3]_x$ , m. p.  $133^\circ$  (sodium salt, sparingly soluble), apparently a molecular compound of the hydroxy-acid,

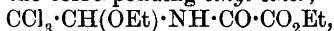


with the corresponding ethoxy-acid. If chloraloxamethane is dissolved in 5—6 times its weight of ice-cold sulphuric acid and then poured into water, there is obtained *chloraloxamolactone*,



m. p.  $236$ — $237^\circ$  (decomp.), which is also produced in the action of phosphorus pentabromide on chloraloxamethane. The lactone gives an acid solution, is soluble in sodium carbonate solution, and on warming with alkalis undergoes fission with formation of chloral or chloroform with oxamide or an oxalate.

When heated with excess of acetyl chloride at  $100^\circ$ , chloraloxamethane gives *acetylchloraloxamethane*,  $\text{CCl}_3 \cdot \text{CH}(\text{OAc}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , m. p.  $60$ — $61^\circ$ , b. p.  $176^\circ/23$  mm. Treatment with an equimolecular quantity of phosphorus pentachloride converts chloraloxamethane into  $\alpha\beta\beta\beta$ -*tetrachloroethyloxamethane*,  $\text{CCl}_3 \cdot \text{CHCl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , colourless needles, m. p.  $53$ — $54^\circ$ , whilst phosphorus tribromide converts it into  $\beta\beta\beta$ -*trichloro- $\alpha$ -bromoethyloxamethane*,  $\text{CCl}_3 \cdot \text{CHBr} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , crystals, m. p.  $62$ — $63^\circ$ . The new halogen atom in these two compounds is very reactive, precipitating silver haloid from silver nitrate solution. The tetrachloro-compound also reacts with methyl alcohol, giving a *methyl ether*,  $\text{CCl}_3 \cdot \text{CH}(\text{OMe}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , crystals, m. p.  $66^\circ$ , with ethyl alcohol giving the corresponding *ethyl ether*,



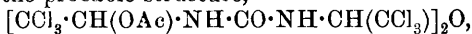
colourless crystals, m. p.  $34$ — $35^\circ$ , with aniline giving *anilinochloraloxamethane*,  $\text{CCl}_3 \cdot \text{CH}(\text{NHPh}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , crystals, m. p.  $172^\circ$ , with phenylhydrazine giving *phenylhydrazinochloraloxamethane*,



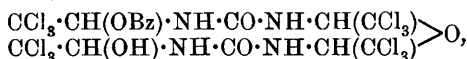
colourless crystals, m. p.  $125^\circ$ , and with ethyl sodioacetoacetate in ether giving *ethyl  $\alpha$ -carbethoxyacetonyl- $\beta'\beta'\beta'$ -trichloroethylaminoglyoxylate*,  $\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{CH}(\text{CCl}_3) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , colourless leaflets, m. p.  $64$ — $65^\circ$ .

Dichloralcarbamide, m. p.  $194^\circ$  (compare Jacobsen, this Journ., 1871, 257; Coppin and Titherley, T., 1914, **105**, 32), obtained by warming together carbamide, chloral and a little water, when its solution in

aqueous sodium hydroxide is gradually treated with acetic anhydride loses the elements of water in an unusual manner, whilst being simultaneously acetylated, with formation of *diacetylanhydrodichloralcarbamide* of the probable structure,

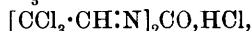


m. p. 137—138°. Proceeding in a similar manner, sodium hydroxide and benzoyl chloride convert dichloralcarbamide into *benzoylanhydrodichloralcarbamide*,



m. p. 146—147° (decomp.).

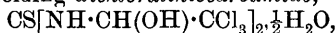
At water-bath temperature, phosphorus pentachloride attacks dichloralcarbamide with formation of hydrogen chloride and a colourless solid *substance*, these two substances probably owing their origin to the decomposition of a primary dichloro-product. The solid, decomp. at 222° without fusion, loses hydrogen chloride very readily, and the alternative structures  $\text{CCl}_3\cdot\text{CHCl}\cdot\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}\cdot\text{CCl}_3$  and



are suggested. The addition of a molecular proportion of alkali to this product gives a *substance*, possibly  $\text{CO}[\text{N}\cdot\text{CH}\cdot\text{CCl}_3]_2$ , which carbonises at 235°; the action of boiling alcohol on this base yields the *diethyl ether* of dichloralcarbamide,  $\text{CO}[\text{NH}\cdot\text{CH}(\text{OEt})\cdot\text{CCl}_3]_2$ , m. p. 242°, whilst acetone gives an amorphous *substance*,  $\text{C}_6\text{H}_8\text{ON}_2\text{Cl}_4$ , decomp. above 230°. The above compound, decomp. at 222°, on treatment with alcohol is converted into an ethoxy-derivative,

m. p. 144—145°, of the probable structure  $\begin{array}{c} \text{NH}\cdot\text{CH}(\text{CCl}_3) \\ \text{CO} \text{---} \text{NH} \end{array} > \text{C}(\text{OEt})\cdot\text{CCl}_3$ .

By heating thiocarbamide with rather more than a bimolecular proportion of chloral at 65° for twenty minutes an *anhydrodichloralthiocarbamide*,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CS}\cdot\text{N}\cdot\text{CH}\cdot\text{CCl}_3$ , m. p. 130—131°, was obtained (compare Nencki and Schaffer, A., 1879, 306). This substance reduces permanganate, decolorises bromine, and on treatment in suspension in carbon tetrachloride with dry chlorine is converted into a hygroscopic *hydrochloride*,  $\text{CS}[\text{NH}\cdot\text{CHCl}\cdot\text{CCl}_3]_2\cdot 2\text{HCl}$ . On heating with excess of acetyl chloride, the anhydrodichloralthiocarbamide gives an *acetyl* derivative, m. p. 103°, whilst treatment with phosphorus pentachloride causes a vigorous reaction, subsequent addition of water yielding *dichloralthiocarbamide*,



m. p. 79—80°.

Phosphorus pentachloride acts on chloralformamide (Feist, *loc. cit.*) when heated on a water bath, giving unstable *formo-αβββ-tetrachloroethylamide*,  $\text{CCl}_3\cdot\text{CHCl}\cdot\text{NH}\cdot\text{CHO}$ , prisms, m. p. 94—95°. The α-chlorine atom is very reactive, so that *N*/10-potassium hydroxide re-forms the original chloralformamide; aniline on warming gives *anilinochloralformamide*,  $\text{CCl}_3\cdot\text{CH}(\text{NHPh})\cdot\text{NH}\cdot\text{CHO}$ , a colourless powder, m. p. 98—99°, and a warm ethereal solution of ethyl sodiummalonate gradually gives *formo-α-trichloromethyl-ββ-dicarboethoxyethylamide*,  $\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{CH}(\text{CCl}_3)\cdot\text{NH}\cdot\text{CHO}$ , m. p. 65—66°, b. p. 172°/0.7 mm.

Anhydrochloralformamide and phosphorus pentachloride react at  $80^{\circ}$  with production of a *hydrochloride*, decomp. above  $400^{\circ}$ , which on titration with alkali liberates the free *base*,  $\begin{array}{c} \text{CH}=\text{N}\cdot\text{CH}(\text{CCl}_3) \\ | \\ \text{CCl}:\text{N}\cdot\text{CH}(\text{CCl}_3) \end{array} > \text{O}$ , m. p.  $157^{\circ}$ . Anhydrochloralacetamide proved indifferent to phosphorus pentachloride, but on treatment in ethereal solution with nitrous fumes gave an unstable additive *compound*,  $\text{C}_8\text{H}_{10}\text{O}_3\text{N}_2\text{Cl}_6\cdot\text{NO}$ , m. p.  $135\text{--}136^{\circ}$  (decomp.).

The condensation of bornylurethane with excess of chloral at water-bath temperature yields *chloralbornylurethane*, a colourless, crystalline powder, m. p.  $187^{\circ}$  (decomp.). D. F. T.

**Thermochromism of Silver Salts of Allylthiourethanes**, WILHELM SCHNEIDER and GUSTAV HÜLLWECK (*Ber.*, 1914, 47, 1246—1248).—The silver salt of ethyl allylthiocarbamate (A., 1912, i, 954) is obtained in a pure condition by crystallisation from a mixture of chloroform and alcohol. It separates in prismatic needles and is thermochromic. At  $0^{\circ}$  it is almost colourless, whilst at temperatures between  $30^{\circ}$  and its m. p. it has a citron-yellow colour, the change being gradual and reversible. A similar change in colour is shown by the silver salts of propyl and methyl allylthiocarbamates (following abstract).

In the case of the salt of the methyl ester the change is reversible almost up to the m. p., but with the silver salt of the propyl ester this is only the case at temperatures not exceeding  $70^{\circ}$ ; above this temperature the latter salt acquires a permanent dark yellow colour.

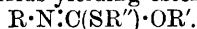
It would appear that the thermochromism of these salts is connected with the presence of the allyl group, for the similarly constituted silver salts of esters of benzylthiocarbamic and  $\gamma$ -methylsulphone-propylcarbamic acids (*loc. cit.*) do not show this phenomenon. F. B.

**Thiocarbimides. V. Thiourethanes and Thiourethane Ethers from Some Naturally Occurring Thiocarbimides.** WILHELM SCHNEIDER, DOUGLAS CLIBBENS, GUSTAV HÜLLWECK, and WERNER STEIBELT (*Ber.*, 1914, 47, 1248—1258. Compare A., 1912, i, 954).—An account of the preparation of a number of thiourethanes of the formula  $\text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{OR}'$  (where  $\text{R}=\text{C}_3\text{H}_5$ ,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot$  or  $\text{SO}_2\text{Me}\cdot[\text{CH}_2]_3\cdot$ )

by the direct combination of allylthiocarbimide, benzylthiocarbimide, and cheiroline with alcohols. The thiourethanes form silver salts,



which react with alkyl haloids yielding esters of the type



*Methyl allylthiocarbamate*,  $\text{C}_3\text{H}_5\cdot\text{N}\cdot\text{CS}\cdot\text{OMe}$ , prepared by heating allylthiocarbimide with methyl alcohol at  $110\text{--}120^{\circ}$ , is a pale yellow liquid, b. p.  $101\text{--}106^{\circ}/14$  mm., and yields with ammoniacal silver solutions a *silver* salt,  $\text{C}_3\text{H}_5\text{N}:\text{C}(\text{SAg})\cdot\text{OMe}$ , which crystallises from a mixture of alcohol and chloroform in yellowish-white prisms, m. p.  $157^{\circ}$ , and reacts with methyl iodide in ethereal solution, yielding *methyl allyliminothiolcarbonate*,  $\text{C}_3\text{H}_5\cdot\text{N}:\text{C}(\text{SMe})\cdot\text{OMe}$ , a colourless oil, b. p.  $70\text{--}75^{\circ}/13$  mm.

*O-Methyl S-ethyl allyliminothiolcarbonate*,  $C_3H_5 \cdot N:C(SET) \cdot OMe$ , prepared from the silver salt and ethyl iodide, has b. p.  $76-80^\circ/12$  mm.

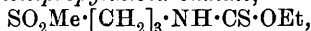
*O-Methyl S-propyl allyliminothiolcarbonate* has b. p.  $91-95^\circ/14$  mm.

The silver salt of ethyl allylthiocarbamate (*loc. cit*) reacts with methyl and propyl iodides in ethereal solution, yielding *O-ethyl S-methyl allyliminothiolcarbonate*,  $C_3H_5 \cdot N:C(SMe) \cdot OEt$ , b. p.  $76-80^\circ/13$  mm., and *O-ethyl S-propyl allyliminothiolcarbonate*, b. p.  $101-105^\circ/15$  mm. respectively.

*Propyl allylthiocarbamate*  $C_3H_5 \cdot NH \cdot CS \cdot OPr^a$ , prepared from allylthiocarbimide and propyl alcohol, is a pale yellow oil, b. p.  $119-123^\circ/12$  mm., and forms a *silver* salt, which crystallises in yellowish-white rhombs, m. p.  $135^\circ$ , and reacts with propyl iodide yielding *propyl allyliminothiolcarbonate*,  $C_3H_5 \cdot N:C(SPr^a) \cdot OPr^a$ , a colourless oil, b. p.  $111-115^\circ/13$  mm.

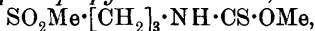
*O-Propyl S-allyl allyliminothiolcarbonate*,  $C_3H_5 \cdot N:C(S \cdot C_3H_7) \cdot OPr^a$ , prepared from the preceding silver salt and allyl iodide, has b. p.  $112-116^\circ/12$  mm. The ethyl and propyl esters of allyliminothiolcarbonic acid are decomposed by silver nitrate in aqueous alcoholic solution with the formation of the silver salts of ethyl and propyl mercaptans respectively.

*Ethyl  $\gamma$ -methylsulphonepropylthiocarbamate*,



obtained from cheirolin and ethyl alcohol at  $120^\circ$ , crystallises from water in needles, m. p.  $71^\circ$ ; the *silver* salt forms colourless needles, m. p.  $150^\circ$ , and on treatment with ethyl iodide is converted into *ethyl  $\gamma$ -methylsulphonepropyliminothiolcarbonate*,  $SO_2Me \cdot [CH_2]_3 \cdot N:C(SET) \cdot OEt$ , lustrous needles, m. p.  $44^\circ$ .

*Methyl  $\gamma$ -methylsulphonepropylthiocarbamate*,



from cheirolin and methyl alcohol, has m. p.  $86^\circ$ , and forms a *silver* salt crystallising in pale yellow plates, m. p.  $141^\circ$ .

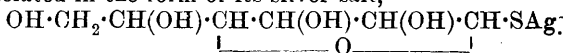
*Ethyl benzylthiocarbamate*,  $C_7H_7 \cdot NH \cdot CS \cdot OEt$ , obtained by heating benzylthiocarbimide with ethyl alcohol, distils undecomposed at  $125-130^\circ/0.3-0.4$  mm., but at 10 mm. undergoes partial decomposition into benzylcarbamide and benzylthiocarbamide. When heated with ethyl iodide it is transformed into the isomeric *ethyl benzylthiolcarbamate*,  $C_7H_7 \cdot NH \cdot CO \cdot SET$ , crystallising in long needles, m. p.  $66^\circ$ . The *silver* salt,  $C_7H_7 \cdot N:C(SAg) \cdot OEt$ , forms long, colourless needles, m. p.  $179^\circ$ , and reacts with ethyl iodide, yielding *ethyl benzyliminothiolcarbonate*,  $C_7H_7 \cdot N:C(SET) \cdot OEt$ , a colourless liquid, b. p.  $164-165^\circ/18$  mm., which on treatment with hydrogen chloride in benzene solution is converted into ethyl benzylthiolcarbamate and ethyl chloride.

F. B.

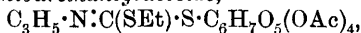
**Mustard Oil Glucosides. III. Synthetic Glucosides from Thiourethanes.** WILHELM SCHNEIDER, DOUGLAS CLIBBENS, GUSTAV HÜLLWECK, and WERNER STEIBELT (*Ber.*, 1914, **47**, 1258—1269. Compare A., 1913, i, 1213).—Attempts have been made to synthesise glucosides of the constitution  $R \cdot N:C(OEt) \cdot S \cdot C_6H_{11}O_5$ , allied to the naturally occurring glucosides, by the condensation of tetra-acetyl-bromoglucose with the silver salts of thiourethanes,  $R \cdot N:C(OEt) \cdot SAg$ ,

and subsequent removal of the acetyl groups from the resulting tetra-acetylglucosides,  $R \cdot N : C(OEt) \cdot S \cdot C_6H_7O_5(OAc)_4$ .

The attempts, however, were not entirely successful, partly on account of the amorphous nature of the products and partly owing to the ease with which the acetyl-free glucosides undergo further hydrolysis into urethanes,  $R \cdot NH \cdot CO_2Et$ , and thioglucose which is readily isolated in the form of its silver salt,

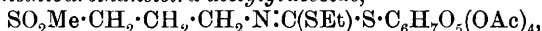


*Tetra-acetylallylthiourethaneglucoside,*



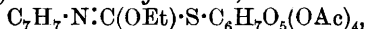
is prepared by evaporating a concentrated solution of the silver salt of ethyl allylthiocarbamate (compare preceding abstract) and tetra-acetyl-bromoglucose in chloroform, and heating the residue at 150—200°. It separates from alcohol in tufts of long, colourless needles, m. p. 99°, and has  $[\alpha]_D^{18} - 17.92^\circ$  in alcohol and  $-1.46^\circ$  in acetylene tetrachloride. When hydrolysed with alcoholic ammonia at 0°, it yields a colourless amorphous product, containing *allylthiourethaneglucoside* and *thioglucose*. The latter compound is obtained as a colourless, amorphous substance of the composition  $C_6H_{12}O_5S \cdot H_2O$  by crystallising the product of hydrolysis from alcohol. On treatment with ammoniacal silver solutions, the product resulting from the hydrolysis of the tetra-acetylglucoside yields the *silver* salt of thioglucose in yellowish-brown, amorphous flocks, of the composition  $C_6H_{12}O_5 \cdot SA_g$ .

*Cheirolinethiourethanetetra-acetylglucoside,*



prepared from the silver salt of ethyl  $\gamma$ -methylsulphonepropylthiocarbamate and tetra-acetyl-bromoglucose, crystallises in tufts of colourless needles, m. p. 113°  $[\alpha]_D^{20} - 4.66^\circ$  in acetylene tetrachloride, and when hydrolysed with alcoholic ammonia yields *cheirolinethiourethaneglucoside*,  $C_{13}H_{25}O_8NS_2$ , as a colourless, amorphous, deliquescent powder, which has  $[\alpha]_D^{22} - 116.77^\circ$  in aqueous solution, and on treatment with ammoniacal silver solution yields the silver salt of thioglucose, which separates from aqueous alcohol with  $1H_2O$  in amorphous flocks (decomp. 80°).

*Tetra-acetylbenzylthiourethaneglucoside,*



from the silver salt of ethyl benzylthiocarbamate, has m. p. 126°,  $[\alpha]_D^{15} - 3.49^\circ$  in *s*-tetrachloroethane, and when hydrolysed with aqueous barium hydroxide yields ethyl benzylcarbamate; hydrolysis with alcoholic ammonia gives rise to a white, amorphous product containing benzylthiourethaneglucoside, which, however, could not be isolated in a pure condition.

The silver salt of thioglucose is obtained in good yield by hydrolysing tetra-acetylbenzylthiourethaneglucoside with alcoholic ammonia in the presence of silver nitrate at the ordinary temperature. F. B.

**Mechanism of the Strecker Reaction.** A. SNESAREV (*J. pr. Chem.*, 1914, [ii], 89, 372—377; *J. Russ. Phys. Chem. Soc.*, 1914, 46, 217—222. Compare following abstract).—In view of the ease with which  $\alpha$ -aminonitriles lose ammonia and pass into  $\alpha$ -imino-

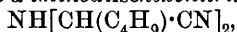
nitriles, the author inclines to the view that the simultaneous formation of the latter compounds in Strecker's synthesis of  $\alpha$ -aminonitriles by the action of hydrocyanic acid on  $\alpha$ -hydroxynitriles is due, in part, to decomposition of the aminonitriles in this manner, and not entirely to the condensation of the hydroxynitrile with the aminonitrile as suggested by Stadnikov. F. B.

**Syntheses in the  $\alpha$ -Iminonitrile Series.** A. SNESAREV (*J. pr. Chem.*, 1914, [ii], 89, 361—371; *J. Russ. Phys. Chem. Soc.*, 1914, 46, 206—217).—An account of the preparation and properties of a number of  $\alpha$ -iminonitriles from the corresponding  $\alpha$ -aminonitriles by the removal of ammonia:  $2\text{NH}_2\cdot\text{CHR}\cdot\text{CN} = \text{NH}(\text{CHR}\cdot\text{CN})_2 + \text{NH}_3$ .

*$\alpha$ -Aminoisobutyronitrile*, prepared by the action of potassium hydroxide on the hydrochloride, has b. p.  $51\text{--}52^\circ/15\text{ mm.}$ , and when kept at the ordinary temperature passes in the course of a month into  *$\alpha$ -iminodiisobutyronitrile*, which crystallises in long, colourless needles, m. p.  $48^\circ$ , and yields a *hydrochloride*, m. p.  $104\text{--}105.5^\circ$ , and a *nitroso-derivative*, m. p.  $51\text{--}52^\circ$ .

The imino-nitrile is accompanied by a *substance*,  $\text{C}_{18}\text{H}_{33}\text{O}_4\text{N}_8$ , crystallising in very slender needles, m. p.  $199\text{--}200^\circ$ , from which it is separated by taking advantage of its solubility in ether. If the condensation of  *$\alpha$ -aminoisobutyronitrile* is carried out at its b. p. only the iminonitrile is produced.

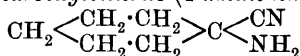
*$\alpha$ -Aminoisohexonitrile*, obtained together with  *$\alpha$ -iminodiisohexonitrile* by the interaction of *isovaleraldehyde*, ammonium chloride and potassium cyanide in aqueous solution, is a viscid, pale yellow liquid. When kept for a month at the ordinary temperature or when heated to its b. p., it passes into  *$\alpha$ -iminodiisohexonitrile*,



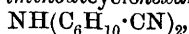
which exists in two stereoisomeric forms. Of these two stereoisomerides one is liquid whilst the other crystallises in needles, m. p.  $68\text{--}70^\circ$ , and yields a *hydrochloride*, m. p.  $151\text{--}153^\circ$ .

*N-Benzyl-di-iminophenylacetoneitrile*,  $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CHPh}\cdot\text{CN})_2$ , formed by the spontaneous condensation of  *$\alpha$ -aminophenylacetoneitrile*, has m. p.  $193\text{--}194^\circ$ , and yields a *hydrochloride*, m. p.  $269\text{--}270^\circ$ .

*$\alpha$ -Aminocyclohexancarboxylonitrile* (*1-aminohexahydrobenzonitrile*),



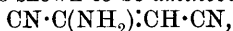
prepared from cyclohexanone, ammonium chloride and potassium cyanide in aqueous solution and purified by means of its *hydrochloride*, m. p.  $187\text{--}189^\circ$  (decomp.), forms large, tabular crystals, m. p.  $26\text{--}27^\circ$ , and readily condenses to  *$\alpha$ -iminodicyclohexancarboxylonitrile*,



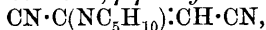
which separates in small, lustrous, tabular crystals and forms a *hydrochloride*, m. p.  $119\text{--}122^\circ$  (decomp.). F. B.

**Carbon Subnitride. Action of Ammonia and Amines.** CHARLES MOUREU and JACQUES CH. BONGRAND (*Compt. rend.*, 1914, 158, 1092—1096).—Carbon subnitride,  $\text{C}_4\text{N}_2$  (compare A., 1910, i, 159), reacts very vigorously with ammonia and with amines even in dilute ethereal solution. A 1% solution of the nitride (1 mol.) in pure dry

ether at  $-70^{\circ}$  is dropped into a  $\frac{1}{4}\%$  solution of ammonia (1 mol.) in ether at  $-70^{\circ}$  in an atmosphere of pure dry hydrogen. At the end of the reaction the mixture is allowed to attain the atmospheric temperature and the ether distilled off in a vacuum over sulphuric acid. The crude product is crystallised from ether and obtained in slender needles, m. p.  $131^{\circ}$ . Its constitution is shown to be *aminobutenedinitrile*,



and on decomposition with aqueous sulphuric acid it yields hydrogen cyanide, ammonia and cyanoacetic acid. Primary and secondary amines behave similarly towards carbon subnitride, but tertiary amines are without action on it. The following compounds have been prepared by the above method: *Diethylaminobutenedinitrile*,  $\text{CN}\cdot\text{C}(\text{NEt}_2)\cdot\text{CH}\cdot\text{CN}$ , prismatic needles, m. p.  $69-70^{\circ}$ ; *piperidylaminobutenedinitrile*,



a viscid oil crystallising slowly; *anilino-butenedinitrile*,



slender needles, m. p.  $120.5-121.5^{\circ}$ , and *benzylaminobutenedinitrile*,  $\text{CN}\cdot\text{C}(\text{NH}\cdot\text{CH}_2\text{Ph})\cdot\text{CH}\cdot\text{CN}$ , a brown oil. All these nitriles on hydrolysis with dilute acids yield hydrogen cyanide, cyanoacetic acid, and the original amine. W. G.

**Preparation and Properties of Sodium Zinc Cyanide.** NATHANIEL HERZ (*J. Amer. Chem. Soc.*, 1914, 36, 912-913).—Sharwood (A., 1903, i, 684) has described experiments on the preparation of sodium zinc cyanide which indicated the existence of two compounds,  $\text{Na}_2\text{Zn}(\text{CN})_4$  and  $\text{NaZn}(\text{CN})_3\cdot 2\frac{1}{2}\text{H}_2\text{O}$ .

It is now shown that when zinc cyanide is dissolved in sodium cyanide solution, both salts being free from potassium salts and carbonates, the compound  $\text{Na}_2\text{Zn}(\text{CN})_4\cdot 3\text{H}_2\text{O}$  separates in efflorescent, orthorhombic crystals and is soluble to the extent of one part in 0.47 part of water at  $15^{\circ}$ . The dry salt is stable in the air and is completely dehydrated at  $105^{\circ}$ . No evidence was obtained of the existence of the compound  $\text{NaZn}(\text{CN})_3\cdot 2\frac{1}{2}\text{H}_2\text{O}$ . E. G.

**Preparation of Fatty Acids containing Arsenic.** FELIX HEINEMANN (D.R.-P. 268829. Compare A., 1913, i, 607).—The compounds described in the chief patent can be obtained by treating a mixture of acids of the acetylene series and arsenious oxide with a halogen hydride in the presence of a dehydrating agent (such as anhydrous copper sulphate or magnesium sulphate). The use of arsenic trichloride is thus avoided. J. C. C.

**Preparation of Fatty Acids containing Arsenic and Phosphorus.** FELIX HEINEMANN (D.R.-P. 271159. Compare A., 1913, i, 607, and preceding abstract).—For the preparation of these compounds reagents may be used which furnish halogen derivatives of arsenic and phosphorus without the formation of water, such as a mixture of phosphorus or arsenic and sulphuryl chloride or a mixture of arsenious oxide and thionyl chloride. J. C. C.

**Influence of the Substituent on the Interaction of Benzene and its Derivatives with Benzyl Chloride in Presence of Antimony Tribromide.** B. N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 259—283).—Experiments with antimony tribromide similar to those with the trichloride (this vol., i, 188) have now been made at 155°. The principal results are given in the following tables of velocity constants :

	2SbBr <sub>3</sub> .		1SbBr <sub>3</sub> .	
C <sub>6</sub> H <sub>6</sub> .....	0·00071	1	0·00018	1
C <sub>6</sub> H <sub>5</sub> Me .....	0·01038	15	0·00265	15
C <sub>6</sub> H <sub>5</sub> Et .....	0·00589	8	0·00151	8
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> .....	0·0140	20	0·00368	20
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> .....	0·0272	38	0·00725	40
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> .....	0·0094	13	0·0026	14
<i>p</i> -C <sub>6</sub> H <sub>4</sub> MePr .....	—	—	0·059	328
1 : 3 : 5-C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> .....	—	—	0·115	639
1 : 2 : 4-C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> .....	—	—	0·0129	71
CH <sub>2</sub> Ph <sub>2</sub> .....	—	—	0·0035	20
C <sub>6</sub> H <sub>5</sub> Ph .....	—	—	0·0037	21
CHPh <sub>3</sub> .....	—	—	0·00052	3
C <sub>6</sub> H <sub>5</sub> Cl .....	—	—	0·000011	0·06
C <sub>6</sub> H <sub>5</sub> Br .....	—	—	0·0000092	0·05
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> .....	—	—	0·000025	0·14

In all cases where parallel experiments have been made with different proportions of antimony trichloride or tribromide, it is found that the ratio of the two velocity constants is equal to the square of the ratio of the two concentrations of the trichloride or tribromide. It may, therefore, be concluded that the latter takes part in the reaction in the proportion of 2 mols. to form the compound 2SbX<sub>3</sub>,ArH. Confirmation of this is afforded by the observation that benzyl chloride acts on this compound with the same velocity as on its constituents. The formation of the compound between the hydrocarbon and the antimony trichloride or tribromide represents, therefore, the first phase in the reaction and takes place very rapidly, if not instantaneously. The second phase of the reaction consists in the action on this compound of benzoyl chloride, with liberation of hydrogen chloride and formation of ketone in combination with antimony trichloride; in the third phase, the ketone and the trichloride are separated under the influence of the high temperature prevailing, tarry products being also formed.

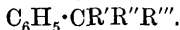
A relation exists, although not a quantitative one, between the stability of the compounds, 2SbCl<sub>3</sub>,ArH, and the course followed by the reactions. The interaction of benzoyl chloride and hydrocarbons or their derivatives in presence of antimony trichloride or tribromide occupies a position intermediate between purely catalytic reactions and those conjugated reactions in which the final products are molecular compounds stable under the experimental conditions employed.

In all probability, the velocity of the reaction of benzene and its substituted derivatives with benzoyl chloride in presence of aluminium chloride varies with the nature of the substituent in the same direction as when the action proceeds in presence of antimony trichloride.

T. H. P.



**Higher Homologues of Benzene.** O. M. HALSE (*J. pr. Chem.*, 1914, [ii], 89, 451—465).—A continuation of Schreiner's work (A., 1910, i, 661) on the synthesis of benzene homologues of the type



$\gamma$ -Methylhexan- $\gamma$ -ol, prepared from methyl ethyl ketone and magnesium propyl bromide, has b. p. 142—144°,  $D_4^{15}$  0.8283, and on treatment with hydrogen chloride yields  $\gamma$ -chloro- $\gamma$ -methylhexane,



which has b. p. 39—40°/15 mm.,  $n_D^{15}$  1.42705,  $D_4^{20}$  0.8787, and is converted by the action of aluminium chloride and benzene into  $\gamma$ -phenyl- $\gamma$ -methylhexane,  $\text{CMeEtPr}^a\text{Ph}$ , a colourless, viscid liquid of aromatic odour, having b. p. 110—112°/15 mm.,  $n_D^{15}$  1.49951,  $D_4^{20}$  0.8819.

In a similar manner,  $\delta$ -methylheptan- $\delta$ -ol, prepared from ethyl acetate and magnesium propyl bromide, gives rise to  $\delta$ -chloro- $\delta$ -methylheptane, which has b. p. 50—51°/12 mm.,  $n_D^{15}$  1.43098,  $D_4^{20}$  0.8690, and is transformed by the Friedel-Crafts reaction into  $\delta$ -phenyl- $\delta$ -methylheptane,  $\text{CMePr}^a_2\text{Ph}$ , b. p. 120—121°/12 mm.,  $n_D^{15}$  1.49326,  $D_4^{20}$  0.8708.

$\gamma$ -Ethylhexan- $\gamma$ -ol from ethyl butyrate and magnesium ethyl iodide has b. p. 158—159°,  $n_D^{15}$  1.43216,  $D_4^{20}$  0.8365;  $\gamma$ -chloro- $\gamma$ -ethylhexane yields  $\gamma$ -phenyl- $\gamma$ -ethylhexane,  $\text{CEt}_2\text{Pr}^a\text{Ph}$ , b. p. 237—238°,  $n_D^{15}$  1.49383,  $D_4^{20}$  0.8748.

$\beta\epsilon$ -Dimethylhexan- $\beta$ -ol from acetone and magnesium isoamyl bromide yields  $\beta$ -chloro- $\beta\epsilon$ -dimethylhexane, b. p. 44—45°/14 mm.,  $n_D^{15}$  1.42495,  $D_4^{20}$  0.8476, and  $\beta$ -phenyl- $\beta\epsilon$ -dimethylhexane,  $\text{CMe}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^a$ , b. p. 116—117°/14 mm.,  $n_D^{15}$  1.50233,  $D_4^{20}$  0.8844.

$\gamma$ -Chloro- $\gamma\zeta$ -dimethylheptane has b. p. 63—64°/15 mm.,  $n_D^{15}$  1.43457,  $D_4^{20}$  0.8692,  $\gamma$ -phenyl- $\gamma\zeta$ -dimethylheptane,  $\text{CMeEtPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^a$ , b. p. 122—123°/14 mm.,  $n_D^{15}$  1.49894,  $D_4^{20}$  0.8788.

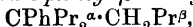
$\delta$ -Ethylheptan- $\delta$ -ol, prepared from ethyl propionate and magnesium propyl bromide, gives rise to  $\delta$ -chloro- $\delta$ -ethylheptane, b. p. 67—68°/12 mm.,  $n_D^{15}$  1.43878,  $D_4^{20}$  0.8821, and  $\delta$ -phenyl- $\delta$ -ethylheptane,  $\text{CEtPr}^a_2\text{Ph}$ , b. p. 127—128°/15 mm.,  $n_D^{15}$  1.49211,  $D_4^{20}$  0.8698.

$\gamma$ -Phenyl- $\epsilon$ -methyl- $\gamma$ -ethylhexane,  $\text{CEt}_2\text{Ph}\cdot\text{CH}_2\text{Pr}^a$ , obtained from  $\gamma$ -chloro- $\epsilon$ -methyl- $\gamma$ -ethylhexane, has b. p. 240—242°,  $n_D^{15}$  1.49097,  $D_4^{20}$  0.8725.

$\delta$ -Chloro- $\beta\delta\zeta$ -trimethylheptane, prepared from methyldiisobutylcarbinol, has b. p. 82—83°/25 mm.,  $n_D^{15}$  1.43336,  $D_4^{20}$  0.8657;  $\delta$ -phenyl- $\beta\delta\zeta$ -trimethylheptane,  $\text{CMePh}(\text{CH}_2\text{Pr}^a)_2$ , b. p. 143—144°/18 mm.,  $n_D^{15}$  1.49497,  $D_4^{20}$  0.8753.

$\delta$ -Propylheptan- $\delta$ -ol, from ethyl butyrate and magnesium propyl bromide, has b. p. 84—85°, and gives rise to  $\delta$ -chloro- $\delta$ -propylheptane, b. p. 80°/12 mm.,  $n_D^{15}$  1.44209,  $D_4^{20}$  0.8779, and  $\delta$ -phenyl- $\delta$ -propylheptane,  $\text{CPhPr}_3^a$ , b. p. 140—141°/15 mm.,  $n_D^{15}$  1.4924,  $D_4^{20}$  0.8694.

$\beta$ -Methyl- $\delta$ -propylheptan- $\delta$ -ol, from ethyl isovalerate and magnesium propyl bromide, has b. p. 86—88°/12 mm.,  $n_D^{15}$  1.43908,  $D_4^{20}$  0.8311, and yields  $\delta$ -chloro- $\beta$ -methyl- $\delta$ -propylheptane, b. p. 90—91°/13 mm.,  $n_D^{15}$  1.44662,  $D_4^{20}$  0.8774, and  $\delta$ -phenyl- $\beta$ -methyl- $\delta$ -propylheptane,



b. p. 143—144°/11 mm.,  $n_D^{15}$  1.496,  $D_4^{20}$  0.8750.

$\epsilon$ -Chloro- $\beta\epsilon\theta$ -trimethylnonane, b. p. 100—101°/12 mm.,  $n_D^{15}$  1.44210,

$D_4^{20}$  0.8625, yields  $\epsilon$ -phenyl- $\beta\theta$ -trimethylnonane,  $\text{CMePh}(\text{CH}_2\cdot\text{CH}_2\text{Pr}^\beta)_2$ , b. p. 153—155°/15 mm.,  $n_D^{15}$  1.49326,  $D_4^{20}$  0.8728.

$\beta\theta$ -Dimethyl- $\epsilon$ -ethylnonan- $\epsilon$ -ol, obtained from magnesium isoamyl bromide and ethyl propionate, has b. p. 119—120°/17 mm.,  $n_D^{15}$  1.44602,  $D_4^{18.5}$  0.8337, and gives rise to  $\epsilon$ -chloro- $\beta\theta$ -dimethyl- $\epsilon$ -ethylnonane, b. p. 117—118°/15 mm.,  $n_D^{15}$  1.44662,  $D_4^{18.5}$  0.8658, and  $\epsilon$ -phenyl- $\beta\theta$ -dimethyl- $\epsilon$ -ethylnonane,  $\text{CEtPh}(\text{CH}_2\cdot\text{CH}_2\text{Pr}^\beta)_2$ , b. p. 170—172°/14 mm.,  $n_D^{15}$  1.50735,  $D_4^{18.5}$  0.8955.

$\beta\theta$ -Dimethyl- $\epsilon$ -propylnonan- $\epsilon$ -ol, from ethyl butyrate and magnesium isoamyl bromide, is a viscid liquid of fruity odour, b. p. 125—126°/13 mm.,  $n_D^{15}$  1.44511,  $D_4^{20}$  0.8347;  $\epsilon$ -chloro- $\beta\theta$ -dimethyl- $\epsilon$ -propylnonane, b. p. 125—126°/15 mm.,  $n_D^{16}$  1.44782,  $D_4^{20}$  0.8672;  $\epsilon$ -phenyl- $\beta\theta$ -dimethyl- $\epsilon$ -propylnonane,  $\text{CPrPh}(\text{CH}_2\cdot\text{CH}_2\text{Pr}^\beta)_2$ , b. p. 180—181°/15 mm.,  $n_D^{15}$  1.48751,  $D_4^{20}$  0.8677.

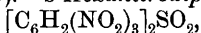
$\epsilon$ -Phenyl- $\beta\theta$ -dimethyl- $\epsilon$ -isobutylnonane,  $\text{CH}_2\text{Pr}^\beta\cdot\text{CPh}(\text{CH}_2\cdot\text{CH}_2\text{Pr}^\beta)_2$ , has b. p. 172—173°/11 mm.,  $n_D^{15}$  1.50623,  $D_4^{20}$  0.89817. F. B.

**Chlorination by means of Aqua Regia.** Chlorination of Benzene, Thiophen, Toluene, and Mesitylene. RASIK LAL DATTA and FRANCIS V. FERNANDES (*J. Amer. Chem. Soc.*, 1914, **36**, 1007—1011).—Hydrocarbons can be rapidly chlorinated by warming them with a mixture of concentrated hydrochloric and nitric acids (2:1). In general, the method can be used for the preparation of a particular chloro-derivative by varying the conditions of the experiment. As a rule, the longer the hydrocarbon is kept in contact with the acid mixture, the greater is the proportion of higher chlorinated products. Chlorobenzene and *p*-dichlorobenzene can be conveniently prepared in this manner. In the case of thiophen, mono-, di-, and tri-chloro-derivatives are produced in proportions varying with the duration of the reaction. The chlorination of toluene by this method results in the formation of either benzyl chloride or of a mixture of *o*- and *p*-chlorotoluene as the principal product, depending on the conditions of the experiments. Mesitylene yields a mixture of the di- and tri-chloro-derivatives together with a very little chloro-mesitylene. E. G.

**Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences. II. Halogen Substitution in the Benzene Nucleus and in the Side-chain.** HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1914, **36**, 1035—1047).—Although various explanations have been offered to account for the phenomena occurring in nucleus and side-chain substitution, the mechanism of the process is not yet definitely understood. The author has now applied his electronic theory (*A.*, 1911, i, 431; 1912, ii, 713; this vol., i, 263) to this subject and has correlated his interpretations with the experimental facts, the conditions of substitution, and the properties of *o*- and *p*-halogen-toluenes and the side-chain substitution products. Certain fundamental distinctions between substitutions in the nucleus and side-chain are developed, and are interpreted in terms of positive and negative

valences. The substitution of negative halogen in the side-chain involves an oxidation of negative valences of carbon to positive valences, but substitution in the nucleus does not involve oxidation. Mechanisms are indicated to account for these facts. The relations between these interpretations and the substitution hypotheses of Bruner, Bancroft, and Holleman are discussed. E. G.

[*s*-Hexanitrodiphenyl Sulphoxide.] SPRENGSTOFF A.-G. CARBONIT (D.R.-P. 269826).—*s*-Hexanitrodiphenyl sulphoxide,



prepared by oxidising a suspension of hexanitrodiphenyl sulphide in nitric acid, forms yellow crystals which detonate at 250—255°. It is suitable for the preparation of explosives. J. C. C.

Friedel and Crafts's Synthesis of Sulphones. S. C. J. OLIVIER (*Chem. Weekblad*, 1914, 11, 372—377).—A theoretical paper discussing the part played by aluminium chloride in the synthesis of sulphones, and citing the results obtained in previous work by the author in which the catalyst was employed in excess and also in equivalent proportions (compare following abstract). A. J. W.

Friedel and Crafts's Synthesis of Sulphones. H. J. PRINS (*Chem. Weekblad*, 1914, 11, 418).—Compare preceding abstract. A criticism of the views expressed by Olivier. A. J. W.

Reduction of Sulphinic Acids by means of Hydrogen Bromide. K. FRIES and G. SCHÜRMANN (*Ber.*, 1914, 47, 1195—1203).—Following up an observation that certain sulphinic acids are reducible by hydrogen bromide (Fries and Vögt, A., 1911, i, 555), it is found that this is a general behaviour of the aromatic sulphinic acids, the products of the reaction being bromine and an aromatic disulphide or sulphur-bromide.

The treatment is effected in acetic acid solution, and requires only a very short time even at the ordinary temperature. Benzene-sulphinic, *p*-nitrobenzenesulphinic,  $\beta$ -naphthalenesulphinic, 1-nitro-naphthalene-5-sulphinic, and 1-hydroxyanthraquinone-4-sulphinic acids all gave the corresponding disulphides, whilst *o*-nitrobenzenesulphinic, *p*-chloro-*o*-nitrobenzenesulphinic, and anthraquinone-1-sulphinic acids gave the corresponding sulphur-bromides. The reactions follow the course  $\text{R}\cdot\text{SO}_2\text{H} + 3\text{HBr} = \text{R}\text{SBr} + 2\text{H}_2\text{O} + \text{Br}_2$  and  $2\text{R}\cdot\text{SO}_2\text{H} + 6\text{HBr} = \text{R}_2\text{S}_2 + 4\text{H}_2\text{O} + 3\text{Br}_2$ . If sodium sulphite is added to the reaction mixture, the product is in all cases the disulphide and by-reactions due to the bromine are effectively checked.

Hydrogen bromide exerts a similar reducing effect on the disulphoxides, the products again being the disulphides or sulphur-bromides. On this account the disulphoxides are regarded as of the symmetrical structure  $\text{ORS}\cdot\text{SRO}$ , and various reasons are given for the probable instability, or labile nature, of the grouping  $\text{R}\cdot\text{S}\cdot\text{SRO}_2$  (compare Hinsberg, A., 1908, i, 875; 1909, i, 6), and for the improbability of an ether structure,  $\text{RSO}\cdot\text{SRO}$  (compare Gutmann, this vol., i, 635).

Anthraquinone-1-sulphinic acid is reduced by hydriodic acid in acetic acid solution with the formation of dianthraquinone di-1-sulphide.

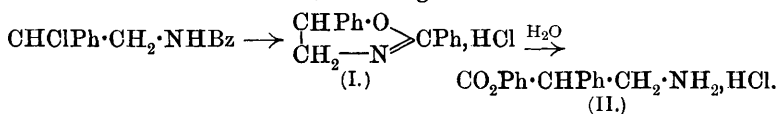
D. F. T.

**$\beta$ -Chloro- $\beta$ -phenylethylamine.** F. WOLFHEIM (*Ber.*, 1914, 47, 1440—1452).—The author has prepared this base from the corresponding  $\beta$ -hydroxyamine, the reduction product of benzaldehyde cyanohydrin, and has found that it is as reactive as the simple halogenated fatty amines. Acyl derivatives were also obtained by reducing acylaminoacetophenones and chlorinating the hydroxy-compounds, but this method was not suited to the preparation of the free base, for the subsequent hydrolysis gave very poor yields or led to other products.

$\omega$ -Benzoylaminoacetophenone was reduced by the method of Pictet and Gams (*A.*, 1910, i, 774), and the phenylbenzoylaminoethylcarbinol was converted by phosphorus pentachloride into *benzo- $\beta$ -chloro- $\beta$ -phenylethylamide*,  $\text{CHClPh}\cdot\text{CH}_2\cdot\text{NHBz}$ , which forms white needles, m. p. 123—124°.  $\omega$ -Acetylaminoacetophenone was prepared by gradually adding sodium hydrogen carbonate to an aqueous solution of the hydrochloride of the base mixed with acetic anhydride, since acetylation in the dry state by Gabriel's method (*A.*, 1910, i, 431) frequently yielded 5-phenyl-2-methylxazole (*ibid.*). Phenylacetylaminomethylcarbinol was obtained from much hot benzene in four-sided thin leaflets, m. p. 122.5—123°, whereas Pictet and Gams described needles, m. p. 104°, which were very soluble in benzene. When heated with fuming hydrochloric acid in a tube, it yielded a small amount of the hydrochloride of the free  $\beta$ -chloroamine.

The reduction of benzaldehyde cyanohydrin, by means of sodium amalgam, to  $\beta$ -hydroxy- $\beta$ -phenylethylamine requires careful manipulation, and details are given of the process which has been patented (Farbwerke vorm. Meister, Lucius & Brüning, D.R.-P. 193634). The ethereal extract of the base is allowed to absorb carbon dioxide, and the indefinite carbonate is used in subsequent experiments. The picrate, m. p. 157—158.5°, and the *hydriodide*, m. p. 121°, are described, and an account of the ready conversion of the base into the above acetyl-amino- and benzoylamino-derivatives of phenylmethylcarbinol is given. A by-product of the reduction is a compound,  $\text{C}_{16}\text{H}_{16}\text{ON}_2$ , which forms white granules, m. p. 103—104°, and is indifferent towards acids and alkalis. The chlorination of the base was effected by heating the carbonate with fuming hydrochloric acid in a sealed tube.  *$\beta$ -Chloro- $\beta$ -phenylethylamine*,  $\text{CHClPh}\cdot\text{CH}_2\cdot\text{NH}_2$ , is a colourless oil. The *hydrochloride* forms long prisms, m. p. 162—164°; the *picrate* crystallises in long, flat needles, m. p. 147.5—148.5°, and the *platinichloride* and *aurichloride* crystallise from water.

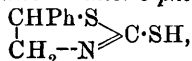
The base was benzoylated by the usual means. When  $\beta$ -chloro- $\beta$ -phenylethylbenzamide (see also above) is boiled with 90% alcohol, it undergoes re-arrangement to an oxazoline and then combines with water to form an *O*-benzoate, according to the scheme :



The *hydrochloride* of  $\beta$ -amino- $\alpha$ -phenylethyl benzoate (II.) crystallises in long, white needles, m. p.  $198^\circ$ . The *platinichloride*, m. p.  $192$ — $194^\circ$ , the red *dichromate*, and the lemon-yellow *picrate*, m. p.  $166.5$ — $167.5^\circ$ , were analysed. On adding alkali to a solution of the hydrochloride, an oil separated which soon solidified. The benzoyl group had migrated to the nitrogen atom and the product was the above phenylbenzoylaminomethylcarbinol. The intermediate 2:5-diphenyloxazoline (I.) was isolated by boiling the benzamide with methyl alcohol containing 4% of sodium. It is a colourless, basic-aromatic oil, b. p.  $229$ — $230^\circ/44$  mm., and forms an amber-yellow *picrate*, m. p.  $141$ — $142^\circ$ , and a pale yellow *platinichloride*.

The hydrochloride of chlorophenylethylamine was evaporated with potassium cyanate, when 2-amino-5-phenylthiazoline, 
$$\begin{array}{c} \text{CHPh}\cdot\text{S} \\ | \\ \text{CH}_2-\text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}\cdot\text{NH}_2$$
 was obtained. This crystallises in long, white needles, m. p.  $111$ — $112^\circ$ , and forms a *hydrochloride*, silvery, rhombic crystals, with  $\frac{1}{2}\text{H}_2\text{O}$ , m. p.  $172$ — $173^\circ$ , a *nitrate*, large, hexagonal tablets, m. p.  $152$ — $153^\circ$ , a *picrate*, m. p.  $202^\circ$ , an *aurichloride*, long, golden-yellow needles, and a *platinichloride*, pale yellow needles, m. p.  $217^\circ$ .

A solution of the same hydrochloride was also mixed with carbon disulphide and then treated with dilute potassium hydroxide until the precipitate redissolved. The clarified solution was then mixed with ammonium chloride, when 2-thiol-5-phenylthiazoline,



was precipitated. This compound crystallises in long, prismatic, highly refractive needles, m. p.  $169$ — $170^\circ$ . The corresponding *methyl ether* is a colourless, sweet smelling oil, which forms an orange-coloured *platinichloride*,  $(\text{C}_{10}\text{H}_{11}\text{NS}_2)_2\cdot\text{H}_2\text{PtCl}_6$ .

The hydrochloride of chlorophenylethylamine was also treated with the theoretical quantity of *N*-sodium hydroxide and then warmed to  $50$ — $60^\circ$ . The free base suddenly dissolved. On adding another equivalent of the *N*-solution, *phenylethyleneimine* [*styreneimine*],

$\text{CH}_2\begin{array}{c} \text{NH} \\ | \\ \text{CHPh} \end{array}$ , was liberated. This was distilled in steam as long as the distillate immediately gave a precipitate with 0.5% picric acid. The free base was extracted from the concentrated distillate as a clear benzylamine-like, strongly basic oil. The *picrate* forms long needles, m. p.  $118$ — $119^\circ$ , whilst the *aurichloride* is amorphous and the *platinichloride* is very soluble. Bismuth-potassium iodide gives a scarlet-red precipitate. The free imine is unstable, even in solution. The ring is opened by a number of agents with the accompaniment of addition. Thus, with hydrochloric acid it forms the hydrochloride of the original  $\beta$ -chloro- $\beta$ -phenylethylamine and with hydrobromic acid, the *hydrobromide* of  $\beta$ -bromo- $\beta$ -phenylethylamine, which crystallises in rhombic plates, m. p.  $163$ — $164^\circ$ , and forms a *picrate*, m. p.  $150$ — $151^\circ$ . When a solution which has been neutralised by nitric acid is evaporated, the nitrate of the above  $\beta$ -hydroxy- $\beta$ -phenylethylamine is obtained, the elements of water having been attached. With sulphurous acid the same addition of water takes place. Sulphuric acid gives no

definite product, but the expected  $\beta$ -amino- $\alpha$ -phenylethylsulphuric acid,  $\text{SO}_3\text{H}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2$ , may be prepared by the interaction of chlorophenylethylamine hydrochloride and silver sulphate. The compound forms feathery aggregates, m. p.  $268\cdot5^\circ$  (decomp.). The aqueous solution is neutral and does not react with barium chloride, from which it appears probable that the substance is an inner ammonium salt.

J. C. W.

**Preparation of Diaryl Ethers.** FRANZ FRITSCHÉ & Co. (D.R.-P. 269543).—Diaryl ethers are prepared by heating a solution of alkali phenoxides in the corresponding phenols with monohalogen substitution products of aromatic hydrocarbons, preferably chlorobenzene, at  $200$ — $220^\circ$  under pressure. Examples are given illustrating the preparation of diphenyl ether, phenyl *o*-, *m*-, and *p*-tolyl ethers, phenyl  $\alpha$ - and  $\beta$ -naphthyl ethers, and phenyl guaiacyl ether. J. C. C.

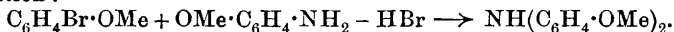
**Some Organic Derivatives of Fluorine.** I. J. RINKES (*Chem. Weekblad*, 1914, 11, 360—364).—Several aromatic fluoro-derivatives have been prepared. *p*-Anisidine has m. p.  $56\cdot2^\circ$ , and b. p.  $128^\circ/11$  mm. Diazotisation in fuming hydrofluoric acid, and decomposition of the product by boiling with this acid, transforms it into *p*-fluoroanisole, a liquid volatile with steam. It has b. p.  $154\cdot5$ — $155^\circ$ , and can be solidified to crystals, m. p.  $-45^\circ$ .

The Sandmeyer reaction converts *p*-fluoroaniline into 4-fluorobenzonitrile, long, colourless, needles, f. p.  $34\cdot8^\circ$ , b. p.  $188\cdot2^\circ/750$  mm. Reduction with stannous chloride of the diazotisation product of *p*-fluoroaniline yields *p*-fluorophenylhydrazine, needles (not analysed), f. p.  $36\cdot8^\circ$ . It decomposes after the lapse of a few weeks.

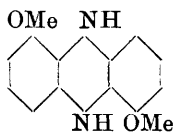
Reduction of *p*-fluoronitrobenzene with ammonium sulphide produces *p*-fluorophenylhydroxylamine, very unstable, colourless, acicular crystals (not analysed), m. p.  $90^\circ$ . It reduces Fehling's solution and an ammoniacal silver solution without application of heat. Oxidation with chromic acid converts it into *p*-fluoronitrosobenzene, yellow needles, f. p.  $35\cdot2^\circ$ , m. p.  $39$ — $40^\circ$ .

A. J. W.

**Preparation of Di-*o*-anisylamine.** H. WIELAND and L. CHUDOSHILOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 194—196).—The interaction of *o*-anisidine and *o*-bromoanisole in presence of potassium hydroxide, copper bronze, and nitrobenzene (compare Goldberg and Nimerovski, A., 1907, i, 621) yields: (1) Principally di-*o*-anisylamine, b. p. above  $200^\circ/25$  mm., the reaction being expressed by the equation:



The amine forms a hydrochloride, m. p.  $125$ — $126^\circ$ , and a cinnamon-red nitroso-derivative,  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_2$ , m. p.  $129\cdot5$ — $130^\circ$ , which gives a blue coloration with concentrated sulphuric acid, and has the normal molecular weight in freezing benzene. (2) A small proportion of the compound (annexed formula), which forms stable red needles, m. p.  $153$ — $154^\circ$ , and has the normal molecular weight in freezing benzene. (3) A small proportion of a compound



which crystallises in yellow needles, m. p.  $159^{\circ}$ , has the molecular weight 212.2 in freezing benzene, and contains 14.2% N; it is probably a bisazo- or azoxy-compound derived from the nitrobenzene and *o*-anisidine. T. H. P.

**Autoxidation of 1-Methyl-2-naphthol.** K. FRIES (*Ber.*, 1914, 47, 1193—1194).—1-Methyl-2-naphthol (Fries and Hübner, A., 1906, i, 190) when exposed to the atmosphere slowly oxidises, and a specimen which had been kept loosely enclosed for eight years was found to have passed to the extent of 43% into methyl-naphthaquinol and 6% into a resin, the remainder being unaltered. The change occurs more rapidly in solution in benzene, and is already perceptible after four weeks.

6-Bromo-1-methyl-2-naphthol in the course of a year was found to undergo similar alteration, but no change was detected in 3 : 6-dibromo-1-methyl-2-naphthol even after eight years. D. F. T.

**Preparation of Di- and Poly-hydric Phenols and Their Substitution Products.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 269544).—When halogenated phenols or their substitution products are heated with aqueous alkalis or alkali carbonates or mixtures of these, in the presence of metallic copper or a copper salt under pressure to a high temperature, the corresponding di- or poly-hydric phenols are obtained. Examples are given of the preparation of catechol from *o*-chloro- or *o*-bromo-phenol, of quinol from *p*-chloro- or *p*-bromo-phenol, and of gallic acid from 3 : 5-dibromo-4-hydroxybenzoic acid. J. C. C.

**Preparation of Carbamic Esters.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 269938).—Carbamic esters are prepared from glycol ethers of the formula  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OR}$  (where R is a simple or substituted aryl group) by employing the usual methods for this conversion.

*Phenoxyethylurethane*,  $\text{NH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$ , prepared by the action of carbonyl chloride on a mixture of phenyl glycol ether and dimethylaniline and treatment of the product with aqueous ammonia, forms colourless crystals, m. p.  $114^{\circ}$ .

The corresponding *urethanes* were also prepared from the following glycol ethers (m. p. of urethane is given in brackets). *p*-Tolyl ( $147^{\circ}$ ), *o*-tolyl ( $119^{\circ}$ ), *m*-tolyl ( $114^{\circ}$ ), *o*-chlorophenyl ( $116^{\circ}$ ), 2-chloro-*p*-tolyl ( $133^{\circ}$ ), 4-chloro-*m*-tolyl ( $132^{\circ}$ ), guaiacyl ( $131^{\circ}$ ). If instead of using ammonia in the above example ethanolamine is employed, a *urethane* is obtained, which forms colourless crystals, m. p.  $85^{\circ}$ , and the *urethane* from 4-chloro-*m*-tolyl glycol ether and ethanolamine has m. p.  $93^{\circ}$ . J. C. C.

**1-Phenol 4-Mercaptan [4-Thiolphenol].** TH. ZINCKE and C. EBEL (*Ber.*, 1914, 47, 1100—1108).—It has been previously shown (Zincke and Glahn, A., 1907, i, 698) that 2 : 6-dibromo-4-thiolphenol can be obtained by acting on 2 : 6-dibromophenol-4-sulphonic acid with phosphorus pentachloride and reduction of the sulphonyl chloride formed; during the process, the bromine atoms protect the phenolic hydroxyl against the action of phosphorus pentachloride. It is now

shown that 4-thiolphenol can be readily prepared by an analogous series of reactions if the hydroxyl group is protected by the introduction of the ethylcarbonato-group according to Fischer's method. The preparation of 4-thiolphenol (Leuckart, A., 1890, 603) and of many of its derivatives is described.

*Sodium p-ethylcarbonatobenzenesulphonate*,  $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\text{Et}$ , shining leaflets or large, transparent crystals, is obtained by the action of ethyl chloroformate on an alkaline solution of sodium *p*-phenolsulphonate, and is converted by phosphorus pentachloride into *p-ethylcarbonatobenzenesulphonyl chloride*, colourless needles, m. p.  $75^\circ$ , which is fairly stable towards dilute alkali hydroxides. Concentrated hydrochloric acid or a solution of hydrogen chloride in glacial acetic acid does not cause elimination of the ethylcarbonato-group. When warmed with an excess of aniline, it yields the corresponding *anilide*, colourless, rhombic plates, m. p.  $102^\circ$ , from which *phenol-4-sulphanilide*, shining needles, m. p.  $141^\circ$ , is obtained by the action of alkali. When boiled with sodium acetate and acetic anhydride, the latter gives a *diacetyl* derivative, needles, m. p.  $152-153^\circ$ .

*p-Ethylcarbonatophenylmercaptan*,  $\text{SH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\text{Et}$ , is obtained by reduction of an alcoholic solution of the sulphonyl chloride by zinc dust and hydrochloric acid. It is an almost colourless oil which has not been obtained in the pure state. When distilled under diminished pressure (17 mm.) it is decomposed. The *benzoyl* derivative has m. p.  $167-168^\circ$ .

*p*-Thiolphenol, m. p.  $29-30^\circ$ , b. p.  $144-146^\circ/20$  mm. (*diacetyl* derivative, m. p.  $66-67^\circ$ ), is prepared by boiling the crude ethylcarbonato-compound with *2N*-sodium hydroxide solution. Oxidation with bromine water, hydrogen peroxide, or alkaline potassium ferricyanide solution transforms it into the disulphide, m. p.  $150-151^\circ$  (compare Leuckart, *loc. cit.*), the *diacetyl* derivative of which, thin needles, has m. p.  $88-89^\circ$ .

*p-Methylthiolphenol*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$ , leaflets, m. p.  $84-85^\circ$ , is obtained by the action of methyl sulphate and *2N*-sodium hydroxide on *p*-thiolphenol. The *acetyl* compound, long, colourless needles, has m. p.  $43-44^\circ$ , whilst the *methyl ether*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$ , leaflets, m. p.  $25-26^\circ$ , is prepared by the action of methyl iodide and sodium methoxide on the methyl sulphide. Nitric acid (*D* 1.15—1.2) converts *p*-methylthiolphenol into 2 : 6-dinitro-4-methylthiolphenol (Zincke and Glahn, *loc. cit.*), whilst a more concentrated acid (*D* 1.4) gives picric acid and resinous products. A solution of *p*-methylthiolphenyl acetate in glacial acetic acid is transformed by perhydrol into *acetoxyphehyl-4-methyl sulphoxide*, leaflets, m. p.  $97-98^\circ$ , from which, *phenol-4-methyl sulphoxide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SMeO}$ , leaflets or needles, m. p.  $90-91^\circ$ , is obtained by the action of *2N*-sodium hydroxide. More drastic oxidation of *p*-methylthiolphenyl acetate by perhydrol in glacial acetic acid solution yields *phenol-4-methylsulphone*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SMeO}_2$ , m. p.  $93-94^\circ$ , from which an acetyl derivative could not be obtained.

*p-Hydroxyphenyldimethylsulphonium iodide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SMe}_2\text{I}$ , m. p.  $123-124^\circ$  with loss of methyl iodide, is prepared by heating *p*-methylthiolphenol with methyl iodide at  $100^\circ$ . The corresponding *chloride*, small, rhombic crystals, has m. p.  $159^\circ$  (decomp.), whilst the



platinum salt, orange-yellow crystals, has m. p. 199°. The hydroxide forms white leaflets, m. p. 107° (decomp.). Nitric acid (D 1.4) converts the iodide or chloride into 2:6-dinitro-1:4-dimethylthioniumquinone (Zincke and Glahn, *loc. cit.*).

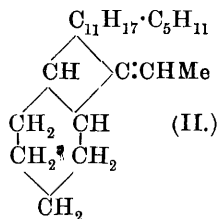
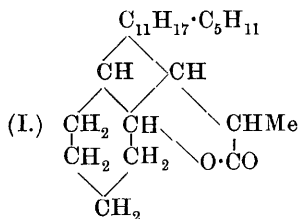
p-Methylthiolphenyl dibromide,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SMeBr}_2$ , is obtained in orange-yellow crystals, which can be preserved for some time in dry air, but evolve hydrogen bromide and partly form the sulphoxide on exposure to moisture, when the calculated quantity of bromine is added to a well-cooled solution of the methyl sulphide in dry chloroform. At a higher temperature and in presence of a larger proportion of bromine, 2:6-dibromo-4-methylthiolphenol, m. p. 47°, is formed (compare Zincke and Glahn, *loc. cit.*) H. W.

Preparation of Diphenylmethylcarbinol by Grignard's Method. JOSÉ GIRAL PEREIRA and J. CESAR SÁNCHEZ (*Anal. Fis. Quim.*, 1914, 12, 208—219. Compare Klages, A., 1902, i, 668).—Diphenylmethylcarbinol has m. p. 81°, b. p. 260°, and  $D_{15}^{25}$  1.1059. The benzoate forms silky, brilliant needles from alcohol, m. p. 115°. By the action of acetyl chloride in the presence of potassium carbonate, and by chromate-sulphuric acid mixture, the chief product is  $\alpha$ -diphenylethylene. G. D. L.

Desoxyns and the Products of their Bromination. I. I. КОТЯКОВ (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 343—348).—The yields of desoxyns (compare A., 1907, i, 413; 1912, i, 762) may be increased by about 50% by carrying out their preparation at the ordinary temperature. The phenyldesoxyns of dextrose and of cellulose have been prepared and are found to exhibit marked differences. The action of bromine on the phenyldesoxyn of cellulose yields compounds which have the empirical formulæ  $\text{C}_{36}\text{H}_{30}\text{O}_{10}\text{Br}_5\text{S}(\text{C}_6\text{H}_4\text{Br})_5$  and  $\text{C}_{10}\text{H}_8\text{O}_4\text{Br}_2(\text{C}_6\text{H}_4\text{Br})_2$ , and represents products of bromination and oxidation of the desoxyn. T. H. P.

Cholesterol. XVIII. Oxidation Experiments with Cholestene. H. WINDAUS and C. RESAU (*Ber.*, 1914, 47, 1229—1231).—When shaken in benzene solution with potassium permanganate dissolved in dilute sulphuric acid, cholestene (Mauthner and Suida, A., 1894, i, 326) is oxidised to a lactone, m. p. 135°, b. p. 280—290°/12 mm., and a yellow, syrupy acid which decomposes on distillation at 320°/26 mm., yielding a hydrocarbon,  $\text{C}_{25}\text{H}_{42}$ , crystallising in long needles, m. p. 65°.

The lactone dissolves in alcoholic potassium hydroxide, but is precipitated from these solutions unchanged.



Taking Windaus's cholesterol formula (A., 1912, i, 854) as their basis, the authors discuss the mechanism of the formation of these compounds and assign to the lactone and hydrocarbon the constitutions represented in (I.) and (II.) respectively.

F. B.

**Oxycholesterol and its Compound with Digitonin.** I. LIFSCHÜTZ and THEODOR GRETHE (*Ber.*, 1914, 47, 1453—1459).—Oxycholesterol, as obtained by oxidation with benzoyl peroxide (A., 1913, ii, 350), is a pale yellow, brittle, transparent, amber-like substance. It has been purified by leaving a solution in methyl alcohol in a cool place for a few hours, filtering if necessary, and evaporating the filtrate to dryness, and the purity of the product has been tested by the following means. I. The substance is treated with acetic and sulphuric acids and ferric chloride, and the dilution at which the band in the red end of the spectrum disappears is ascertained (*ibid.*). The greatest value obtained is 1 to 49430. II. The crystals of the digitonin compound (below) are examined under the microscope. The presence of uniform rhombic plates shows the absence of cholesterol, which does not combine with digitonin. III. The gradual development of the absorption spectrum of cholesterol in the "cholesterol" reaction (A., 1913, ii, 886) indicates that the oxycholesterol is not pure. The formula, calculated from new analyses, is  $C_{27}H_{46}O_2$ .

When a 2% solution of oxycholesterol in 95% alcohol is left with an equimolecular quantity of digitonin in the form of a 1% solution in 90% alcohol, *digitoninoxysteride*,  $C_{54}H_{92}O_{28}$ ,  $C_{27}H_{46}O_2$ , separates in silvery, rhombic leaflets, m. p. 215—218°. The amount of oxycholesterol in the compound was estimated by comparison with a test solution before the spectroscope (*loc. cit.*), and found to agree very closely with the above formula.

J. C. W.

**Preparation of Esters of Aromatic Carboxylic Acids.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 268621).—The interaction between salts of carboxylic acids and alcohol halogenides often proceeds more smoothly if it is carried out in the presence of an organic base such as trialkylamines, pyridine, quinoline, piperidine, dimethylaniline, aniline, etc. Very small amounts of the latter are necessary, and the free carboxylic acid or an internal salt (as occurs in many phthaleins) may be used instead of the ordinary carboxylate. Benzyl benzoate is easily obtained by warming a mixture of potassium benzoate (100 parts), benzyl chloride (120 parts), and triethylamine (1 part) to 95—100°. Other examples are given of the preparation of *isoamyl benzoate*, benzyl diethylrhodamine, *carbethoxymethyl anthraquinone-2-carboxylate*, pale yellow needles, m. p. 139—140°, and *benzyl-1-chloroanthraquinone-2-carboxylate*, pale yellow needles, m. p. 135—136°.

J. C. C.

**Reactions in Non-aqueous Solutions.** VII. In Benzonitrile. ALEX. NAUMANN (*Ber.*, 1914, 47, 1369—1376. Compare this vol., i, 259).—In continuation of the earlier work the author finds that many chlorides, bromides, iodides, and cyanides, as well as bromine, iodine, and sulphur, are soluble in benzonitrile. In some

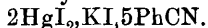
cases the solid separates from solution with combined benzonitrile; the following *compounds* were isolated:  $\text{CdCl}_2 \cdot 2\text{PhCN}$ ,  $\text{CdBr}_2 \cdot 2\text{PhCN}$ ,  $\text{HgCl}_2 \cdot 2\text{PhCN}$ ,  $3\text{HgBr}_2 \cdot 2\text{PhCN}$ ,  $\text{CoBr}_2 \cdot 2\text{PhCN}$ , and also  $\text{CoBr}_2 \cdot 2\text{PhCN} \cdot 6\text{H}_2\text{O}$ .

The deep blue solution of cobalt bromide reacted in the normal manner with chlorine, giving a solution of cobalt chloride. Hydrogen sulphide gave only a slight precipitate of black cobalt sulphide, but on subsequent treatment with dry ammonia the solution yielded a copious precipitate of cobalt sulphide and ammonium bromide. Ammonia alone gave a blue precipitate and then a rose-red *compound*,  $\text{CoBr}_2 \cdot 4\text{NH}_3$ . Cadmium iodide and mercuric chloride each gave solutions containing double salts with cobalt bromide. Silver nitrate gave a deposit of silver bromide leaving a red solution of cobalt nitrate.

Mercuric chloride failed to react in benzonitrile solution with the halogens or sulphur, but hydrogen sulphide gave a colourless precipitate,  $\text{HgCl}_2 \cdot 2\text{HgS}$ , ammonia produced a deposit of  $\text{HgCl}_2 \cdot 4\text{NH}_3$ , and silver nitrate in the normal manner yielded a precipitate of silver chloride.

Mercuric bromide in warm solution gave with hydrogen sulphide a yellow, crystalline *precipitate* of the composition  $\text{HgBr}_2 \cdot 2\text{HgS} \cdot 2\text{PhCN}$ , whilst with silver nitrate a precipitate of silver bromide was obtained.

Mercuric iodide gave a yellow turbidity with hydrogen sulphide, subsequent treatment with ammonia giving a black precipitate of mercuric sulphide. The solubility of mercuric iodide in benzonitrile is increased approximately twenty-fold by the presence of approximately 5% of potassium iodide in the benzonitrile, and on evaporation the solution gave yellow crystals of the composition



Mercuric cyanide failed to react with ammonia, but cadmium chloride, bromide, and iodide gave deposits of the general composition  $\text{CdX}_2 \cdot 2\text{NH}_3$ ; the iodide also gave a colourless precipitate,  $\text{CdI}_2 \cdot 2\text{CdS}$ , on treatment with hydrogen sulphide.

A solution of silver nitrate was converted by chlorine, bromine, or iodine into the corresponding haloid, whilst in warm solution it reacted with sulphur giving silver disulphide. Hydrogen sulphide in a rapid stream gave a black precipitate containing some free sulphur, whilst nitrous fumes were evolved. Treatment with ammonia gave a precipitate,  $\text{AgNO}_3 \cdot 2\text{NH}_3$ , whilst with cobalt chloride the behaviour of the silver nitrate solution was analogous to that with cobalt bromide (above).  
D. F. T.

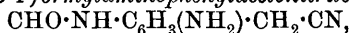
**Some Monoacyl-*o*-phenylenediamine-acetonitriles and their Conversion into the Corresponding Diacyl and Benziminazole Derivatives.** D. MARON, MARIE KONTÓROWITSCH and JEAN-JACQUES BLOCH (*Ber.*, 1914, **47**, 1347—1352).—An extension of the recent investigation (Maron and Bloch, this vol. i, 576), in which it has been shown that the monoacyl derivatives of the aromatic ortho-diamines lend themselves well to synthetic experiments.

3-Amino-4-acetylaminophenylacetonitrile,  $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CN}$ , m. p. 137—138°, was obtained by the steps  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CN} \rightarrow \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CN} \rightarrow \text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CN} \rightarrow \text{NHAc} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{CN}$ , followed by reduction of the last with iron

and acetic acid; when treated in hydrochloric acid solution with sodium nitrite, it yielded an *azimino*-compound, m. p. 109—110°; on treatment in benzene suspension with acetic anhydride it gave 3:4-di-acetylaminophenylacetoneitrile,  $C_6H_3(NHAc)_2 \cdot CH_2 \cdot CN$ , m. p. 177—178°, whilst boiling acetic acid converted it into 2-methyl-5-cyanomethylbenziminazole,  $CN \cdot CH_2 \cdot C_6H_3 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \diagdown \end{smallmatrix} > CMe$ , a colourless solid, m. p. 206—207°, of which the *hydrochloride* was sparingly soluble in cold water.

The cyanomethylmethylbenziminazole could be nitrated by fuming nitric acid at  $-5^\circ$  to  $-10^\circ$ , giving *nitro-2-methyl-5-cyanomethylbenziminazole*, m. p. 215—217°, which on reduction with iron and acetic acid passed into *amino-2-methyl-5-cyanomethylbenziminazole*, an unstable, brown powder, m. p. 235—237°. This gives a violet solution in sulphuric acid, a yellow solution with blue fluorescence in alcohol, and is converted by treatment with acetic anhydride and benzene at 30—40° into the corresponding *acetyl* derivative, m. p. 222—223°.

On keeping *p*-aminophenylacetoneitrile with formic acid in benzene solution, *p*-formylaminophenylacetoneitrile,  $CN \cdot CH_2 \cdot C_6H_4 \cdot NH \cdot CHO$ , m. p. 135—136°, gradually separates. Fuming nitric acid at  $-10^\circ$  to  $-5^\circ$  converts this into 3-nitro-4-formylaminophenylacetoneitrile, a yellow powder, m. p. 154—155°, which on reduction with iron and acetic acid passes into 3-amino-4-formylaminophenylacetoneitrile,



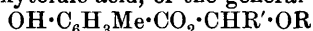
needles, m. p. 124°. This substance when treated in hydrochloric acid solution with sodium nitrite gives an *azimino*-compound, whilst with acetic anhydride in suspension in benzene, 3-acetyl-amino-4-formylaminophenylacetoneitrile,  $CHO \cdot NH \cdot C_6H_3(NHAc) \cdot CH_2 \cdot CN$ , m. p. 173°, is produced; with boiling acetic or formic acid condensation is effected to 5-cyanomethylbenziminazole,  $CN \cdot CH_2 \cdot C_6H_3 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \diagdown \end{smallmatrix} > CH$ , m. p. 150°.

D. F. T.

**Preparation of Ethyl  $\alpha\beta$ -Dibromo- $\beta$ -phenylpropionate in a Stable Form.** E. MERCK (D.R.-P. 271434).—This ester, as usually prepared, undergoes decomposition on keeping owing to the presence of certain impurities. It is obtained in a pure and stable form if ethyl cinnamate is mixed with light petroleum and bromine added, whereby the bromo-ester is precipitated after some time. It is collected and melted once or twice under hot water. By this process the impurities remain dissolved in the light petroleum and water.

J. C. C.

**Preparation of Alkyloxyalkylidene Esters of Hydroxy-toluic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 269335. Compare A., 1903, i, 485; 1904, i, 318).—Alkyloxyalkylidene esters of hydroxytoluic acid, of the general formula



(where R and R' are the same or different alkyl groups or R' denotes hydrogen), are more suitable as anti-rheumatic agents than the corresponding esters of salicylic acid previously described. They are

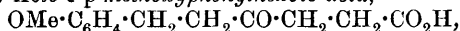
prepared by treating salts of hydroxytoluic acids with  $\alpha$ -halogen-dialkyl ethers.

*Methoxymethyl 3-hydroxy-p-toluate*, prepared from sodium 3-hydroxy-*p*-toluate and monochlorodimethyl ether, is a colourless oil, b. p. 125—131°/5 mm.; *α-ethoxyethyl 4-hydroxy-m-toluate*, prepared from potassium 4-hydroxy-*m*-toluate and  $\alpha$ -monochlorodiethyl ether, is a yellow oil. J. C. C.

**Condensation of  $\gamma$ -Ketonic Acids with Aldehydes.** W. BORSCHKE *Ber.*, 1914, **47**, 1108—1121).—The condensation of  $\beta$ -benzoylpropionic acid and its derivatives with aromatic aldehydes has been investigated. Reaction can occur in two directions. When hydrochloric acid gas or alkali hydroxide is used as condensing agent, the methylene group most distant from the carboxyl enters into reaction, and substances such as  $\beta$ -benzoyl- $\beta$ -benzylidenepropionic acid,  $\text{CHPh}\cdot\text{C}(\text{COPh})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , are formed, the constitution of which is deduced from their ability to pass into naphthalene derivatives by loss of water. On the other hand, under the conditions used in Perkin's syntheses of cinnamic acid, the methylene group adjacent to the carboxyl group is acted on and crystalline neutral substances are obtained by the loss of two molecules of water. Thus sodium benzoylpropionate, acetic anhydride, and benzaldehyde yield phenylbenzylidenecrotonolactone, 
$$\begin{array}{c} \text{CPh}\cdot\text{CH}\cdot\text{C}\cdot\text{CHPh} \\ \text{O} \quad \text{CO} \end{array}$$
, identical with the sub-

stance described by Thiele (*A.*, 1899, i, 609). It is possibly formed by the dehydration of primarily produced  $\alpha$ -phenacylcinnamic acid, but the author considers that, more probably, the initial product of the reaction is 3-phenylcrotonolactone which subsequently condenses with the aldehyde.

[With H. SAUERNHEIMER and G. HEIMBURGER.]— $\beta$ -Benzoylpropionic acid and  $\beta$ -*p*-toluoylpropionic acids are obtained by the action of aluminium chloride on succinic anhydride and benzene, or toluene, and purified by esterification and fractionation of the esters. *Ethyl p-toluoylepropionate*, long, colourless needles, has b. p. 183°/14 mm., m. p. 50°, whilst the corresponding free acid, leaflets, melts at 127°.  $\delta$ -Anisylidenelævulic acid,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , yellow needles, m. p. 131—132°, is readily prepared from anisaldehyde and lævulic acid by the method described by Erlenmeyer (*A.*, 1890, 495) for  $\delta$ -benzylidenelævulic acid. Its *ethyl* ester crystallises in white needles, m. p. 64·5°, and yields with phenylhydrazine in glacial acetic acid solution, a substance,  $\text{C}_{21}\text{H}_{24}\text{O}_3\text{N}_2$ , yellowish-white crystals, m. p. 70—71°, which is probably a pyrazoline derivative.  $\gamma$ -Keto- $\epsilon$ -*p*-methoxyphenylhexoic acid,



long, white needles, m. p. 87—88°, is obtained by the reduction of a solution of  $\delta$ -anisylidenelævulic acid in aqueous sodium hydrogen carbonate by hydrogen in the presence of colloidal palladium. Its *ethyl* ester has b. p. 209—210°/12 mm., and solidifies in a mixture of ice and salt; with phenylhydrazine it yields a *phenylhydrazone*, white needles, m. p. 108°.

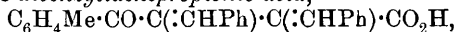
$\beta$ -Benzoyl- $\beta$ -benzylidenepropionic acid, colourless needles from

alcohol, white crystalline powder from carbon tetrachloride, m. p. 130—131°, is best obtained by cautious addition of a mixture of ethyl benzoylpropionate and benzaldehyde to an ice-cold solution of sodium in alcohol (96%). Its *oxime*, white needles, and *phenylhydrazone*, pale yellow prisms, have m. p.'s 117—118° and 150—151° (decomp.) respectively. When heated at its boiling point (under 16 mm.), the acid yields 3-benzoyl- $\alpha$ -naphthol, yellow, silky needles, m. p. 169°. Reduction of  $\beta$ -benzoyl- $\beta$ -benzylidenepropionic acid by hydrogen in the presence of colloidal palladium gives  $\beta$ -benzoyl- $\gamma$ -phenylbutyric acid,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{COPh})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , colourless needles, m. p. 100—101°.

$\gamma$ -Phenyl- $\alpha$ -benzylidenecrotonolactone, m. p. 150—151°, is obtained by heating sodium benzoylpropionate, acetic anhydride, and sodium acetate on the water-bath for a day. When added to a solution of sodium methoxide, which is immediately acidified with very dilute hydrochloric acid, it yields methyl  $\alpha$ -phenacylcinnamate, m. p. 79—80° (compare Thiele, *loc. cit.*). If, however, the solution is first diluted with water and subsequently acidified,  $\alpha$ -phenacylcinnamic acid, m. p. 171°, is obtained.  $\gamma$ -Phenyl- $\alpha$ -anisylidenecrotonolactone, yellow needles, m. p. 168°, and  $\gamma$ -phenyl- $\alpha$ -cinnamylidenecrotonolactone, orange-red, crystalline powder, m. p. 154°, are obtained by the action of sodium benzoylpropionate and acetic anhydride with anisaldehyde and cinnamaldehyde respectively. Aqueous alcoholic sodium carbonate solution transforms the latter into  $\beta$ -benzoyl- $\alpha$ -cinnamylidenepropionic acid,  $\text{COPh}\cdot\text{CH}_2\cdot\text{C}(\text{:CH}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CO}_2\text{H}$ , yellow crystals, m. p. 219—220°.

$\gamma$ -Tolyl- $\alpha$ -benzylidenecrotonolactone, yellow needles, m. p. 133—134°, is prepared in a similar manner to the corresponding phenyl compound, and, like the lower homologue, is decomposed by sodium methoxide solution with the formation of methyl  $\alpha$ -tolacylcinnamate,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{:CHPh})\cdot\text{CO}_2\text{Me}$ , m. p. 78—79°, or  $\alpha$ -tolacylcinnamic acid, white needles, m. p. 166—167°, according to the mode of operation. When an alcoholic suspension of the lactone is reduced by hydrogen in the presence of colloidal palladium, an oil is obtained which does not solidify after several months and which has not been further investigated.  $\alpha$ -Tolacylcinnamic acid is readily reduced to phenyl- $\alpha$ -tolacylpropionic acid, white leaflets, m. p. 120°.

$\beta$ -Toluoyl- $\alpha\beta$ -dibenzylidenepropionic acid,



prisms, m. p. 184—185°, is prepared by the condensation of tolylbenzylidenecrotonolactone with benzaldehyde in the presence of alcoholic sodium ethoxide.

$\gamma$ -Tolyl- $\alpha$ -anisylidenecrotonolactone, golden-yellow needles, m. p. 168—169°, is formed in the usual manner from sodium  $\beta$ -toluoylpropionate and anisaldehyde, and yields methyl  $\alpha$ -tolacyl-*p*-methoxycinnamate, yellowish-white needles, m. p. 92°.

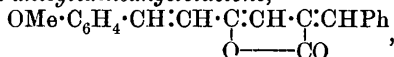
$\gamma$ -Tolyl- $\alpha$ -cinnamylidenecrotonolactone forms orange-red needles, m. p. 180°. It is converted in the usual manner into methyl  $\beta$ -toluoyl- $\alpha$ -cinnamylidenepropionate,



needles, m. p. 102°, and into the corresponding acid, white needles, m. p. 232—233°. The latter combines with semicarbazide and

phenylhydrazine, giving well characterised products, and, in alkaline solution, is readily converted into  $\delta$ -phenyl- $\alpha$ -tolacylvaleric acid, white needles, m. p. 115°.

*$\alpha$ -Benzylidene- $\delta$ -anisylidenangelolactone,*

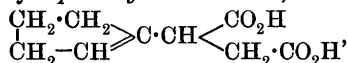


dark yellow needles, m. p. 160—161°, is prepared by the condensation of sodium  $\delta$ -anisylidenelævulate with benzaldehyde in the presence of acetic anhydride. The corresponding 1:4-dianisylidenangelolactone, reddish-yellow needles, m. p. 176°, is prepared in an analogous manner. It is not converted by sodium methoxide into the methyl ester of the corresponding ketonic acid; in the cold, little action occurs, and when the solution is warmed, resinous substances are formed. On the other hand,  *$\alpha\delta$ -dianisylidenelævulinic acid*, yellow needles, m. p. 188—189°, is readily obtained by the action of aqueous alcoholic sodium carbonate on the lactone. The acid is dehydrated to the lactone when heated above its m. p., when boiled with acetic anhydride containing sulphuric acid, when its solution in hot acetic acid is treated with a solution of hydrogen chloride in the same solvent, and when an equimolecular quantity of benzoyl chloride is added to its solution in pyridine. It reacts with an alcoholic solution of phenylhydrazine, yielding a substance,  $\text{C}_{27}\text{H}_{26}\text{O}_4\text{N}_2$ , yellowish-white crystals, m. p. 194—196°.

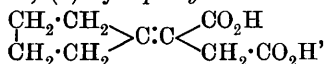
*$\gamma$ -Hydroxy- $\alpha\delta$ -dianisylidenevalerolactone*, white crystals m. p. 68—69°, is prepared by the reduction of *dianisylidenangelolactone* by hydrogen according to Skita's method. In similar circumstances, *dianisylidenelævulinic acid* yields  *$\alpha\delta$ -dianisyl-lævulinic acid*, white prisms, m. p. 133—134°.

*$\delta$ -Anisylidene- $\alpha$ -cinnamylideneangelolactone* is obtained in red leaflets, m. p. 186—187°, by the condensation of sodium  $\delta$ -anisylidenelævulate, cinnamaldehyde and acetic anhydride. H. W.

**Unsaturated Acids from cyclopentanone and Ethyl Succinate.** HANS STOBBE (*J. pr. Chem.*, 1914, [ii], 89, 329—341).—Under the influence of sodium ethoxide, cyclopentanone condenses with ethyl succinate in ethereal solution, yielding the following compounds: (1)  $\Delta^1$ -cyclopentenylylsuccinic acid,



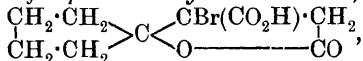
which has m. p. 157—159°, forms a granular calcium salt, and is oxidised by alkaline potassium permanganate to acetic acid and an acid having m. p. 132°; (2) cyclopentylidenesuccinic acid,



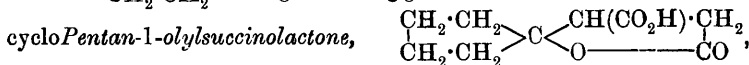
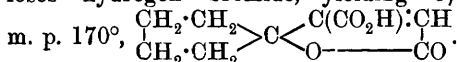
crystallising in long, colourless needles, m. p. 205—207° (decomp.); (3) a lactonic acid,  $\text{C}_{14}\text{H}_{18}\text{O}_4$ , m. p. 131—132°.

cyclopentylidenesuccinic acid forms a granular barium salt, and on treatment with acetyl chloride at the ordinary temperature is converted into the anhydride, crystallising in short, lancet-shaped needles,

m. p. 53—54°. An aqueous suspension of the acid reacts with bromine, yielding  $\beta$ -bromo- $\beta$ -cyclopentan-1-olylsuccinolactone,



which has m. p. about 170° (decomp.), and when boiled with water loses hydrogen bromide, yielding cyclopentan-1-olylfumarolactone,



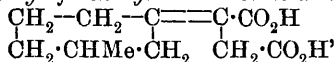
obtained by reducing the last-named compound with sodium amalgam in aqueous solution, or by the action of hydrobromic acid on cyclopentylidenesuccinic acid, crystallises in lustrous scales, m. p. 133—134°.

The constitution of cyclopentylidenesuccinic acid has been established by its oxidation with alkaline permanganate to cyclopentanone, formic, acetic, oxalic, and malonic acids. F. B.

**Unsaturated Acids and Stereoisomeric Lactonic Acids from Active 1-Methylcyclohexan-3-one and Ethyl Succinate.** HANS STOBBE (*J. pr. Chem.*, 1914, [ii], 89, 341—361. Compare preceding abstract).—From the product obtained by condensing ethyl succinate with active 3-methylcyclohexanone by means of sodium ethoxide in ethereal solution, two isomeric dibasic acids,  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , and three monobasic acids,  $\text{C}_{18}\text{H}_{26}\text{O}_4$ , have been isolated.

The dicarboxylic acids form sparingly soluble barium salts, and are thus readily separated from the monocarboxylic acids, the barium salts of which are readily soluble in water. The final separation of the two acids is then accomplished by taking advantage of their different solubilities in cold ether.

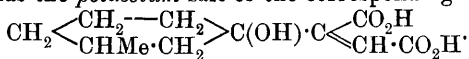
*Tetrahydro-m-tolylsuccinic acid* [3-methyl- $\Delta^1$ -cyclohexenylsuccinic acid],  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{C} - \text{CH} \cdot \text{CO}_2\text{H} \\ | \quad | \quad | \\ \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH} \quad \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$  or  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 = \text{C} - \text{CH} \cdot \text{CO}_2\text{H} \\ | \quad | \quad | \\ \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \quad \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$  is the more readily soluble acid and has m. p. 111—113°. The less soluble acid consists of 3-methylcyclohexylidenesuccinic acid,



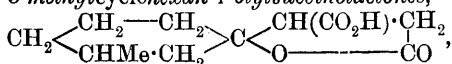
which crystallises in clusters of short prisms, m. p. 162° (decomp.), and resembles other  $\gamma$ -disubstituted itaconic acids in being difficultly reducible (solubility in water = 0.0875:100 at 25°; dissociation constant, 0.02089). It is feebly laevorotatory, and on treatment with acetyl chloride forms an *anhydride*, m. p. 104—105°; the *ethyl* ester is a colourless oil, b. p. 176°/16 mm; the *calcium* and *barium* salts are also described. The constitution of the acid has been established by its oxidation with alkaline permanganate to 3-methylcyclohexanone, acetic, malonic and oxalic acids. When triturated with bromine and water, it is converted into  $\beta$ -bromo- $\beta$ -3-methylcyclohexan-1-olylsuccinolactone,  $\text{CH}_2 \begin{array}{c} \nearrow \text{CH}_2 - \text{CH}_2 \\ \searrow \text{CHMe} \cdot \text{CH}_2 \end{array} \text{C} \begin{array}{l} \nearrow \text{CBr}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \\ \searrow \text{O} \text{-----} \text{CO} \end{array}$ , which is decomposed



by boiling with water, yielding 3-methylcyclohexan-1-olylfumarolactone,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$  This crystallises in slender needles, m. p. 198—199°, and when heated with aqueous potassium hydroxide yields the *potassium* salt of the corresponding hydroxy-acid,



On reduction, the fumarolactone should theoretically give rise to four stereoisomeric 3-methylcyclohexan-1-olylsuccinolactones,



of which three have up to the present been isolated. Two of these, isomerides, having m. p. 228° (decomp.) and 128° respectively, are formed by reducing the sodium salt of the fumarolactone with sodium amalgam in aqueous solution. The former sublimes slowly at 180° in very slender needles, whilst the latter crystallises from benzene in long, lustrous needles.

The third isomeride is obtained together with the acid of m. p. 228° by the action of concentrated hydrobromic acid at the ordinary temperature, or of 50% sulphuric acid at 100° on  $\beta$ -methylcyclohexylidenesuccinic acid. It crystallises in lustrous leaflets, m. p. 265° (decomp.), which sublime at 220—230° in slender needles. In aqueous solution the *sodium* salt has  $[\alpha]_{\text{D}}^{20} - 10.57^\circ$ .

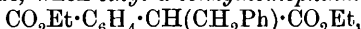
The three *monocarboxylic acids*,  $\text{C}_{18}\text{H}_{26}\text{O}_4$ , formed by the condensation of ethyl succinate and 3-methylcyclohexanone have m. p. 259—261° (with previous sintering at 251°), 237°, and 221° respectively, and are separated by fractional crystallisation from benzene and alcohol. They are probably lactonic acids produced by the condensation of two molecules of the ketone with one molecule of the ester. The less fusible acid separates from alcohol in cubes and forms a well-crystallised *piperidine* salt. F. B.

**Homophthalic Acid.** W. DIECKMANN (*Ber.*, 1914, 47, 1428—1434).—In a previous communication (*A.*, 1908, i, 894) it was shown that, in contrast to ethyl glutaconate, ethyl homophthalate does not couple with benzenediazonium salts, and cannot be alkylated in alcoholic solution by the action of sodium ethoxide and an alkyl haloid. The conclusion was drawn that the benzene linking was not so able to carry over the activating influence of the ortho-carbonyl group to the methylene group, as is the ethylene linking in ethyl glutaconate. It is now found, however, that such an influence on the acidity of the methylene group in ethyl homophthalate may be demonstrated, for, in a suitable medium, a potassium salt and, from this, a benzyl derivative have been prepared. Another contrast to ethyl phenylacetate is in the fact that a benzylidene derivative may be obtained, although only under unusual conditions.

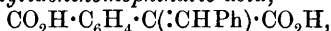
The analogy to glutaconic acid is still more marked in the case of the anhydrides. They both form coloured, neutral salts of the enol form (compare Bland and Thorpe, *T.*, 1912, 101, 863). The imides of homophthalic acid (Gabriel, *A.*, 1887, 50, 725, 1112) also behave on

titration as monobasic acids. The free anhydrides and imides of homophthalic acid, unlike the derivatives of glutamic acid, however, do not react with bromine or ferric chloride and are therefore normal in structure.

Ethyl homophthalate was added to a solution of potassium in a mixture of ether and alcohol when the potassium salt separated as a yellow, crystalline precipitate. It was suspended in ether and warmed with benzyl bromide, when *ethyl α-benzylhomophthalate*,

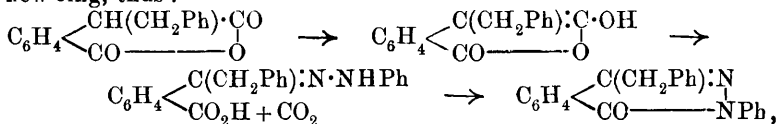


was obtained in colourless crystals, m. p. 59–60°, b. p. 220–230°/20 mm. The free acid was prepared in colourless crystals, m. p. 164°, which dissolved in alkali without colour, whereas Eichelbaum (A., 1888, 1300) described m. p. 154°, and yellow salts, which were no doubt due to the presence of the anhydride. The acid is best obtained by the reduction of *benzylidenehomophthalic acid*,



which is prepared by warming an alcoholic solution of ethyl homophthalate with benzaldehyde and sodium ethoxide, followed by hydrolysis with excess of alkali. The benzylidene derivative forms almost colourless crystals, m. p. 210°, and its *anhydride* is pale yellow, has m. p. 135°, and is hydrolysed without coloration by alkalis.

Like homophthalic anhydride (A., 1908, i, 894), the colourless, crystalline *benzylhomophthalic anhydride*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \cdot (\text{CH}_2\text{Ph}) \cdot \text{CO} \\ \text{CO} \text{-----} \text{O} \end{smallmatrix}$ , m. p. 112°, forms deep yellow solutions of the salts of 3-hydroxy-4-benzylisocoumarin, which couple with benzenediazonium acetate to form 3-phenyl-1-benzylphthalazone (Ephraim, A., 1893, i, 522). This remarkable reaction is explained by the opening of the link between the active –CH and the carbonyl groups, following by the closing of a new ring, thus :



Homophthalic acid was also condensed with aniline. The *anil*,  $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}$ , is colourless, has m. p. 188°, and may be titrated as a monobasic acid. The alkali salts, that is, the salts of 3-hydroxy-2-phenylisocarbostyryl,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \cdot \text{C} \cdot \text{OH} \\ \text{CO} \text{-----} \text{NPh} \end{smallmatrix}$ , give deep yellow solutions with green fluorescence and couple with diazobenzene to form *benzene-azohomophthalanil* [*phenylhydrazone of phthalonic acid anil*],  $\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_3$ , which crystallises in yellow needles, m. p. 240°.

The anhydride of β-phenylglutamic acid, 6-hydroxy-4-phenyl-α-pyrone, also couples with benzenediazonium acetate in alkaline solution, yielding *benzene-azo-β-phenylglutamic anhydride* [*β-phenyl-α-ketoglutamic anhydride phenylhydrazone*],  $\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_2$ , in yellow needles, m. p. 201°. J. C. W.

Colour Reactions During the Hydrolysis of Acid Anhydrides. W. DIECKMANN (*Ber.*, 1914, 47, 1435–1440).—The author

indicates that in all the cases in which the development of deep colours has been observed during the hydrolysis of the anhydrides of dicarboxylic acids by alkali hydroxides there is present a  $-\text{CH}_2$  or  $-\text{CH}$  group between the activating groups  $\text{C}:\text{C}$  and  $\text{C}:\text{O}$ , and that the activity of this methylene group is increased by ring formation (compare Stobbe, A., 1908, i, 985, and preceding abstract).

Phenylitaconic anhydride couples with benzenediazonium acetate in acetone solution in presence of excess of alkali acetate, yielding

*benzylideneoxalacetic anhydride phenylhydrazone*, 
$$\begin{array}{c} \text{CHPh}:\text{C}:\text{CO} \\ \text{NHP}:\text{N}:\text{C}:\text{CO} \end{array} > \text{O},$$

which forms yellowish-red crystals, m. p.  $193^\circ$ . It requires one molecule of alkali for the titration in alcoholic solution, and then acid precipitates the *phenylhydrazone* of *ethyl benzylideneoxalacetate*,

$$\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$$
 m. p.  $177^\circ$ , which is hydrolysed by excess of alkali to the *phenylhydrazone* of the free acid,  $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2$ , m. p.  $179^\circ$ . Attempts were made to rearrange the acid into a pyrazolone or pyrazoline derivative, but without success.

Phenylcrotonolactone (Thiele and Sulzberger, A., 1902, i, 157) also couples with diazobenzene under the above conditions. The *phenylhydrazone*,

$$\begin{array}{c} \text{CPh}:\text{CH}:\text{C}:\text{N}:\text{NHP} \\ \text{O} \text{-----} \text{CO} \end{array}$$
, forms orange needles, m. p.  $227^\circ$ ,

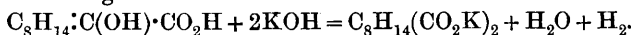
and may be converted into 1:5-diphenylpyrazole-3-carboxylic acid by the action of alcoholic alkali or hydrogen chloride in acetic acid.

Benzaldehyde and phthalide were condensed in alcoholic solution in presence of sodium ethoxide, and the deep red solution yielded 2-phenyl-1:3-diketohydrindene on acidifying. Benzylidenephthalide could not be obtained.

J. C. W.

**Direct Formation of Camphenic (Camphenecamphoric) Acid from Camphenylic Acid.** OSSIAN ASCHAN (*Ber.*, 1914, 47, 1121—1123. Compare A., 1910, i, 709).—It has been previously shown that camphenylic acid mixed with an excess of camphenic acid is obtained by the oxidation of camphene with permanganate in dilute alkaline solution, and further that the latter cannot be obtained from the former by the same operation. Since, however, camphene has been shown to be a uniform product (Aschan, A., 1911, i, 796) and camphenylic acid is its primary oxidation product, it follows that camphenic acid must be obtainable from the latter. This transformation has been indirectly effected by Hintikka (this vol., i, 409).

The author now shows that the change can be directly effected in solution by adding sodium camphenylate to a highly concentrated aqueous solution of potassium hydroxide and cautious heating of the mixture in a silver crucible until the water is driven off. The clear melt is dissolved in water, and acidified with dilute sulphuric acid, when camphenic acid, m. p.  $134$ — $135^\circ$ , is obtained, which shows no alteration in m. p. when mixed with *cis-dl*-camphenic acid. Reaction occurs according to the scheme :



H. W.

**The Condensation of Valerolactone with Aromatic Aldehydes and Fatty-Aromatic Ketones.** M. S. LOSANITSCH (*Monatsh.*, 1914, 35, 311—318).—Although the condensation of  $\Delta^2$ -unsaturated lactones with aromatic aldehydes has been investigated (Thiele, A., 1902, i, 152), there appears to have been no attention paid to the condensation of saturated lactones with aldehydes and ketones. The author finds that valerolactone, under the influence of sodium ethoxide, forms condensation products with such substances as benzaldehyde and acetophenone. The method applied was to add an ethereal solution of an equimolecular mixture of valerolactone and the ketonic substance to a suspension of the equivalent quantity of alcohol-free sodium ethoxide in the same solvent; a deposit of a sodium compound separates, and on acidifying yields a hydrated product which easily loses the elements of water to give the final condensation product.

In this manner, benzaldehyde gave rise to *α-benzylidenevalerolactone*,  $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{array} > \text{C}:\text{CHPh}$ , yellow, prismatic crystals, m. p. 61·5—62°, b. p. 204—205° (corr.) /15 mm., accompanied by a certain quantity of oily by-products.

*α-Piperonylidenevalerolactone*,  $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{array} > \text{C}:\text{CH}\cdot\text{C}_7\text{H}_5\text{O}_2$ , obtained similarly from piperonal, forms lemon-yellow rhombohedra, m. p. 122·5—123·5° (corr.).

With acetophenone the condensation is far from complete under the above conditions, and a double proportion of sodium ethoxide is necessary for a good yield. The product is *α-phenylethylidenevalerolactone*,  $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{array} > \text{C}:\text{CMePh}$ , large prisms, m. p. 55—57°, b. p. 196—198°/13 mm., 325—328° (corr.) /ord. pressure.

Condensation of valerolactone with heptaldehyde gave an oily substance, b. p. 179—184°/13 mm., in barely 40% yield. This product, which was accompanied by more complex substances, had a composition  $\text{C}_{24}\text{H}_{42}\text{O}_5$ , and the action of *m*-nitrobenzoyl chloride and pyridine produced only *m*-nitrobenzoic anhydride, for which the m. p. 164·5—165·5° (corr.) was obtained.

Valerolactone also failed to condense satisfactorily with ethyl acetate.  
D. F. T.

**Constitution of Carminic Acid.** C. LIEBERMANN and HANS LIEBERMANN (*Ber.*, 1914, 47, 1213—1219).—The authors advance the following arguments against Dimroth's (A., 1913, i, 977) view that carminic acid is a derivative of anthraquinone:

(1) The extreme solubility of carminic acid in water is not shared by any other hydroxyanthraquinone derivative with the possible exception of the glucosides, and even these possess a much smaller solubility than carminic acid.

(2) In the whole of the anthraquinone series no example is known of a compound showing the characteristic behaviour of carminic acid of being quantitatively converted by loss of water at 145° into an insoluble dye which cannot be reconverted into the acid.

(3) The very small yields of anthracene hydrocarbons formed by the distillation of carminic acid and its derivatives with zinc dust (5% from carminic acid, almost 0% from carminic anhydride), in comparison with the much larger yields given by other anthraquinone derivatives, point to the occurrence of an anthracene condensation during the distillation rather than to the presence of an anthraquinone group in the carminic acid molecule.

Further, the small yields of trihydroxymethylanthraquinonecarboxylic acid and coccinin, obtained by the action of sulphuric acid and potassium hydroxide respectively on carminic acid, are also in agreement with the view that the anthraquinone group is not already present in the molecule, but is produced by condensation during the action of these reagents. The authors have reinvestigated the ruficoccin of Liebermann and van Dorp (this Journ., 1871, 913; 1872, 704), and find that it consists of a mixture of trihydroxymethylanthraquinonecarboxylic acid and trihydroxymethylanthraquinone.

*Carminic anhydride*,  $C_{22}H_{20}O_{12}$ , prepared by heating carminic acid with thionyl chloride, is a vivid red powder, and, with the exception of its sparing solubility in water, closely resembles the original acid into which it is reconverted by boiling with aqueous alkalis.

F. B.

**Preparation of Basic Bismuth Gallo-carboxylate.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 268932).—Basic *bismuth gallo-carboxylate* is prepared by treating an aqueous or alcoholic solution of gallo-carboxylic acid with bismuth hydroxide or bismuth salts in acid solution. It forms a yellow powder, and is a valuable anti-diarrhoeic.

J. C. C.

**"Paired" Glycuronic Acids. II. Phloroglucinolglycuronic Acid.** YOSHITA SERA (*Zeitsch. physiol. Chem.*, 1914, 90, 258—260. Compare this vol., i, 290).—When rabbits are fed with phloroglucinol their urine contains a phloroglucinolglycuronic acid, which can be isolated in the same way as the orcinolglycuronic acid already described (*loc. cit.*). *Barium phloroglucinolglycuronic acid* crystallises in thin, colourless needles. The *potassium salt*,  $C_{12}H_{15}O_{10}K$ , forms prisms, and has  $[\alpha]_D -80.82^\circ$  (in water). On hydrolysis it yields phloroglucinol and glycuronic acid. Phloroglucinolglycuronic acid, unlike phlorin, is not hydrolysed by emulsin.

R. V. S.

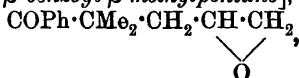
**Catalytic Hydrogenations in the Presence of Platinum-black. Conversion of Aldehydes and Ketones into Alcohols.** G. VAYON (*Ann. Chim.*, 1914, [ix], 1, 144—200).—A résumé of work already published (compare A., 1912, i, 260, 628, 749).

W. G.

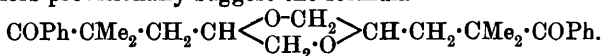
**Syntheses by means of Sodamide. Action of Epihalohydrins on Dialkylacetophenones. Oxypropylenedimethylacetophenone and Derivatives.** (Mme.) RAMART-LUCAS and A. HALLER (*Compt. rend.*, 1914, 158, 1302—1306. Compare A., 1903, i, 318, 714; 1904, i, 180).—Acetophenone reacts with epihalohydrins in

the presence of sodamide to give only tarry products. Dialkyl-acetophenones behave normally, giving substitution products.

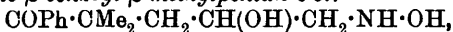
Phenyl isopropyl ketone, treated in ether with sodamide, and then at the boiling point with the theoretical quantity of epibromohydrin, added gradually, yields  $\alpha\beta$ -oxypropylenedimethyl-acetophenone [ $\delta\epsilon$ -oxido- $\beta$ -benzoyl- $\beta$ -methylpentane],



white prisms, m. p.  $59^\circ$ , b. p.  $139-140^\circ/12$  mm. On boiling this substance with water it gives  $\beta$ -benzoyl- $\beta$ -methylpentane- $\delta\epsilon$ -diol,  $\text{COPh} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , slender needles, m. p.  $99-100^\circ$ . Sodamide in benzene or toluene is without action on the ketone, but with a trace of acid the latter substance undergoes more or less rapid polymerisation, giving the dimeride,  $(\text{C}_{18}\text{H}_{16}\text{O}_2)_2$ , m. p.  $214-215^\circ$ , which crystallises from acetyl chloride in slender needles. For this dimeride the authors provisionally suggest the formula



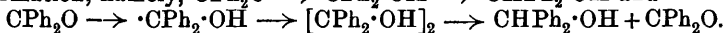
The monomeride reacts with Crismer's salt to give, not an oxime, but  $\epsilon$ -hydroxylamino- $\beta$ -benzoyl- $\beta$ -methylpentan- $\delta$ -ol.



slender needles, m. p.  $122-123^\circ$ . Semicarbazide hydrochloride, on the other hand, gives the dimeride, m. p.  $214^\circ$ , mentioned above.

W. G.

**The Reduction of Aromatic Ketones. II.** J. BÖESEKEN and W. D. COHEN (*Proc. R. Akad. Wetensch. Amsterdam*, 1914, 16, 962-968).—In the earlier paper (A., 1913, i, 1062) it was shown that the reduction of benzophenone in the presence of hydroxyl ions always gave rise to some benzhydrol. The present investigation renders possible a decision between the two possible courses for the benzhydrol formation, namely,  $\text{CPh}_2\text{O} \rightarrow \cdot\text{CPh}_2 \cdot \text{OH} \rightarrow \text{CHPh}_2 \cdot \text{OH}$  and



If the latter representation were correct, it would be expected that the pinacones of the ketones which most readily give rise to the corresponding benzhydrols would be most readily decomposed by alkalis. This is now proved to be the case; the decomposition-velocity of the various pinacones by  $N/10$ ,  $N/100$ , and  $N/1000$  ethereal-alcoholic solutions of sodium ethoxide has been measured at  $25^\circ$ , and the results show that the greater the decomposition-velocity of the pinacone by alkali, the smaller the quantity produced in the reduction of the corresponding ketone by aluminium amalgam. The pinacones examined were those derived from 2-, 3-, and 4-chloro-, 4-bromo-, 4-methoxy-, 4-methyl-, 4:4'-dichloro-, 4:4'-dimethyl-, 2'-chloro-4-methyl-, and 4'-chloro-4-methyl-benzophenones together with benzophenone itself. D. F. T.

**Halochromy with Anils.** G. REDDELIEN (*Ber.*, 1914, 47, 1355-1364).—The anils exhibit considerable analogy to the aldehydes and ketones in chemical behaviour (Reddelien, A., 1913, i, 1202), and the resemblance extends to the occurrence of halochromy.

From an examination of the colour of the hydrochlorides and the sulphuric acid solutions of certain anils, the author finds that the deepening in colour on salt formation is affected in the same manner as with the ketones, the halochromy being strengthened by the methoxyl group and weakened by the nitro-group (compare Reddelien, A., 1912, i, 986). The colours of the salts of an anil also deepen in the order: hydrochloride, hydrobromide, hydriodide.

The constitution of the salts is formulated in accordance with Pfeiffer's theory (A., 1910, i, 788), for example, benzophenoneanil hydrochloride is represented  $\leftarrow \text{CPh}_2\text{:N} \begin{smallmatrix} \text{Ph} \\ \text{HCl} \end{smallmatrix}$ , the colour being referred to the unsaturation of the carbon atom in the C:N group. As the  $\text{-C:NPh}$  group is more basic than the  $\text{-CO}$  group, the amount of free affinity at the carbon atom should be less with the salts of the anils than of the ketones, which agrees with the stronger halochromy of the latter. The absorption spectra of the anil salts also indicate only a slight displacement of the absorption of the free anil towards the red. It is also found that as a fairly general rule the anil salts in which halochromy is most marked and in which therefore the characteristic carbon atom is most unsaturated, undergo hydrolysis most readily into ketone and amine hydrochloride.

*p*-Methoxybenzophenoneanil (Hantzsch and Kraft, A., 1891, i, 338) was obtained for the first time as a solid, greenish-yellow prisms, m. p.  $72^\circ$ , b. p.  $225\text{--}240^\circ/11\text{ mm.}$

*Benzophenone-p-nitroanil*, obtained by heating benzophenone, nitroaniline, and a little hydrobromic acid at  $200^\circ$  in a current of carbon dioxide, forms greenish-yellow needles, m. p.  $156^\circ$ .

*Benzophenone-p-anisil*,  $\text{CPh}_2\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , stout, yellow prisms, m. p.  $70^\circ$ , was obtained in a similar manner.

The hydrochlorides were prepared by passing hydrogen chloride into a benzene solution of the anil.

Benzophenoneanil *hydrochloride*, yellow; *hydrobromide*, yellow crystals, m. p.  $264\text{--}266^\circ$  (decomp.); *hydriodide*, deep yellow.

Fluorenoneanil *hydrochloride*, orange-red, m. p.  $198^\circ$  (decomp.); *hydrobromide*, red, m. p.  $214\text{--}216^\circ$  (decomp.); *hydriodide*, deep red, m. p.  $218\text{--}220^\circ$  (decomp.).

Benzophenone- $\alpha$ -naphthil *hydrochloride*, orange-yellow, m. p.  $175\text{--}176^\circ$  (decomp.). Benzildianil *hydrochloride*, orange-coloured, m. p.  $146\text{--}147^\circ$  (decomp.). Dypnoneanil *hydrochloride*, deep yellow, m. p.  $125\text{--}126^\circ$  (decomp.). Benzophenone-*p*-anisil *hydrochloride*, golden-yellow. *p*-Methoxybenzophenoneanil *hydrochloride*, yellow. Benzophenone-*p*-nitroanil *hydrochloride*, yellow, m. p.  $183\text{--}184^\circ$  (decomp.). Benzophenoneanil *nitrate*, yellow, m. p.  $166\text{--}167^\circ$  (decomp.). Fluorenoneanil *nitrate*, orange-coloured crystals, m. p.  $136\text{--}137^\circ$  (decomp.).

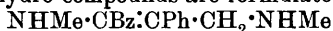
D. F. T.

**Secondary  $\alpha$ -Amino-ketones.** S. GABRIEL (*Ber.*, 1914, 47, 1336—1347).—The ease with which  $\alpha$ -aminoacetophenone and some of its derivatives containing a substituent in the benzene ring undergo condensation (this vol., i, 51; Rudenburg, this vol., i, 52) has led the

author to examine compounds of the type  $C_6H_5 \cdot CO \cdot CH_2 \cdot NHX$ , where X represents an aliphatic radicle.

The required bases were synthesised by Hinsberg's method. An aqueous solution of  $\alpha$ -aminoacetophenone hydrochloride was well stirred with an acetone solution of *p*-toluenesulphonyl chloride in the presence of potassium hydrogen carbonate, when *p*-toluenesulphophenacylamide,  $C_7H_7 \cdot SO_2 \cdot NH \cdot CH_2 \cdot CPh$ , rhombic tablets, m. p. 116—117°, was obtained; by methylating with methyl iodide and an aqueous-alcoholic solution of sodium hydroxide, this substance was converted into *p*-toluenesulphophenacylmethylamide,  $C_7H_7 \cdot SO_2 \cdot NMe \cdot CH_2 \cdot CPh$ , needles, m. p. 122°, which was rather more conveniently prepared by the interaction of the potassium derivative of *p*-toluenesulphomethylamide and  $\omega$ -bromoacetophenone. By hydrolysis with fuming hydrochloric acid at 100° under pressure, the last product is transformed into methylaminoacetophenone *p*-toluenesulphonate, needles (with  $1H_2O$ ), m. p. 88° with previous sintering at 80°, but the anhydrous salt has m. p. 133—134°. The toluenesulphonate was converted into the *picrate*, m. p. 136°, and thence into the *hydrochloride*, rhombic tablets, m. p. 219° (decomp.).

When the toluenesulphonate was treated with sodium hydroxide solution, the resulting solution deposited a granular crystalline solid which rapidly reddens and then resinifies in the air; analysis indicated this product to be *anhydrobisphenacylmethylamine*,  $C_{18}H_{20}ON_2$ , m. p. near 128° (decomp.). This substance possesses basic properties, but no salts were isolable on account of the readiness with which it passes into *bisanhydrobisphenacylmethylamine*,  $C_{18}H_{18}N_2$ , yellow prisms, m. p. 133°. The last compound, which was obtained most conveniently by heating the previous base at 100° in a vacuum, can be distilled in a vacuum without decomposition; it gave a *hydrochloride*, m. p. 241° (decomp.), with previous assumption of a green colour at 200°, a *picrate*, m. p. 178°, and an *acetyl* derivative, needles, m. p. 156°. The above behaviour of the unisolated methylaminoacetophenone recalls that of aminoacetophenone itself (Gabriel, A., 1908, i, 464), and the above anhydro- and bisanhydro-compounds are formulated



and  $\begin{matrix} CH=CPh \\ | \\ NMe \cdot CPh \end{matrix} \gg C \cdot NHMe$  respectively. Bisanhydrobisphenacylmethylamine differs from its analogue bisanhydrobisphenacylamine, however, in its behaviour towards hydriodic acid, by which it is converted into a *hydriodide*,  $C_{18}H_{20}N_2 \cdot 2HI$ , yellow, rhombic tablets or prisms, m. p. 227° (decomp.); potassium hydrogen carbonate converts this salt into a carbon dioxide derivative,  $C_{18}H_{20}N_2 \cdot CO_2$ , which, on distillation under 2—3 mm. pressure, gives a colourless mass presumably containing at least some of the *dihydrobisanhydrobisphenacylmethylamine*; of this base the *perchlorate*, microscopic, rectangular plates, and *picrate*, needles, m. p. 132° (decomp. commencing at 125°), were also prepared.

By the interaction of benzylamine and *p*-toluenesulphonyl chloride in the presence of sodium hydroxide solution, *p*-toluenesulphobenzylamide,  $C_7H_7 \cdot SO_2 \cdot NH \cdot CH_2Ph$ , plates, m. p. 116°, was produced; this was converted into its *potassium* derivative and shaken with bromoacetophenone in suspension in acetone, when *p*-toluenesulphobenzyl-



*phenylacetylamine*,  $C_7H_7 \cdot SO_2 \cdot N(CH_2Ph) \cdot CH_2 \cdot CPh$ , colourless needles or leaflets, m. p. 116—116.5°, was obtained. Hydrolysis of this product with fuming hydrochloric acid under pressure at 100° gave a mixture of the *hydrochloride*, colourless scales, m. p. 219°, and the *p-toluene-sulphonate*, needles, m. p. 206—207°, of benzylaminoacetophenone. The hydrochloride, on treatment with aqueous sodium hydroxide, gave a yellow oil which gradually changed to a solid containing a *substance*,  $C_{15}H_{15}ON$  (polymeride?), m. p. 83—86°, and also an *oil*. The nature of the latter was not certain, but on treating its acetone solution with hydrochloric acid the original hydrochloride was regenerated, whilst the solid, m. p. 83—86°, could be reconverted into the hydrochloride only by distillation under 2—3 mm., and acting on the resulting oil with acetone and hydrochloric acid. When the crude solid, from which the preceding solid and oil can be separated, was dissolved in warm sulphuric acid, colourless, rhombic tablets of a *sulphate* were obtained on cooling; the corresponding *base* was isolated by treating the aqueous alcoholic solution with ammonia, when it was obtained in the form of yellow prisms, m. p. 110—112° (decomp.), and of the composition  $(C_{10}H_{10}N)_x$ . D. F. T.

**Zinc Chloride as a Condensation Agent. IV. The Interaction of Propiophenone and Aromatic Amines.** G. REDDELIEN (*Ber.*, 1914, 47, 1364—1368).—The author has already shown (*A.*, 1913, i, 1202, 1203; 1912, i, 363) that acetophenone and aniline give various condensation products according to the condensation agent applied, and he has now examined the behaviour of propiophenone from the same point of view.

[With CONRAD WEYGAND.]—When a mixture of propiophenone and aniline with a little aniline zincchloride was kept in gentle ebullition in a stream of carbon dioxide, phenyl ethyl ketone-anil,  $CPhEt \cdot NPh$ , pale yellow needles, m. p. 50°, b. p. 169°/11 mm. (compare Busch and Fleischmann, *A.*, 1910, i, 728) was obtained.

A similar reaction to the last, but using *p*-toluidine in place of aniline, gave *phenyl ethyl ketone-p-tolil*,  $CPhEt \cdot N \cdot C_6H_4Me$ , b. p. 172°/10 mm., m. p. 72—73°, which crystallises less readily than the corresponding anil.

In an analogous manner anisidine gave *phenyl ethyl ketone-p-anisil*,  $CPhEt \cdot N \cdot C_6H_4 \cdot OMe$ , yellow needles, b. p. 205—206°/11 mm., m. p. 96°.

These results are in accordance with those obtained earlier with acetophenone, but on heating a mixture of propiophenone and aniline with a little aniline hydrochloride, a mixture of phenyl ethyl ketone-anil and a deep yellow oil, b. p. 240°/18 mm., was obtained instead of the expected triphenyltrimethylbenzene. When heated with a little aniline hydrochloride in a stream of carbon dioxide at 200°, phenyl ethyl ketone-anil underwent condensation to a viscous, yellow oil, b. p. 242—244°/13 mm., probably  $\alpha\gamma$ -diphenyl- $\beta$ -methyl- $\Delta^2$ -buten- $\alpha$ -anil,  $CPhEt \cdot CMe \cdot CPh \cdot NPh$ .

The relative difficulty with which this last condensation is effected and the absence of formation of triphenyltrimethylbenzene in the preceding condensation leads the author to the opinion that it is in the

enolic form that acetophenone condenses, and that the presence of a methyl radicle at the double bond greatly reduces the tendency of the bond to additive processes. A similar effect of the methyl radicle is also seen in the absence of interaction between  $\beta\delta$ -diphenyl- $\Delta^{\beta}$ -buten- $\delta$ -one,  $\text{CPhMe}:\text{CH}\cdot\text{COPh}$  (dypnone), and aniline in alcohol containing a little alkali at the ordinary temperature or at  $100^{\circ}$ , whilst phenyl styryl ketone,  $\text{CHPh}:\text{CH}\cdot\text{COPh}$ , at the ordinary temperature gave a copious deposit of phenyl styryl ketone-anil (compare Tambor and Wildi, A., 1898, i, 314).

D. F. T.

**Formation of Ketones by the Spontaneous Elimination of Hydrogen Chloride from Aryl-aliphatic Acid Chlorides. I.** W. BORSCHÉ and W. EBERLEIN (*Ber.*, 1914, 47, 1460—1470).—It has been previously shown (Borsche, A., 1911, i, 1018) that tetrahydropiperyl chloride, in contrast to  $\delta$ -phenylvaleryl chloride, is decomposed on distillation under reduced pressure, yielding hydrogen chloride and a colourless oil. The latter is now shown to be methylenedioxybenzosuberone (Borsche, *loc. cit.*), identical with the product obtained by the action of aluminium chloride on a solution of tetrahydropiperyl chloride in carbon disulphide. The chlorides of  $\gamma$ -methylenedioxyphenylbutyric acid and of  $\beta$ -methylenedioxyphenylpropionic acid undergo decomposition in an analogous manner.

The recent work of Leuchs, Wutke, and Gieseler (A., 1913, i, 855) and of Lecher (A., 1913, i, 1166) suggests that the elimination of hydrogen chloride may be greatly influenced by the presence of phosphorus compounds in the acid chloride. This is, however, shown to be improbable, since when the product of the action of phosphorus trichloride on tetrahydropiperic acid is distilled without removal of chloride or of phosphorous acid, complete decomposition occurs without formation of methylenedioxybenzosuberone. Further,  $\delta$ -phenylvaleryl chloride,  $\gamma$ -phenylbutyryl chloride, and  $\beta$ -phenylpropionyl chloride, prepared under exactly the same conditions as the chlorides of the methylenedioxy-acids, can be distilled under diminished pressure without suffering decomposition and, although addition of phosphoric oxide previous to distillation causes considerable decomposition to occur, even then the presence of a bicyclic ketone cannot be demonstrated. Lastly, tetrahydropiperyl chloride obtained from thionyl chloride and sodium tetrahydropiperate decomposes in exactly the same manner as the chloride obtained with the help of phosphorus trichloride. The deciding factor for the formation of ketones appears to be the nature of the substituents in the benzene nucleus.

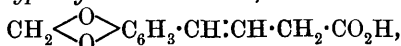
When tetrahydropiperyl chloride is distilled under diminished pressure, a practically colourless, viscous oil is obtained, together with a small quantity of crystalline tetrahydropiperic acid, m. p.  $95\text{--}96^{\circ}$ . The former, after purification through its semicarbazone, m. p.  $236\text{--}238^{\circ}$  (decomp.), has b. p.  $206\text{--}208^{\circ}/18\text{ mm.}$ , and consists of methylenedioxybenzosuberone. Experiments on the mechanism of this change show that tetrahydropiperic acid is practically undecomposed when distilled under diminished pressure (12 mm.), but yields methylenedioxybenzosuberone when warmed in benzene solution with phosphoric oxide (compare Perkin and Robinson, T., 1907, 91,

1073). Further, the decomposition of tetrahydropiperyl chloride into methylenedioxybenzosuberone does not occur to an appreciable extent previous to distillation.

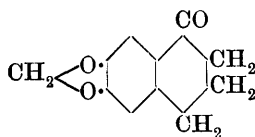
Tetrahydropiperic acid reacts with thionyl chloride to yield a viscous, reddish-brown oil, which is almost completely carbonised by distillation under reduced pressure. The chloride can, however, be obtained by the action of thionyl chloride on an ethereal suspension of sodium tetrahydropiperate at the ordinary temperature (compare Kopetschni and Karczag, this vol., i, 180).

$\delta$ -Phenylvaleryl chloride, when distilled with phosphoric oxide under 22 mm., yields a yellow distillate from which a condensation product cannot be isolated. When similarly treated,  $\delta$ -phenylvaleric acid gives a small quantity of  $\alpha\beta$ -benzosuberone (semicarbazone, m. p.  $216^\circ$  [decomp.]: compare Kipping, Hall, and Hunter, T., 1899, 75, 144; 1901, 79, 602).

$\gamma$ -Methylenedioxyphenylisocrotonic acid,



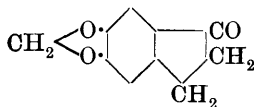
shining leaflets, m. p.  $117-118^\circ$  after softening at about  $114^\circ$ , is prepared by heating piperonal, sodium succinate, and acetic anhydride for ten hours at  $115^\circ$ . It can be distilled without decomposition in a vacuum, but is completely decomposed at the ordinary temperature. Reduction with hydrogen in the presence of colloidal palladium yields



$\gamma$ -methylenedioxyphenylbutyric acid, prisms, m. p.  $83^\circ$ , which, when treated with phosphorus trichloride and subsequently distilled, gives  $\alpha$ -keto-methylenedioxytetrahydronaphthalene (annexed formula), colourless needles, m. p.  $77-78^\circ$ , b. p.  $191^\circ/18$  mm. (semi-

carbazone, crystalline powder, m. p.  $258^\circ$  [decomp.]). The slight evolution of hydrogen chloride during the heating of the crude product and the general course of the distillation make it probable that formation of the ketone occurs largely previous to the distillation. This is confirmed by the fact that the action of ammonia on a dry ethereal solution of the crude product of the action of phosphorus trichloride on the acid leads to the formation of only minimal amounts of a substance, m. p.  $145^\circ$ , whilst the isolation of the ketone is readily effected.

Piperonylpropionyl chloride, on distillation, behaves in the same



manner as tetrahydropiperyl chloride and yields methylenedioxy- $\alpha$ -hydrindone (annexed formula), m. p.  $161^\circ$  (semicarbazone, m. p.  $253^\circ$ ; benzylidene compound, m. p.  $198-199^\circ$ ). Perkin and Robinson (*loc. cit.*) give m. p.'s  $160^\circ$  and  $200^\circ$  respectively for

the ketone and the benzylidene derivative. Proof that formation of the ketone takes place in this instance during the distillation of the chloride is furnished by the facts that the undistilled chloride is completely soluble in sodium carbonate solution, and that on treatment with ammonia in dry ethereal solution it yields  $\beta$ -piperonylpropion-

*amide*, white, crystalline powder, m. p. 123·5°, whilst aniline converts it into *β-piperonylpropionanilide*, silky needles, m. p. 122—123°.

H. W.

**Action of Sodamide on Some Diketones.** ÉDOUARD BAUER (*Ann. Chim.*, 1914, [ix], 1, 342—376; 377—393).—For the most part an elaboration of work already published on the action of sodamide on *αδ*-dibenzoylbutane (compare A., 1913, i, 724). *αδ*-Dibenzoyl-*γ*-methylbutane similarly undergoes cyclisation in the presence of sodamide, giving a compound,  $C_{19}H_{18}O$ , b. p. 211°/12 mm., m. p. 55°,  $\alpha_D^{15} - 0^\circ 10'$ . It does not decolorise bromine water, and only slowly reduces potassium permanganate. In all its properties it closely resembles the behaviour of 1-benzoyl-2-phenyl- $\Delta^1$ -cyclopentene, but its constitution has not yet been definitely settled.

W. G.

**Synthesis of Acetylenic *γ*-Diketones.** GEORGES DUPONT (*Compt. rend.*, 1914, 158, 1349—1351).—Aromatic acetylenic *γ*-diketones are readily prepared by the oxidation of aromatic acetylenic *γ*-glycols in acetic acid solution with chromic acid. The oxidising agent is added until a yellow colour persists, and then, after 2 hours, the mixture is poured on to water, the precipitate collected, and recrystallised from benzene or alcohol. The reaction:  $OHR \cdot CH \cdot C \equiv C \cdot CHR \cdot OH + O_2 = COR \cdot C \equiv C \cdot COR + 2H_2O$  has, so far, failed with aliphatic acetylenic *γ*-glycols, but has yielded the following diketones.

*Dibenzoylacetylene*,  $COPh \cdot C \equiv C \cdot COPh$ , pale yellow crystals, m. p. 112°, which on hydrogenation in the presence of platinum-black yields *s*-dibenzoylthane, m. p. 144°. A trace of the acetylenic diketone with concentrated sulphuric acid gives first a yellow and then a green coloration, turning to reddish-brown on warming.

*di-p-Toluyloacetylene*,  $C_6H_4Me \cdot CO \cdot C \equiv C \cdot CO \cdot C_6H_4Me$ , small, elongated, white prisms, m. p. 92—93°, of which a trace with sulphuric acid gives a yellow coloration, disappearing at first on warming and then reappearing as a brown coloration.

*Di-p-anisoylacetylene*,  $OMe \cdot C_6H_4 \cdot CO \cdot C \equiv C \cdot CO \cdot C_6H_4 \cdot OMe$ , slender, white needles, m. p. 138°. The colour with sulphuric acid is eosin-red, changing on warming progressively first to Prussian-blue, then to wine-red, and finally to a brownish-violet.

W. G.

**Simultaneous Chlorination and Oxidation by means of Aqua Regia.** Preparation of Chloroanil from *p*-Phenylenediamine and Quinol. RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1914, 36, 1011—1013).—It has been shown by Datta and Fernandes (this vol., i, 675) that aqua regia reacts with hydrocarbons as a chlorinating agent. In cases in which oxidation is possible as well as chlorination, both processes take place simultaneously. By this means pure chloroanil (tetrachloro-*p*-benzoquinone) can be rapidly and simply prepared from either *p*-phenylenediamine or quinol.

E. G.

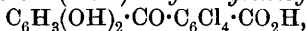
**Physico-chemical Investigation of the Hydroxy- and Dihydroxy-anthraquinones particularly with regard to their Lake-forming Power.** GUSTAV F. HÜTTIG (*Zeitsch. physikal. Chem.*, 1914, 87, 129—168).—The author has determined the dissociation constant

of the following derivatives of anthraquinone, alizarin, 1-hydroxy-anthraquinone, 2-hydroxyanthraquinone, 2 : 6-dihydroxyanthraquinone; 1 : 4-dihydroxyanthraquinone, 1 : 5-dihydroxyanthraquinone, and 1 : 6-dihydroxyanthraquinone. The determination is based on a method which involves the determination of the solubility of the substances in water, in a strong base (KOH), and in a weak base (ammonia). The solubilities were determined in the case of water solutions colorimetrically, and in the other cases by precipitation with dilute acid and filtration in a Gooch crucible and subsequent weighing. The dissociation constants are found to be in the following order : 2nd dissociation constant of alizarin  $1.1 \times 10^{-12}$ ; 1-hydroxyanthraquinone  $3.2 \times 10^{-12}$ ; 1 : 5-dihydroxyanthraquinone  $4.4 \times 10^{-11}$ ; 1 : 4-dihydroxyanthraquinone  $3.1 \times 10^{-10}$ ; alizarin 1st constant  $6.6 \times 10^{-9}$ ; 1 : 6-dihydroxyanthraquinone  $7.9 \times 10^{-9}$ ; 2-hydroxyanthraquinone  $2.4 \times 10^{-8}$ , and 2 : 6-dihydroxyanthraquinone  $8.8 \times 10^{-7}$ . The order of the power of lake formation is alizarin, 1 : 4-dihydroxyanthraquinone, 1-hydroxyanthraquinone, 2-hydroxyanthraquinone, 1 : 5-dihydroxyanthraquinone, 1 : 6-dihydroxyanthraquinone and 2 : 6-dihydroxyanthraquinone, the last of which has no power at all of lake formation. A relationship is given in tabular form of the dissociation constant with the positions of the hydroxyl groups, and theories are propounded on the nature of lakes.

J. F. S.

**1 : 2 : 3 : 4-Tetrachloroquinizarin.** HENNY HÖVERMANN (*Ber.*, 1914, 47, 1210—1213).—Contrary to the statement in D.R.-P. 172105, tetrachlorophthalic acid can be condensed with quinol to form tetrachloroquinizarin (5 : 6 : 7 : 8-tetrachloro-1 : 4-dehydroxyanthraquinone).

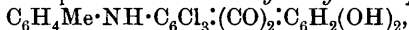
**2 : 3 : 4 : 5-Tetrachloro-6-(2' : 5')-dihydroxybenzoylbenzoic acid,**



prepared by heating tetrachlorophthalic acid or its anhydride with quinol at 195—230° in the presence of boric acid, crystallises in slender, citron-yellow needles, m. p. 231°, and when warmed with sulphuric acid is converted into 5 : 6 : 7 : 8-tetrachloro-1 : 4-dihydroxyanthraquinone,  $\text{CCl}_4 : (\text{CO})_2 : \text{C}_6\text{H}_2(\text{OH})_2$ . This crystallises in lustrous, red leaflets, m. p. 270°, forms a *diacetyl* derivative (yellow needles, m. p. 209°), and dissolves in sulphuric acid, yielding carmine-red solutions having an orange fluorescence.

*Dichlorotetrahydroxyanthraquinone*,  $\text{C}_6\text{Cl}_2(\text{OH})_2 : (\text{CO})_2 : \text{C}_6\text{H}_2(\text{OH})_2$ , obtained by heating the tetrachloro-compound with water and calcium hydroxide at 250° in the presence of a little copper powder, crystallises in red needles, and gives violet solutions in alkalis and purple-red solutions in strong sulphuric acid; the hydroxyl groups are probably in the  $\alpha$ -positions.

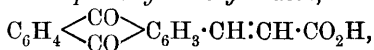
**6 : 7 : 8-Trichloro-5-p-toluidino-1 : 4-dihydroxyanthraquinone,**



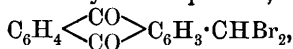
prepared by heating the tetrachloro-compound with *p*-toluidine in the presence of copper powder and sodium carbonate, crystallises in slender, deep violet needles.

F. B.

**Anthraquinone-2-aldehyde.** ALFRED ECKERT (*Monatsh.*, 1914, 35, 289—300).—When anthraquinone-2-aldehyde is heated for one to one and a-half hours with sodium acetate and acetic anhydride under a reflux condenser, *anthraquinonyl-2-acrylic acid*,



pale yellow needles, m. p. 335°, is obtained; *sodium* salt, yellow needles sparingly soluble in water and alcohol. The acid is also produced when  $\omega$ -dibromomethylanthraquinone,



is heated with acetic anhydride and potassium acetate for forty hours. Oxidation of the acid by potassium permanganate in alkaline solution regenerates anthraquinone-2-aldehyde. If the anthraquinonylacrylic acid or the anthraquinonealdehyde is treated in the cold with a mixture of sulphuric and nitric acids it is converted into 5-nitroanthraquinone-2-aldehyde, pale yellow needles, m. p. 268°; this is insoluble in alkali hydroxides, but dissolves in warm sulphuric acid to a red solution which on dilution with water gives a deposit soluble in alkali hydroxide to a violet solution; *phenylhydrazone*, deep violet needles, m. p. 312°; *hydrazone*, yellow; *bisulphite* compound, pale yellow, crystalline solid.

On oxidation of 5-nitroanthraquinone-2-aldehyde in acetic acid by chromic acid there is obtained 5-nitroanthraquinone-2-carboxylic acid, long, yellow needles (*sodium* salt, yellow needles), of which the nitro-group is replaced by methoxyl with production of 5-methoxyanthraquinone-2-carboxylic acid, yellow needles, m. p. 279°, on heating with methyl-alcoholic potassium hydroxide; this by reduction passes into 5-aminoanthraquinone-2-carboxylic acid, brownish-red needles, m. p. 338°.

The position occupied by the nitro-group in the above compounds was determined as follows. The nitroanthraquinonecarboxylic acid was converted by thionyl chloride into the corresponding acid *chloride* from which the *amide*, scales, m. p. 330°, was produced by treatment, in suspension in benzene, with ammonia. The amide was then converted into the corresponding *amine* by the action of potassium hypobromite, the product forming reddish-orange scales, m. p. 274°, and giving a *diaminoanthraquinone*, red needles, m. p. 292°, on reduction.

The easy replacement of the nitro-group in the above nitroanthraquinonecarboxylic acid by methoxyl is suggestive of an  $\alpha$ -position, and the diaminoanthraquinone just described has therefore in all probability its substituents in the 1:3-, 1:6-, or 1:7-positions, as the compound of the remaining possible constitution, 1:2-diaminoanthraquinone, is already known.

In order to decide this point, 1:6-dinitroanthraquinone, almost colourless needles, m. p. 257—259°, and 1:7-dinitroanthraquinone, pale yellow needles, m. p. 295°, were prepared by nitration of anthraquinone (D.R.P., 167699), the former of which was found to be reducible to the above diaminoanthraquinone, m. p. 292°. This

result was confirmed by the conversion of the diaminoanthraquinone, obtained by the above process of degradation, into a dihydroxyanthraquinone agreeing with the earlier description of 1:6-dihydroxyanthraquinone (Frobenius and Hepp, A., 1907, i, 428).

In an appendix it is stated that the bromination of 2-methylanthraquinone with a large excess of bromine gives rise to *ω*-tribromomethylanthraquinone, yellow scales, m. p. 281°, which on treatment with milk of lime at 180° yields anthraquinone-2-carboxylic acid, and is converted in nitrobenzene solution by copper powder into 2:2'-diphthaloyltolane (compare Ullmann and Klingenberg, A., 1913, i, 375).

D. F. T.

**Specific Rotation of Camphor Dissolved in Olive Oil.** HENRI MALLOSSE (*Bull. Soc. chim.*, 1914, [iv], 15, 358—360).—The author has examined the specific rotation of solutions of camphor in olive oil at concentrations varying from 1.125 to 24.866 grams per 100 grams of solvent at 18°.

The specific rotation is found to be nearly independent of the concentration when *q* (grams of oil in 100 grams of solution) increases from 75 to 83; from 83 to 90, it increases slowly, more rapidly from 90 to 95 and very rapidly above 95. For values of *q* between 75 and 95, the specific rotation can be very approximately expressed by the following empirical formulæ:  $[\alpha]_D^{18} = 57.9 - 0.53399c + 0.02834c^2 - 0.0005023c^3$ ;  $[\alpha]_D^{18} = 57.9 - 0.4894p + 0.023805p^2 - 0.0003867p^3$ ;  $[\alpha]_D^{18} = -139.69 + 7.3294q - 0.092205q^2 + 0.0003867q^3$ , where *c* and *p* = grams of camphor in 100 c.c. and 100 grams of solution respectively.

H. W.

**The Constituents of Ethereal Oils. Separation and Properties of the Sesquiterpene Gurjunene Occurring in East Indian Oil of Copaiba Balsam. Derivatives of this Sesquiterpene.** F. W. SEMMLER and W. JAKUBOWICZ (*Ber.*, 1914, 47, 1141—1153).—An investigation of the constituents of gurjun balsam oil or so-called East Indian oil of copaiba balsam (compare Deussen and Philipp, A., 1910, i, 575; Deussen, A., 1909, i, 815).

The crude sesquiterpene gurjunene was submitted to partial oxidation by chromic acid in acetic acid solution, when the laevorotatory constituent is more easily destroyed, and by repetition of the processes of oxidation and distillation a fraction was finally obtained of tricyclogurjunene or  $\beta$ -gurjunene,  $C_{15}H_{24}$ , b. p. 120—123°/13 mm.,  $D_4^{20}$  0.9348,  $n_D^{20}$  1.50275,  $n_D^{25}$  1.4974,  $n_D^{30}$  1.4925. Oxidation of this sesquiterpene by chromic acid or potassium permanganate yielded a substance, gurjunene ketone,  $C_{15}H_{22}O$  (compare Deussen, *loc. cit.*), m. p. 43°, b. p. 163—166°/10 mm.,  $D_4^{20}$  1.017,  $n_D^{20}$  1.52700,  $n_D^{25}$  1.5220,  $n_D^{30}$  1.5170, of which when heated with an alcoholic solution of sodium ethoxide for eight hours at 160° regenerates the original  $\beta$ -gurjunene. On reduction by sodium and alcohol the ketone is transformed into gurjunene alcohol,  $C_{15}H_{24}O$ , m. p. 104°, b. p. 155—159°/11 mm.,  $D_4^{20}$  1.001,  $n_D^{20}$  1.51859,  $n_D^{25}$  1.5135,  $n_D^{30}$  1.5085. The presence of only one ethylenic linking in  $\beta$ -gurjunene was confirmed by reduction with hydrogen and platinum, which produced only a dihydro-derivative,

tricyclodihydrogurjunene,  $C_{15}H_{26}$ , b. p.  $120^{\circ}/8$  mm.,  $D_{20} 0.9258$ ,  $n_D 1.49775$ ,  $\alpha_D - 37.5^{\circ}$ .

Of the crude gurjunene, the above  $\beta$ -gurjunene constitutes approximately 33%; the remaining 67% consists of another tricyclic sesquiterpene,  $C_{15}H_{24}$ , b. p.  $114-116^{\circ}/10$  mm.,  $D_{20} 0.918$ ,  $n_D 1.5010$ ,  $\alpha_D$  approx.  $-110^{\circ}$ , termed  $\alpha$ -gurjunene or tricyclenegurjunene, which can be separated in a fairly pure condition from the mixture by fractional distillation. This sesquiterpene fails to give the above-mentioned ketone on oxidation, and, unlike its  $\beta$ -isomeride, it responds to Turner's colour reaction (Deussen and Philipp, A., 1910, i, 687) with sodium nitrite and sulphuric acid.

No indication of any bicyclic constituent in crude gurjunene was obtained. D. F. T.

**The Chemistry of Tobacco. The Ethereal Oils of Tobacco. (Tobacco Aroma).** WALTER HALLE and ERNST PRIBRAM (*Ber.*, 1914, 47, 1394—1398).—A preliminary account of an investigation of an extract of Hungarian tobacco (compare Traetta-Mosca, A., 1913, i, 1432).

The extract from approximately 300 kilos. of tobacco yielded about 140 grams of a yellow oil with a strong odour of tobacco. The oil was acid to litmus and contained no nitrogen; it was shaken with sodium carbonate solution and then the neutral residue was separated by distillation under reduced pressure into several fractions which all became acid on keeping; the higher fractions contained oxygen compounds, whilst the lower ones were oxygen-free. By repeated distillation a liquid, b. p.  $72-89^{\circ}/18$  mm., was obtained from the lower fractions, which did not become acid in the air and did not attack sodium.

The acid produced in the various fractions by atmospheric oxidation appears to be isovaleric acid. From the above neutral fraction a hydrocarbon,  $C_{10}H_{18}$  or  $C_{10}H_{20}$ , b. p.  $73-76^{\circ}/20$  mm., was isolated, which by oxidation with potassium permanganate was made to yield terephthalic acid together with another substance possibly isobutylacetic acid. D. F. T.

**Preparation of Hydrocarbons Suitable for Conversion into Caoutchouc or the Like.** KURT GOTTLÖB (Austrian Patent 63613).—Dipentene or substances that are converted into dipentene by pyrogenetic reactions are converted by pyrogenetic or electro-thermic reactions into caoutchouc or masses resembling it. J. C. C.

**The Vulcanisation of Solutions of Caoutchouc by Ultra-violet Rays.** ANDRÉ HELBRONNER and GUSTAVE BERNSTEIN (*Compt. rend.*, 1914, 158, 1343—1345. Compare A., 1913, i, 638).—On submitting a solution of caoutchouc and sulphur to the action of ultra-violet rays, the caoutchouc is vulcanised, but, instead of being precipitated after a short time, furnishes a very stable gel, which is not precipitated by heating to  $80^{\circ}$ , but separates as a skin on allowing the solution to evaporate. Examined under the ultramicroscope there is very little difference between the unvulcanised and the vulcanised solution. The authors suggest that the process of vulcanisation is as



follows. The soluble sulphur is converted, under the influence of the ultraviolet rays, into an insoluble form, which, as fast as it is formed, combines with or is absorbed, in the nascent state, by the caoutchouc, which is thus vulcanised. The skin formed on evaporating the solution, whilst having all the characters of well-vulcanised rubber, is remarkable for its low sulphur content, which is only 0.6% of combined sulphur. The re-polymerisation of the caoutchouc in the process of vulcanisation is apparently a catalytic reaction produced by the sulphur, and the combination of the sulphur with the caoutchouc is only a secondary reaction. W. G.

**Biochemical Synthesis of  $\beta$ -Anisylglucoside ( $\beta$ -*p*-Methoxybenzylglucoside).** EM. BOURQUELOT and ALEX. LUDWIG (*Compt. rend.*, 1914, 158, 1377—1379, and *J. Pharm. Chim.*, 1914, [vii], 9, 542—547).— $\beta$ -Anisylglucoside can be prepared by the action of emulsin on solutions of anisyl alcohol and dextrose in acetone, containing a certain proportion of water. The proportion of dextrose combined at the end of the reaction increases with the percentage of anisyl alcohol in the solvent. The glucoside was isolated in the crystalline form by the usual process (compare A., 1913, i, 663). So obtained it crystallises in long, colourless needles. It is odourless and possesses a slightly bitter taste. The crystals contain  $1\text{H}_2\text{O}$ , which they lose at  $100^\circ$ , and the anhydrous substance has m. p.  $137\text{—}138^\circ$ ,  $[\alpha]_D - 53.33^\circ$ . It is hydrolysed by boiling dilute sulphuric acid, and in aqueous solution by emulsin. W. G.

**The Galactosides of the Brain. II. The Preparation of Phrenosin and Kerasin by the Pyridine Method.** OTTO ROSENHEIM (*Biochem. J.*, 1914, 8, 110—120).—The galactoside mixture obtained by extracting brain with cold pyridine can be separated into a phrenosin and a kerasin fraction by temperature fractionation from acetone. Phrenosin is obtained by recrystallisation of the phrenosin fraction at  $37^\circ$  from a chloroform-glacial acetic acid mixture, followed by recrystallisation from a chloroform-acetone mixture. Kerasin is obtained from the kerasin fraction by recrystallisation at room temperature from the chloroform-glacial acetic acid mixture, followed by a mixture of pyridine and acetone. A test is described with a selenite plate in which the differences in the polarisation colour of the two materials are seen; by means of this test the progress of purification is controlled. The differences in colour are figured. W. D. H.

**The Galactosides of the Brain. III. Liquid Crystals and the Melting Point of Phrenosin.** OTTO ROSENHEIM (*Biochem. J.*, 1914, 8, 121—127).—The galactosides phrenosin and kerasin exist in the liquid crystalline condition at temperatures from below  $100^\circ$  up to  $180^\circ$  (kerasin) and  $215^\circ$  (phrenosin). This explains the divergent statements with regard to their melting points. Instead of a melting point, they possess a clearing point at which the anisotropic liquid crystalline phase passes into the isotropic liquid-amorphous phase. They give rise to "myelin forms" on warming with water which possess the same optical properties as the "myelin forms" of lecithin, etc. True crystals of phrenosin can be obtained, and the

conditions under which this can be done are described: the data given furnish an explanation of Thierfelder's transformation of phrenosin. The paper contains a note by Lehmann who examined the materials.

W. D. H.

**The Optical Isomerides of Homonataloin and Nataloin; their Reciprocal Transformations.** E. LÉGER (*Compt. rend.*, 1914, 158, 1189—1191).—Homonataloin and nataloin each yield three isomeric penta-acetyl derivatives (compare this vol., i, 309), of which in each case one crystallises in octahedra, a second in prismatic needles, and the third is amorphous. These are named  $\beta$ ,  $\gamma$ ,  $\delta$  respectively. They are obtained mixed on warming the aloins at 105—110° for one hour with acetic anhydride. At higher temperatures the yield of the  $\beta$ -derivative diminishes, none of the  $\gamma$  is produced, the  $\delta$ -form predominating. Further, on warming the  $\beta$ -acetyl compound under a reflux apparatus with sodium acetate and acetic anhydride for two hours, 80% of it is converted into the  $\delta$ -form, whilst the  $\gamma$ -acetyl compound under similar conditions yields a mixture of the  $\beta$ - and  $\delta$ -isomerides. The three penta-acetylhomonataloins have the following properties: the  $\beta$ -isomeride has m. p. 247° (corr.), and is inactive; the  $\gamma$ -isomeride has m. p. 199—200° (corr.) and  $[\alpha]_D - 54.2^\circ$ , and the  $\delta$ -isomeride is amorphous. The corresponding derivatives of nataloin have respectively,  $\beta$ -, m. p. 245°, and is inactive;  $\gamma$ -, m. p. 198° (corr.),  $[\alpha]_D - 53^\circ$ , and  $\delta$ -,  $[\alpha]_D - 56.1^\circ$ .

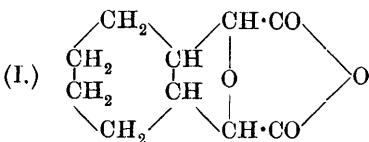
These penta-acetyl derivatives on saponification yield the corresponding nataloins and homonataloins:

	$[\alpha]_D$ .		$[\alpha]_D$ .
Natural nataloin .....	- 145.0°	Natural homonataloin.....	- 149.7°
$\beta$ -Nataloin .....	+ 10.0	$\beta$ -Homonataloin .....	0.0
$\gamma$ -Nataloin .....	- 143.7	$\gamma$ -Homonataloin .....	- 146.2
$\delta$ -Nataloin .....	- 146.0	$\delta$ -Homonataloin .....	- 110.8

If these  $\beta$ -,  $\gamma$ -, and  $\delta$ -aloins are again treated separately with acetic anhydride at 105—110°, they yield not a single penta-acetyl derivative, but each yields a mixture of the three isomerides, as do the natural aloins.

W. G.

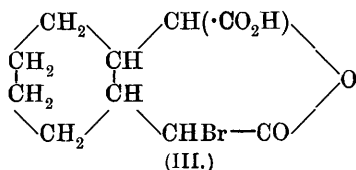
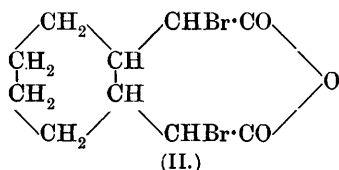
**Cantharidin.** J. GADAMER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), 2, 494—498).—From a discussion of the results of



previous investigators together with those detailed below, the author arrives at the given constitution (I.) for cantharidin. The symmetry of the molecule accounts for the absence of optical activity.

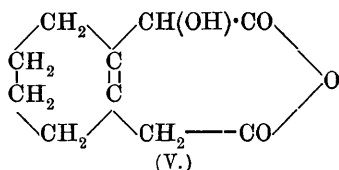
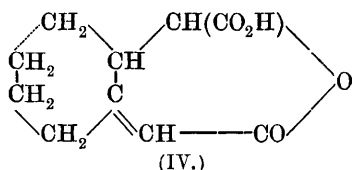
The anhydride nature of cantharidin is indicated by its gradual neutralisation on treatment with alkali; the normal salts of the corresponding acid show great tendency to hydrolysis, so that in solution there is an equilibrium between the normal salt and the anhydride. The normal *brucine* salt is fairly stable, but is not capable of resolution into stereoisomerides.

By heating cantharidin with an acetic acid solution of hydrogen bromide, a dibromo-compound,  $C_{10}H_{12}O_3Br_2$  (formula II.), analogous to the di-iodo-compound of Piccard was obtained, together with a substance,  $C_{10}H_{11}O_3Br$ , and a compound,  $C_{10}H_{13}O_4Br$ , designated *bromohydrocantharic acid*, probably of formula III. This acid can be resolved by



means of its brucine salt into *d*- and *l*-stereoisomerides. The active forms of the acid on reversion into cantharidin yield an inactive product, thus indicating the symmetrical nature of the latter substance.

The feebly active isocantharidin obtained by heating active cantharic acid (formula IV.) with acetyl chloride is represented by formula V.



D. F. T.

**Preparation of Saline Double Compounds from Cantharidyl-ethylenediamine.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269661).—The base,  $C_{12}H_{18}O_3N_2$ , obtained by the condensation of cantharidin with ethylenediamine (Anderlini, A., 1893, i, 483), gives compounds with gold salts which have a strong bactericidal action. The *aurichloride* forms golden-yellow leaflets, m. p. 218—220°, the *auricyanide* forms large, colourless needles, m. p. 226—227°, and the *aurithiocyanate* crystallises in colourless leaflets, m. p. 168—170°.

J. C. C.

**Chlorophyll. XXIV. Pigments of Brown Algæ.** RICHARD WILLSTÄTTER and HAROLD J. PAGE (*Annalen*, 1914, 404, 237—271).—In 1865 Cohn regarded the brown pigment in the phæophyceæ and the diatomaceæ as a substance nearly related to chlorophyll and called it phæophyll. This view was supported by Molisch in 1905. The existence in brown algæ of a pigment nearly allied to and transformable into chlorophyll, however, has been doubted by Cvet (A., 1906, i, 873), and more recently by Czapek and by Kylin.

The authors have established beyond doubt that chlorophyll as such is present in brown algæ; in addition, three yellow non-nitrogenous pigments, fucoxanthin, carotin, and xanthophyll, occur. The molecular proportion of the chlorophyll to the yellow pigments is about 1 : 1, not 3—5 : 1 as in many land plants. If brown algæ contained a pigment similar to the substance produced in the brown phase of chlorophyll as

suggested by Molisch, it ought to yield derivatives of the chlorophyllin or the *isochlorophyllin* series by suitable treatment; this is not the case, the chlorophyll after such treatment being isolated as phytochlorin-*e*. Molisch's suggestion is also contradicted by spectroscopic and microscopic evidence which show respectively that the absorption spectrum of brown algæ is not considerably different from that of ordinary leaves, and that the green colour produced when brown algæ are treated with hot water is not due to the formation of chlorophyll from a brown derivative, but is a specially pronounced example of the paling which all leaves experience by such treatment. In brown algæ, the thallus is thick and contains below the cuticle a considerable quantity of yellow pigment in granules overlying the chloroplasts; by the action of hot water the yellow pigments are diffused among the oily cell-contents and the underlying chlorophyll is thereby rendered more visible.

Cvet's chlorophyll- $\gamma$  (*loc. cit.*) is not a natural pigment; the authors have obtained it from dried phæophyceæ, but never a trace of it by rapidly extracting fresh brown algæ with cold solvents.

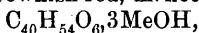
The chlorophyll in the phæophyceæ differs remarkably from that of land plants and of green algæ in consisting almost exclusively of chlorophyll-*a*, the amount of the *b* component being 5% at most.

The phæophyceæ, unlike land plants, cannot be extracted in the dried state. Fresh brown algæ (*Fucus virsoides*) are treated with 40% aqueous acetone which removes a large quantity of slimy matter; after this treatment the algæ can be readily disintegrated, and all the colouring matter can be removed by extracting five times with 85% acetone. The first of these 85% acetone extracts is yellowish-brown, is almost free from chlorophyll, and is worked up for fucoxanthin. The subsequent extracts, which are olive-green and finally pure green, are combined and treated with talc and sufficient water to precipitate the chlorophyll, the fucoxanthin for the most part remaining in the solution. The chlorophyll, which is precipitated almost quantitatively, is converted into potassium chlorophyllin and phæophytin by the methods of Willstätter and Stoll. By treatment with boiling concentrated methyl-alcoholic potassium hydroxide and subsequent acidification, the phæophytin yields phytochlorin-*e* and only a trace of phytorhodin-*g*, and consists, therefore, almost entirely of the *a* component; it contains 31.81% of phytol (theory for phæophytin-*a*, 33.7). The crude potassium chlorophyllin is converted by methyl-alcoholic potassium hydroxide at 125–160° into rhodophyllin (and a little pyrrophyllin) containing 4.24% of magnesium (theory 4.23).

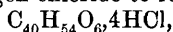
A method is described by which all of the four pigments in brown algæ are extracted by aqueous acetone and subsequently brought into solution in ether. The ethereal solution is mixed with its own volume of petroleum, b. p. 30–50°, and the mixture is treated with an equal volume of 70% methyl alcohol. After further and somewhat complicated treatment, the partition results in the collection of the fucoxanthin in the aqueous methyl alcohol and of the chlorophyll, xanthophyll, and carotin in the ether-petroleum layer. By colorimetric measurements, it is found that the phæophyceæ contain much less chlorophyll than land plants, and much more yellow pigments

than land plants and green algæ. Fucoxanthin is the most abundant of the yellow pigments. Fresh fucus contains approximately 0.05% of chlorophyll-*a*, 0.017% of fucoxanthin, 0.009% of carotin, and 0.009% of xanthophyll.

Fucoxanthin cannot be successfully extracted from algæ-meal which has been kept for a few weeks; it is then obtained accompanied by Cvet's so-called chlorophyll- $\gamma$ , from which it is separated only with very great difficulty and loss of material. It has a more pronounced basic character than other carotinoids, but is not acidic. It crystallises from methyl alcohol in brownish-red, monoclinic prisms,



or in large, hexagonal plates containing  $2\text{H}_2\text{O}$ ; the two forms are interconvertible under suitable conditions. Fucoxanthin crystallises from ether-petroleum in stout needles, without solvent of crystallisation. It has m. p.  $159.5\text{--}160.5^\circ$  (corr.), develops a dark blue coloration with concentrated sulphuric acid, and is converted by alcoholic alkalis into a substance from which fucoxanthin cannot be recovered. Fucoxanthin reacts with ethereal hydrogen chloride to form a *hydrochloride*,



m. p. about  $215^\circ$ , blue flocks with a copper lustre, and with iodine in carbon disulphide to form a *tetra-iodide*,  $\text{C}_{40}\text{H}_{54}\text{O}_6\text{I}_4$ , m. p.  $134\text{--}135^\circ$  (corr.), violet-black prisms with a copper lustre. C. S.

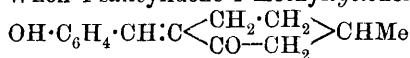
**A Dye from *Lycoperdon Gemmatum* (Batsch).** YASHIRŌ KOTAKE and KŌICHI NAITŌ (*Zeitsch. physiol. Chem.*, 1914, **90**, 254—257).—By extraction of this fungus with hot alcohol, a brown dye can be readily obtained in crystalline form, although not free from ash. On hydrolysis this product yields dextrose and a dye, which the authors name *gemmatein*, which crystallises in dark brown needles and has the composition  $\text{C}_{17}\text{H}_{12}\text{O}_7$ . Gemmatein yields on fusion with potassium hydroxide another coloured substance and *p*-hydroxyphenyl-acetic acid. Oxidation of gemmatein by boiling with hydrogen peroxide (3%) for five hours yields homogentisic anhydride. R. V. S

**Allyl Furylacrylate.** F. F. BLICKE (*Ber.*, 1914, **47**, 1353—1355).—*Allyl furylacrylate*,  $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\cdot\text{C}_3\text{H}_5$ , was prepared by the interaction of the corresponding acid and alcohol in the presence of sulphuric acid; the ester is a colourless oil, b. p.  $130\text{--}132^\circ/15\text{ mm.}$ , which is rapidly affected by light and air; it gives a *dibromide*, m. p.  $46^\circ$ , probably of the structure  $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\cdot\text{C}_3\text{H}_5\text{Br}_2$ . When heated in a sealed exhausted glass tube at  $210^\circ$ , the ester slowly polymerises to a syrupy liquid from which, by pouring its benzene solution into ether, an amorphous substance,  $(\text{C}_{10}\text{H}_{10}\text{O}_3)_x$ , can be separated. This polymeride on heating with a little of the unimolecular ester passes into a second *polymeride*, which is insoluble in benzene. Hydrolysis of the unimolecular ester regenerates the original furylacrylic acid, but the first of the polymerides gives an amorphous acid product which appears to be richer in carbon and hydrogen than furylacrylic acid (compare Liebermann and Kardos, A., 1913, i, 476).

Methyl furylacrylate, which was prepared similarly to the allyl

ester, does not undergo polymerisation in the above manner when heated.  
D. F. T.

Partly-hydrogenated Xanthen and a New Xanthen Synthesis. I. W. BORSCHÉ and A. GEYER (*Ber.*, 1914, 47, 1154—1161).—When 4-salicylidene-1-methylcyclohexan-5-one,



(Borsche and Geyer, A., 1912, i, 891), is treated with hydrogen chloride in acetic acid or ethereal solution, it undergoes conversion into 3-methyl-1:2:3:4-tetrahydroxanthylum chloride,

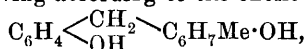


of which the corresponding carbinol,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ \text{O} \end{array} > \text{C}_6\text{H}_7\text{Me} \cdot \text{OH}$ , on distillation with zinc chloride gives a colourless liquid which soon crystallises. The same liquid can also be obtained by distilling the original 4-salicylidene-1-methylcyclohexan-5-one with twice its weight of zinc chloride under a pressure of 12—15 mm. The distillate is a mixture from which colourless leaflets, m. p. 121°, of 3-methylxanthen,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{O} \end{array} > \text{C}_6\text{H}_3\text{Me}$ , can be separated by recrystallisation from methyl alcohol. The mother liquors yielded a colourless solid, m. p. 68—74°, the composition of which indicated a mixture of methyl-dihydro- and methyltetrahydro-xanthen.

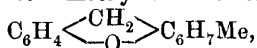
Oxidation of the above methylxanthen by chromic anhydride in glacial acetic acid produced 3-methylxanthone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \text{O} \end{array} > \text{C}_6\text{H}_3\text{Me}$ , long, colourless needles, m. p. 98°, whilst bromination in chloroform solution yielded 6(?)-bromo-3-methylxanthen,  $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CH}_2 \\ \text{O} \end{array} > \text{C}_6\text{H}_3\text{Me}$ , colourless leaflets, m. p. 172°, which was oxidisable to 6(?)-bromo-3-methylxanthone,  $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CO} \\ \text{O} \end{array} > \text{C}_6\text{H}_3\text{Me}$ , colourless needles, m. p. 173°.

The probable course of the above synthesis is a primary formation of a 3-methyldihydroxanthen, which passes by autoxidation and reduction into a mixture of the corresponding tetrahydroxanthen with the non-hydrogenated substance.

Although the methyldihydro- and methyltetrahydro-xanthenes in the mother liquors could not be separated, the latter substance was obtained in a pure condition starting from 4-salicyl-1-methylcyclohexan-5-one. This was now produced by the reduction of the corresponding salicylidene derivative with hydrogen and colloidal palladium. When distilled under reduced pressure with twice its weight of zinc chloride, this substance, behaving according to the enolic structure

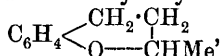


undergoes condensation to 3-methyl-1:2:3:4-tetrahydroxanthen,



colourless leaflets, m. p. 75°.

An attempt to extend this last method of synthesis to simpler substances was not altogether satisfactory. Phenyl *o*-hydroxyphenyl-ethyl ketone, obtained by reduction of phenyl *o*-hydroxystyryl ketone by Paal's method, on distillation in the usual way with zinc chloride gave 2-phenyldihydrocoumaran,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CHPh} \end{smallmatrix}$ , instead of the desired 2-phenyl-1:4-coumaran which had evidently undergone auto-oxidation and reduction, the product or products of the former process being resinous. In a similar manner methyl *o*-hydroxyphenyl ethyl ketone yielded 2-methyldihydrocoumaran,



instead of 2-methylcoumaran.

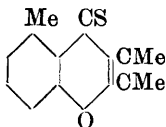
D. F. T.

**Thiochromones.** H. SIMONIS and S. ROSENBERG (*Ber.*, 1914, **47**, 1232—1237. Compare A., 1913, i, 890; this vol., i, 424).—The dimethyl- and trimethyl-chromones described previously have been converted into the corresponding thiochromones by the action of phosphorus pentasulphide.

The thiochromones form greenish-yellow additive compounds with mercuric chloride and react with hydroxylamine and phenylhydrazine, yielding the oxime and phenylhydrazone of the original chromones.

2:3-Dimethylthiochromone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CS} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CMe} \end{smallmatrix}$ , prepared from 2:3-dimethylchromone and phosphorus pentasulphide at 110°, forms long, lustrous, cinnabar-red needles, m. p. 120°, and combines with mercuric chloride in ethereal solution, yielding a green additive compound,  $\text{C}_{11}\text{H}_{10}\text{OS}, \text{HgCl}_2$ . When heated with alcoholic phenylhydrazine in the presence of a little potassium hydroxide, it is converted into 1:2-dimethylchromonephenylhydrazone,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CMe} : \text{CMe} \end{smallmatrix} \text{C:N} \cdot \text{NHPh}$ , which crystallises in pale yellow prisms, m. p. 209°.

2:8-Dimethylthiochromone crystallises in bordeaux-red needles, m. p. 134°, 2:3:6-trimethylthiochromone in long, ruby-red, spear-like forms, m. p. 125°.



2:3:5-Trimethylthiochromone (annexed formula) forms dark red, flat needles, m. p. 116°, and react with phenylhydrazine, yielding 2:3:5-trimethylchromonephenylhydrazone, which crystallises in yellow prisms, m. p. 202°.

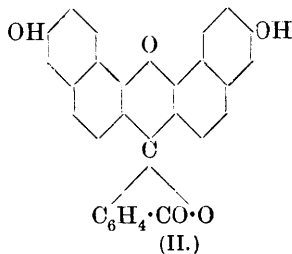
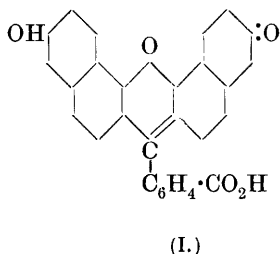
2:3:8-Trimethylthiochromone separates from alcohol in red needles, m. p. 139°.

2:3:8-Trimethylchromonephenylhydrazone crystallises in yellow prisms, m. p. 149°.

F. B.

**Action of Phthalic Anhydride on 1:6-Dihydroxynaphthalene.** Formation of 3:11-Dihydroxynaphthaffluoran. O. FISCHER and E. KÖNIG (*Ber.*, 1914, **47**, 1076—1084).—By the interaction of phthalic anhydride and 1:6-dihydroxynaphthalene, the authors have

prepared a fluoran, the lactone and quinonoid forms of which can readily be isolated, the former, however, being somewhat unstable. From its mode of formation, this substance must be derived either from a  $\alpha\beta$ - or a  $\beta\alpha$ -naphthafluoran and, since it yields bisazo-dyes which do not dissolve in alkali carbonate or hydroxide, the authors are led to prefer the latter alternative and to ascribe the following formulæ to the two forms.



When phthalic anhydride is heated with 1 : 6-dihydroxynaphthalene for thirty to forty minutes at 180—200°, a dark red mass is obtained, which, after purification by steam distillation in the presence of sodium hydroxide and acidification of the solution with acetic acid, yields a bulky red precipitate. When treated with ether, acetone, methylal, pyridine, benzene, etc., the latter yields colourless *crystals*, such as,  $C_{28}H_{16}O_5 \cdot 2Et_2O$ ,  $C_{28}H_{16}O_5 \cdot 2COMe_2$ , which, when deprived of solvent of crystallisation, pass into the red form. The latter is also favoured by water, traces of acid, light petroleum, or ether. When the colourless form is heated it becomes dark red; at about 300° the colour deepens, whilst, at a higher temperature, the substance becomes completely decomposed. 3 : 11-Dihydroxynaphthafluoran dissolves in aqueous alkalis and alkaline carbonates, forming blue solutions with a slight greenish tint, and exhibits a red fluorescence in dilute solution. These solutions probably contain the mono-metallic salts. In alcoholic sodium hydroxide, the fluoran dissolves to green solutions which become blue when largely diluted with water, and contain the dimetallic salts.

3 : 11-Dihydroxynaphthafluoran diacetate, colourless needles, m. p. 180°, is obtained by the action of acetic anhydride on the colourless fluoran. The corresponding *benzoyl* derivative forms colourless needles.

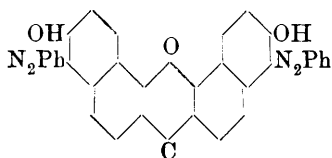
The methylation of 3 : 11-dihydroxynaphthafluoran yields a variety of colourless and coloured compounds which have not been completely investigated. The *dimethyl ether* can be isolated from the products of the action of methyl iodide and potassium hydroxide or of diazomethane on the fluoran in the form of colourless needles which become red on exposure to air. Above 200° the substance darkens in colour and is completely decomposed at about 293°. It exhibits halochromism. When treated with hydrochloric acid, it becomes red. Concentrated sulphuric acid yields eosin-coloured solutions with red fluorescence. The pale pink, fluorescent solution in glacial acetic acid becomes deep red on addition of hydrochloric acid.



Reduction of 3:11-dihydroxynaphthafluoran by the successive action of zinc dust and sodium hyposulphite on the alkaline solution yields a substance,  $C_{28}H_{18}O_5$ , colourless prisms.

3:11-Dihydroxynaphthafluoran readily yields oxonium salts with acids. The *hydrochloride* forms a scarlet, crystalline precipitate which loses some hydrogen chloride when washed with water or preserved in a vacuum. The *perchlorate* forms dark red, almost black plates.

The following bisazo-dyes are obtained by the cautious addition of

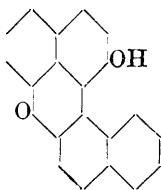


a solution of the requisite diazonium chloride to an alkaline solution of 3:11-dihydroxynaphthafluoran: 4:10-bisbenzeneazo-3:11-dihydroxynaphthafluoran (annexed formula), scarlet needles; 4:10-bis-p-tolueneazo-3:11-dihydroxynaphthafluoran, dark red

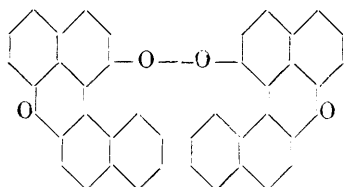
leaflets, which, like the previous compounds have no definite m. p., but darken and slowly decompose when heated above 300—350°; 4:10-bis-p-nitrobenzeneazo-3:11-dihydroxynaphthafluoran, dark red needles; 4:10-bis-p-chlorobenzeneazo-3:11-dihydroxynaphthafluoran, red, crystalline powder. H. W.

### The Oxidation of Phenols. I. A New Organic Radicle.

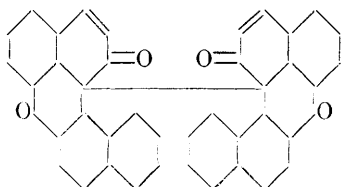
RUDOLF PUMMERER and FRITZ FRANKFURTER (*Ber.*, 1914, 47, 1472—1493).—The oxidation of monohydric phenols by reagents such as silver oxide or potassium ferricyanide has as yet been but little investigated. In a number of cases, it has been shown to lead to the union of two benzene nuclei with the formation of diphenyl- or dinaphthyl derivatives, but it is doubtful whether this reaction is general, since the colourless products, insoluble in alkali, which are frequently obtained by oxidation with ferricyanide are neither hydroxydiphenyls nor dibenzoquinones; particularly in the case of  $\beta$ -naphthol, the authors find that oxidation with potassium ferricyanide in



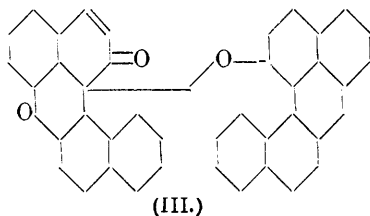
the presence of the smallest possible quantity of sodium hydroxide does not yield  $\beta$ -dinaphthol, but a variety of other substances. The possibility that these substances are produced by the further oxidation of  $\beta$ -dinaphthol has been investigated by a study of the direct action of oxidising agents on the latter; *hydroxydinaphthylene oxide* (annexed formula) is first formed, which readily loses an atom of hydrogen and passes into a yellowish-brown substance of quinonoid character for which one of the three following formulæ is proposed.



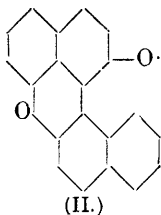
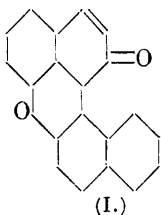
(I.)



(II.)



In neutral solvents, the latter dissociates frequently to a considerable extent with the formation of a radicle which is notably stable towards air, but otherwise exceedingly reactive. The latter possesses a tervalent carbon atom (formula I), but can apparently react in the tautomeric form (formula II) with a univalent oxygen atom.



A solution of dinaphthol in benzene is heated on the water-bath for fifteen minutes with ignited sodium sulphate and silver oxide. After filtration the solvent is removed, whereby a brown residue of a *quinhydrone* (see later) is obtained in 75% yield. This is converted into hydroxydinaphthalene oxide by reduction with zinc dust in warm glacial acetic acid solution all operations being effected in an atmosphere of carbon dioxide. The product so obtained generally contained small quantities of dinaphthalene dioxide. The pure substance, lemon-yellow, four-sided prisms, has m. p. 152°. Its solutions have a greenish-blue fluorescence. Sodium hydroxide dissolves it with difficulty, yielding a *sodium salt*,  $C_{20}H_{11}O_2Na$ , long, yellowish-brown needles. Benzoyl chloride converts it into a *monobenzoyl derivative*,  $C_{27}H_{16}O_3$ , prisms, m. p. 172°. The action of methyl iodide and sodium methoxide on a solution of the hydroxy-oxide in methyl alcohol gives a small quantity of the corresponding *mono-methyl ether*,  $C_{21}H_{14}O_2$ , lemon-yellow plates, m. p. 144°, but leaves the greater part of the substance unattacked; methyl sulphate in alkaline solution is without action. Both the methyl ether and the benzoyl derivative are relatively stable towards permanganate in neutral solution. Phosphorus pentachloride converts the hydroxy-oxide into a yellow *product* which is apparently a mixture of tetra- and pentachlorodinaphthalene dioxides, the m. p. of which could not be ascertained in a sulphuric acid bath.

The previously-mentioned quinhydrone is readily obtained in well-defined, blackish-brown prisms with metallic glance, m. p. 161°, on partial concentration of the benzene solution. It dissolves in hot benzene, yielding intensely red solutions, which become pale brown when cooled. Reducing agents convert it into hydroxydinaphthalene oxide. The solution of the brown quinhydrone in benzene is readily decolorised by ethereal hydrogen chloride or quinol solution; titrations have therefore been effected with *N/10*-solutions of these reagents, which, on the assumption that one molecule of the reagent is required for each molecule of dehydroxynaphthalene oxide, show the presence of

about 40% of the latter, and lead to the formula  $C_{40}H_{22}O_4 + 3C_{20}H_{12}O_2$  for the quinhydrone. Addition of pyridine to a solution which has been decolorised by ethereal hydrogen chloride causes a recurrence of the colour, but subsequent titration proves a regeneration of only 30—40% of the dehydro-compound. Evaporation of a solution decolorised by ethereal hydrogen chloride leaves a brownish residue, which does not contain chlorine, and consists of a mixture of hydroxy-oxide, quinhydrone, and dioxide. Determinations of the molecular weight of the quinhydrone in nitrobenzene solution by the freezing-point method give results in agreement with those required for a dissociation into four molecules; in naphthalene solution, a gradual decomposition of the dehydro-substance into hydroxy-oxide and dioxide is observed.

The preparation of dehydro-hydroxydinaphthalene oxide is rendered difficult by reason of its extreme sensitiveness to acid and light. It is best obtained by oxidising a dilute alkaline solution of the yellow hydroxydinaphthalene oxide with an equimolecular quantity of potassium ferricyanide at  $0^\circ$ , followed by immediate extraction with a large amount of ether. The dried solution is concentrated with exclusion of light, when the substance is obtained in yellowish-brown prisms, *m. p.*  $149^\circ$ . The percentage of dehydro-product in the crude materials can be estimated by titration with quinol solution, the purest substance obtained showing in this way a content of 97.4% dehydro-product. Oxidation of hydroxydinaphthalene oxide can also be effected by means of dehydroindigotin, and, since the indigotin formed separates quantitatively from solution in benzene or nitrobenzene, this method of formation has been used in determinations of molecular weight. Such determinations, as well as those effected directly in benzene or nitrobenzene solution, point to a dissociation of dehydro-hydroxydinaphthalene oxide.

The remarkable behaviour of dehydro-hydroxydinaphthalene oxide in different solvents points to a dissociation of the molecule into two radicles similar to that observed with the hexa-arylethanes or tetra-arylhydrazines. The yellowish-brown crystals are soluble in different media with different colours; light petroleum yields brownish-yellow solutions, and the coloration deepens in ether, benzene, nitrobenzene and chloroform, the last being of a pure reddish-violet colour. Complete dissociation occurs when the cold reddish-brown solution in benzene is sufficiently diluted, and the colour changes to violet (compare Piccard, A, 1911, ii, 561). Such completely dissociated solutions show no deepening in colour when warmed, whereas this phenomenon is well-marked in more concentrated solution. The solution in nitrobenzene has no measurable conductivity, so that ionic dissociation cannot have occurred. All the solutions of the radicle have an intensely blue fluorescence and a characteristic band spectrum (a strong band at  $\lambda$  515—555  $\mu\mu$ , a weaker one at  $\lambda$  590—600  $\mu\mu$ ). In general, dissociation appears to take place with extreme rapidity. In one isolated instance, however, an almost colourless product has been obtained, which possibly represents the pure ethane form of dehydro-hydroxydinaphthalene oxide; this dissolved very readily in

benzene to a colourless solution which in about half a minute became brownish-red.

A solution of dehydro-hydroxydinaphthalene oxide is only slowly affected by air. When shaken for two hours with oxygen, however, it yields a pale, ochre-yellow, micro-crystalline *precipitate*, which melts with evolution of oxygen when brought into a bath heated at 116°. The product appears to be a peroxide, mixed, however, with a product richer in oxygen. The unusually slow absorption of oxygen by a substance possessing a bivalent carbon atom is probably explained by the close neighbourhood of the electronegative keto-group. Dissociation of the peroxide into oxygen and two molecules of the ketomethyl does not appear to take place; instead, the oxygen appears to attack the portion of the molecule containing the keto-group and to cause rupture of the ring; thus, on shaking the benzene solution with oxygen at 40°, a colourless, crystalline substance of high m. p. is obtained, which does not regenerate the initial material and which yields an acid after treatment with warm sodium hydroxide.

Iodine does not react rapidly with a solution of the radicle in benzene. Similarly, bromine and chlorine (as also permanganate) react only after some seconds, yielding very unstable halogen compounds, which rapidly decompose in solution with formation of dinaphthalene dioxide. They may, however, be precipitated as violet double salts by the addition of mercuric chloride or stannic chloride. They react very readily with water, amines, and phenols. With hydroxydinaphthalene oxide they immediately regenerate dehydro-hydroxydinaphthalene oxide if the acid is suitably absorbed. The benzene solution of the bromo-compound partly regenerates the radicle on treatment with zinc dust, copper powder, or aqueous solutions of thiosulphate, potassium iodide or sodium carbonate.

In the course of a few hours, hydrogen chloride converts dehydro-hydroxydinaphthalene oxide into the corresponding chloromethane and methane, the reaction being reversible under the influence of light. Hydroxy-acids also cause fission; in presence of moisture, a yellow solution is formed from which pyridine does not regenerate the radicle. In anhydrous sulphuric, perchloric, formic, and trichloroacetic (but not acetic) acids, violet solutions are obtained. The spontaneous decomposition of the radicle does not take place very rapidly in the cold, but is catalysed by small quantities of acids, notably picric acid, and by light, hydroxydinaphthalene oxide and dinaphthalene dioxide being formed in equal quantities.

Quinol appears to react with dehydro-hydroxydinaphthalene oxide in one of two directions. Either decolorisation occurs without quinone formation due in all probability to a coupling action of the radicle or, in addition, benzoquinone is produced. The latter takes place when a solution of quinol is poured over the solid dehydro-compound. On the other hand, when a solution of the latter is used, benzoquinone is not generally formed except in the cases of chloroform and glacial acetic acid solutions. This is most simply explained by the supposition that the solid yellow dehydro-hydroxydinaphthalene oxide contains a reactive oxygen linking which, at the moment of solution, can yield by

dissociation the aryloxy radical with univalent oxygen; this shows powerful oxidising action, but, in general, is immediately isomerised into the ketomethyl form.

The usual reducing agents convert the radical into hydroxydinaphthalene oxide. Reactive hydrocarbons, such as triphenylmethyl, cyclopentadiene or pinene, immediately give additive compounds. Nitric oxide is without perceptible action on a solution of the radical in chloroform; in benzene or ether, on the other hand, a yellow, unstable solution is immediately formed from which only traces of the radical are recovered by evaporation. A transitory green coloration due to a tertiary nitroso-compound, as in the case of triphenylmethyl (Schlenk and Mair, A., 1911, i, 434), has not been observed.

Dinaphthalene dioxide (Bünzly and Decker, A., 1905, i, 884) is the ultimate product of the oxidation of  $\beta$ -dinaphthol, hydroxydinaphthalene oxide or of the dehydro-substance by silver oxide in neutral solution. It has m. p.  $242^\circ$ , whereas Bünzly and Decker give  $245^\circ$ . When dissolved in glacial acetic acid and treated with perchloric acid or a persulphate, it yields a bluish-violet solution which shows three absorption bands ( $520$ — $525\ \mu\mu$ ,  $560$ — $585\ \mu\mu$ , and  $650$ — $660\ \mu\mu$ ), and thus contains a doubly quinonoid oxonium salt which is immediately decolorised by reducing agents. H. W.

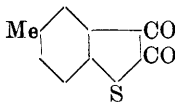
**Methylthionaphthenquinone.** R. STOLLÉ (*Ber.*, 1914, 47, 1130—1132).—The method recently described by the author (this vol., i, 200) for the preparation of 1-substituted isatins by the action of oxalyl chloride on mono-substituted anilines can also be adapted to the production of thionaphthenquinones.

If a sesquimolecular proportion of oxalyl chloride in ethereal solution is gradually introduced into an ethereal solution of *p*-tolyl mercaptan and the mixture is then warmed for a time, *p*-tolylthiolglyoxylyl chloride  $C_6H_4Me \cdot S \cdot CO \cdot COCl$ , is formed and by evaporation can be obtained as a viscous liquid which solidifies in a freezing mixture.

When warmed in carbon disulphide solution with aluminium chloride, the tolylthiolglyoxylyl chloride undergoes intramolecular condensation with formation of 1:2-diketo-4-methylthionaphthen (annexed formula), red leaflets, m. p.  $144^\circ$ , which dissolves in alkalis, but is reprecipitated by acids.

If in the action of oxalyl chloride on tolylmercaptan, equimolecular quantities are used, the product is ethyl *p*-tolylthiolglyoxylate, yellow, rectangular tablets, m. p.  $178^\circ$ , of which the corresponding *p*-tolylthiolglyoxylic acid,  $C_6H_4Me \cdot S \cdot CO \cdot CO_2H$ , colourless leaflets or needles, m. p.  $100^\circ$  (decomp.), can be obtained by treatment of the above tolylthiolglyoxylyl chloride with water; the *anilide*, needles, m. p.  $137^\circ$ , was produced by reaction of the acid chloride and aniline.

The action of oxalyl chloride or phenol in ethereal solution gave rise to a chloride, probably *phenoxyglyoxylyl chloride*, m. p.  $56$ — $57^\circ$ , which produced an *anilide*, m. p.  $136^\circ$ , but its condensation under the influence of aluminium chloride appeared to give a mixture of substances in



which the oxalyl radicle had undergone attachment at the ortho- and para-positions respectively.  
D. F. T.

**Aporeine and its Salts.** VITTORIO PAVESI (*Gazzetta*, 1914, **44**, i, 398—405. Compare A., 1907, i, 870).—From a supersaturated solution in light petroleum aporeine is deposited in faintly yellowish-green, monoclinic prisms [ $\text{BRUGNATELLI} : a : b : c = 2.219 : 1 : 3.03$ ;  $\beta = 46^\circ 45'$ ] melting at  $88-89^\circ$  to a fluorescent, yellowish-green liquid, which in the air turns brown at  $225^\circ$  and blackens at  $280-290^\circ$ , whilst in an inert gas such as hydrogen or carbon dioxide it preserves its characteristic fluorescence and appears capable of distillation. In solution in most solvents it exhibits marked blue fluorescence which resembles that shown by quinine salts, and is especially pronounced in magnesium light.

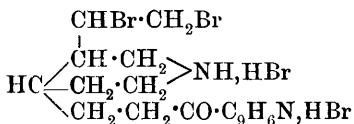
The following salts of aporeine have been prepared: hydrochloride, white, nacreous scales; hydrobromide, yellow, nacreous scales, turning greenish-black at  $190-210^\circ$ , and melting and decomposing at a higher temperature; hydriodide, pale, greenish-yellow, nacreous scales, which begin to change at  $200-210^\circ$ , and melt at  $250-255^\circ$ ; sulphate, slender, white filaments, giving a yellow mass on drying, and being rapidly converted into a reddish-brown powder when exposed to the air and light; nitrate, m. p.  $240^\circ$  (decomp.); hydrogen oxalate, m. p.  $89-90^\circ$ ; hydrogen malate, m. p.  $198^\circ$  (decomp.); hydrogen tartrate, m. p.  $190^\circ$  (decomp.); citrate, m. p.  $81-82^\circ$ ; benzoate and salicylate.

*Papaver dubium* contains another alkaloid, *aporeidine*, which crystallises in rhombic plates, m. p.  $176-178^\circ$ , and is apparently formed by the action of light and air on aporeine or by alteration of the portion of the crude alkaloidal extract insoluble in light petroleum.  
T. H. P.

**Characters of Double Halogen Salts of Quinine and Carbamide.** P. G. GOLUBEV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 189—193).—The double hydrobromide of quinine and carbamide,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{CH}_4\text{ON}_2 \cdot 2\text{HBr} \cdot 3\text{H}_2\text{O}$ , forms needles or drusy masses of prismatic crystals, m. p.  $70-75^\circ$ , loses its water of crystallisation at  $80^\circ$  or over sulphuric acid at the ordinary temperature, and decomposes into quinine hydrobromide, ammonium bromide, carbon dioxide, ammonia, and water at  $130-140^\circ$ . The corresponding double hydrochloride,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{CH}_4\text{ON}_2 \cdot 2\text{HCl} \cdot 3\text{H}_2\text{O}$ , which is employed as a local anæsthetic, loses its water of crystallisation at  $100^\circ$ , and decomposes at  $130-140^\circ$  in a similar manner to the hydrobromide.  
T. H. P.

**Addition of Bromine to Cinchotoxine.** G. ROHDE and ST. MEISSNER (*Ber.*, 1914, **47**, 1507—1515).—The action of bromine on cinchotoxine in the presence of hydrobromic acid has been investigated. A partial account has been published in the dissertations of König (Munich, 1901) and Bartz (Munich, 1909).

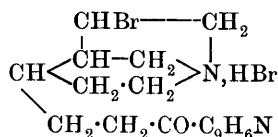
A solution of bromine in hydrobromic acid is added slowly and with vigorous agitation to a solution of cinchotoxine in the same



solvent. A yellowish-brown resinous perbromide is precipitated, which is gradually redissolved with the formation of a mixture of two stereoisomeric *hydrobromides* (annexed formula) which can be separated, partly mechanically and partly by taking advantage of the different solubilities in 5% hydrobromic acid, into a white salt, long white needles, and a yellow salt. Each of these contain  $2\text{H}_2\text{O}$ . The former melts according to the rate of heating at about  $124^\circ$ ; the latter melts indefinitely at about  $120$ — $125^\circ$ . The corresponding anhydrous salts are intensely yellow and have m. p.'s  $151^\circ$  and  $162^\circ$  respectively; on exposure to air, water is re-absorbed. When these salts are crystallised from water, a partial dissociation into hydrobromic acid and the mono-acid *salts* takes place, and this dissociation can be made quantitative by the addition of the calculated quantity of sodium carbonate, or a small excess of pyridine. The basic salt,  $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{,HBr}$ , corresponding with the yellow salt, forms white needles or rods, m. p. about  $178^\circ$  ( $190^\circ$ , or above when rapidly heated). That derived from the white salt forms white ill-defined crystals which become yellow at about  $155^\circ$ , and have m. p. about  $168^\circ$  (up to  $185^\circ$  when rapidly heated). Protracted heating with water converts it into a more soluble salt which remains as a yellow pasty mass on evaporating the solution, and which has not been further investigated. Recrystallisation from aqueous hydrobromic acid converts each salt into the corresponding normal salt. In the basic salts the hydrogen bromide is probably attached to the nitrogen atom of the piperidine ring.

The *base*, corresponding with the yellow normal salt and with the basic salt, m. p.  $178^\circ$ , is obtained when an aqueous solution of either salt is added to a well-agitated mixture of aqueous sodium carbonate and ether. It forms white needles which soften at about  $95^\circ$ , and have m. p. about  $105^\circ$ . Attempts to recrystallise it show it to be unstable when dissolved; in hot benzene or in cold chloroform solution it is gradually decomposed with formation of the basic salt, m. p.  $178^\circ$ , and of an *oil* which has not been further investigated. On treatment with an excess of hydrobromic acid, the base yields the dihydrobromide which is readily convertible into the basic salt, m. p.  $178^\circ$ .

The second pair of salts, on the other hand, yields a ditertiary *base* formed by elimination of hydrogen bromide from within the molecule, a salt of the annexed formula being probably first formed. It is best obtained by the addition of an aqueous solution of the white normal salt to an excess of sodium carbonate solution, and forms white, rhombohedric crystals, m. p.  $124$ — $125^\circ$ . The ditertiary nature of the base follows from the fact that it does not yield a nitroso-, benzoyl-, or methyl compound, and does not yield a purple coloration with nitrobenzene containing dinitrothiophen (a reaction which according to Miller and Rohde is characteristic of piperidine bases which



contain a free imino-group); on the other hand, with methyl iodide (1 mol.) it yields a *methiodide*, white platelets, m. p. 216°.

The isolation of an analogous base, m. p. 90°, from the basic salt, m. p. 178°, has been described by Bartz, who obtained it by the gradual addition of a hot aqueous solution of the latter to a well stirred boiling solution of an excess of sodium carbonate; on repetition of this experiment, the authors have not succeeded in obtaining a crystalline compound, an oil being produced which could not be caused to solidify, and has not been thoroughly investigated. H. W.

**An Alkaloid Obtained from Galega officinalis.** GEORGES TANRET (*Compt. rend.*, 1914, 158, 1182—1184).—An alkaloid, *galegine* is readily isolated from the seeds of *Galega officinalis* in the form of its sulphate by the following process. The seeds are extracted with 60% alcohol, and the extract defecated by basic lead acetate. In the filtrate the lead is precipitated by sulphuric acid and the acetic acid removed by ether. The sucrose and stachyose are precipitated by barium hydroxide (compare A., 1913, i, 235), and the filtrate, slightly acidified with sulphuric acid, is again filtered and evaporated to a clear syrup, from which the *galegine sulphate*,  $(C_6H_{13}N_3)_2 \cdot H_2SO_4$ , crystallises in needles, m. p. 227°. The sulphate on decomposition with sodium hydroxide yields the free *base* as an oil which slowly crystallises. It has m. p. 60—65°, is optically inactive, and absorbs moisture and carbon dioxide from the air. Analysis gives it the formula  $C_6H_{13}N_3$ , and its salts show it to be monobasic. The following salts were prepared: the *hydrochloride*,  $C_6H_{13}N_3 \cdot HCl$ , m. p. 60°, very hygroscopic; the *nitrate*,  $C_6H_{13}N_3 \cdot HNO_3$ , crystallising in long needles, m. p. 108°; the *hydrogen carbonate*,  $(CO_2, 2C_6H_{13}N_3)CO_2$ , m. p. 138°, decomposing slowly on heating and losing one half of its carbon dioxide; the *oxalate*,  $(C_6H_{13}N_3)_2 \cdot H_2C_2O_4$ , m. p. 192—195°; the *picrate*, yellow needles, m. p. 180°; the *silicotungstate*,  $4C_6H_{13}N_3 \cdot 12WO_3 \cdot SiO_2 \cdot 2H_2O$ , greenish-yellow crystals; and the *platinichloride*,  $(C_6H_{13}N_3)_2 \cdot H_2PtCl_6$ , m. p. 123°. W. G.

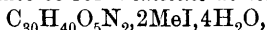
**Emetine.** I. A. WINDAUS and L. HERMANN (Ber., 1914, 47, 1470—1472).—An aqueous solution of emetine hydrochloride is gradually added to a hot 4% solution of potassium permanganate. The solution is filtered and concentrated, and organic matter is removed by successive extractions with ether and ethyl acetate. The ethereal extract yields *m*-hemipinic acid, m. p. 179—185°, according to the rate of heating, which is further identified by conversion into the corresponding anhydride, long needles, m. p. 175°, and ethylimide, white needles, m. p. 227°. Cephæline does not yield *m*-hemipinic acid.

The portion soluble in ethyl acetate yields *m*-hemipinimide, m. p. 318—320°, identical with the hemipinisoimide of Goldschmiedt (A., 1888, 302, 1118).

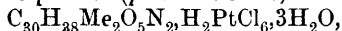
The presence of a di-substituted dimethoxy-benzene ring in emetine is thus established, and, since the oxidation of *isoquinoline* derivatives yields the corresponding phthalic acids and their imides, it is probable that emetine contains a dimethoxyisoquinoline ring. H. W.



**Alkaloids in Ipecacuanha Root.** O. HESSE (*Annalen*, 1914, **405**, 1—57).—The author has isolated five alkaloids from ipecacuanha roots, namely, emetine, cephaeline, psychotrine, and two new alkaloids, ipecamine and hydroipecamine. Analyses of carefully purified emetine give results which agree best with the formula  $C_{31}H_{42}O_5N_2$ , but the examination of the following derivatives points to the formula  $C_{30}H_{40}O_5N_2$  for emetine (compare Paul and Cownley, A., 1894, i, 155; Kunz-Krause, A., 1887, 980; 1895, i, 118). The alkaloid must be purified through its hydrobromide, not the hydrochloride. It forms an *oxalate*,  $C_{30}H_{40}O_5N_2 \cdot H_2C_2O_4$ , and *nitrate*,  $C_{30}H_{40}O_5N_2 \cdot 2HNO_3 \cdot 4H_2O$ , yields *noremetine hydriodide*, probably  $C_{26}H_{32}O_5N_2 \cdot 2HI$ , by boiling with hydriodic acid, D 1.7, and reacts with methyl iodide and boiling aqueous sodium carbonate to form *emetine dimethiodide*,



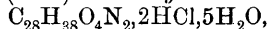
the anhydrous form of which melts at 222—225°, resolidifies, and finally has m. p. 245° (decomp.). From the dimethiodide the corresponding *platinichloride*,  $C_{30}H_{40}O_5N_2 \cdot Me_2PtCl_6 \cdot 3H_2O$ , has been prepared; these two substances have been erroneously described by Keller as methylemetine dimethiodide and platinichloride respectively (A., 1911, i, 1014; this vol., i, 428). The *hydroxide*,  $C_{30}H_{40}O_5N_2 \cdot Me_2(OH)_2$ , is an almost white powder and readily changes in aqueous or alcoholic solution to *dimethylemetine*,  $C_{30}H_{38}Me_2O_5N_2$ , m. p. 52°, a white, apparently crystalline powder (*platinichloride*,



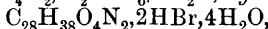
yellow powder).

*Acetylemetine*,  $C_{32}H_{42}O_6N_2$ , m. p. 99—100°, is obtained by heating emetine with acetic anhydride at 50° and finally at 90—100°, and also by heating the hydrobromide with sodium acetate and acetic anhydride at 90—100°. The author is unable to confirm Keller's experiment with emetine and benzoic anhydride (*loc. cit.*). On the contrary, with these substances at 100°, or by treating emetine with benzoyl chloride and aqueous sodium hydroxide, or by heating emetine with benzoyl chloride in benzene, he obtains *benzoylemetine*,  $C_{37}H_{44}O_6N_2$ , m. p. 118°, which resembles emetine itself in containing four methoxy-groups. The benzoyl derivative does not yield emetine and benzoic acid by boiling with alcoholic potassium hydroxide and forms a *platinichloride*,  $2C_{37}H_{44}O_6N_2 \cdot H_2PtCl_6 \cdot 6H_2O$ .

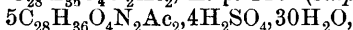
The author's analyses of cephaeline agree with the formula  $C_{25}H_{29}ON_2(OMe)_3$ . The anhydrous alkaloid has m. p. 107—108°, and  $[\alpha]_D^{15} - 21.2^\circ$  in alcohol ( $c = 2$ ). The *hydrochloride*,



*platinichloride*,  $C_{28}H_{38}O_4N_2 \cdot H_2PtCl_6 \cdot 3H_2O$ , *hydrobromide*,



*thiocyanate*,  $C_{28}H_{38}O_4N_2 \cdot 2HCNS \cdot 2H_2O$ , *nitrate*, and *acetate* are described. Cephaeline forms a *dimethiodide*, m. p. 225—228° and again at about 250° after resolidifying (*platinichloride*,  $C_{28}H_{38}O_4N_2 \cdot Me_2PtCl_6 \cdot 4H_2O$ ), from which the *hydroxide* has been obtained. The alkaloid forms a *diacetyl* derivative,  $C_{28}H_{38}O_4N_2 \cdot Ac_2$ , m. p. 116° (*sulphate*,



colourless needles), which yields *acetylcephaeline*,  $C_{28}H_{37}O_4N_2 \cdot Ac$ , m. p. 125° (*platinichloride*,  $2C_{28}H_{37}O_4N_2 \cdot Ac \cdot H_2PtCl_6 \cdot 6H_2O$ ), by warming

with alcoholic potassium hydroxide (4 mols.). *Dibenzoylcephaeline*,  $C_{28}H_{36}O_4N_2Bz_2$ , m. p.  $128^\circ$  (sulphate,  $5C_{28}H_{36}O_4N_2Bz_2 \cdot 4H_2SO_4 \cdot 25H_2O$ , colourless, crystalline powder; *hydrochloride*,  $C_{28}H_{36}O_4N_2Bz_2 \cdot HCl$ ; *platinichloride*,  $2C_{28}H_{36}O_4N_2Bz_2 \cdot H_2PtCl_6 \cdot 5H_2O$ ), yields *benzoylcephaeline*,  $C_{28}H_{37}O_4N_2Bz$ , m. p.  $135^\circ$  (*platinichloride*,  $2C_{28}H_{37}O_4N_2Bz \cdot H_2PtCl_6 \cdot 5H_2O$ ),

in a similar manner.

*Psychotrine*,  $C_{25}H_{27}ON_2(OMe)_3 \cdot 4H_2O$ , crystallises in prisms or double pyramids which appear colourless or faintly yellow in one direction and red or steel-blue in other directions; this property, which is particularly noticeable when the crystals are in their mother liquor, is lost when the substance is warmed in the air. The anhydrous alkaloid has m. p.  $122^\circ$  (Paul and Cownley give  $138^\circ$ ). *Dibenzoylpsychotrine*,  $C_{28}H_{34}O_4N_2Bz_2$ , m. p.  $132-135^\circ$ , greyish-white, amorphous powder (*platinichloride*,  $2C_{28}H_{34}O_4N_2Bz_2 \cdot H_2PtCl_6 \cdot 4H_2O$ ), yields *benzoylpsychotrine* by treatment with aqueous sodium hydroxide.

*Ipecamine*,  $C_{25}H_{27}ON_2(OMe)_3$ , m. p.  $89-90^\circ$ ,  $[\alpha]_D^{15} - 22.5^\circ$  in alcohol ( $c=2$ ), has been isolated from the first mother liquor of the emetine hydrobromide. It is a white, crystalline powder, which has an intensely bitter taste, is insoluble in dilute sodium hydroxide, and forms a *platinichloride*,  $C_{28}H_{36}O_4N_2 \cdot H_2PtCl_6 \cdot 4H_2O$ . The alkaloid reacts with methyl iodide in benzene to form the *dimethiodide*,

$C_{28}H_{36}O_4N_2 \cdot 2MeI \cdot 4H_2O$   
(*platinichloride*,  $C_{28}H_{36}O_4N_2 \cdot Me_2PtCl_6 \cdot 3H_2O$ ), and yields a *benzoyl derivative*,  $C_{28}H_{35}O_4N_2Bz$ , m. p.  $104^\circ$  (*platinichloride*,  $2C_{28}H_{35}O_4N_2Bz \cdot H_2PtCl_6 \cdot 4H_2O$ ).

*Hydroipecamine*,  $C_{25}H_{29}O_4N_2(OMe)_3$ , m. p.  $91-92^\circ$ ,  $[\alpha]_D^{15} - 42.2^\circ$  in alcohol ( $c=2$ ), is precipitated in the form of its hydrobromide, together with emetine hydrobromide, and is separated therefrom by the greater solubility of its hydrobromide in water. The alkaloid is a white powder, which becomes highly electrified by friction. In solution it is readily decomposed by light. The *hydrochloride*, *platinichloride*,  $C_{28}H_{38}O_4N_2 \cdot H_2PtCl_6 \cdot 4H_2O$ , and *benzoyl derivative*,  $C_{28}H_{37}O_4N_2Bz$ , m. p.  $112^\circ$  (*platinichloride*,  $2C_{28}H_{37}O_4N_2Bz \cdot H_2PtCl_6 \cdot 3H_2O$ ), are described.

The colour reactions of the four preceding alkaloids with calcium hypochlorite and with concentrated sulphuric acid (alone and with ammonium molybdate) are described (compare Allen and Scott-Smith, A., 1903, ii, 117).

The amounts of the individual alkaloids in ipecacuanha root (Minas, Matto Grosso, Johore, and Carthagena) have been determined: emetine, from 0.61 to 1.62%; cephaeline, from 0.46 to 0.81%; ipecamine and hydroipecamine, from 0.22 to 0.53% (by difference), and psychotrine, 0.04 to 0.06%, calculated on the air-dried drug.

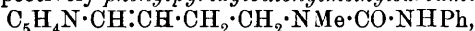
C. S.

**Metanicotine.** EMIL MAASS and KARL ZABLINSKI (*Ber.*, 1914, 47, 1164-1173).—An examination of certain reactions of metanicotine,  $NHMe \cdot CH_2 \cdot CH_2 \cdot CH \cdot CH \cdot C_5H_4N$ , mainly involving the secondary nitrogen atom present in the side-chain.

The metanicotine was prepared by the method of Pinner (A., 1894,

i, 388), and benzoylmetanicotine, colourless needles, m. p. 82°, was isolated as an intermediate product.

Metanicotine condenses with phenylcarbimide and phenylthiocarbimide producing respectively *phenylpyridylbutenylmethylcarbamide*,



colourless crystals, m. p. 108°, and *phenylpyridylbutenylmethylthiocarbamide*, colourless crystals, m. p. 137°.

Nitrous acid converts metanicotine in hydrochloric acid solution into *nitrosometanicotine*,  $\text{C}_5\text{H}_4\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{NO}$ , colourless, silky crystals, m. p. 116°, which readily decomposes; *platinichloride*, m. p. 201°.

Cautious treatment of metanicotine with hydriodic acid, and red phosphorus in a sealed tube, first at 180°, and subsequently at 250—260°, effected a reduction in which approximately equal quantities of *dihydrometanicotine* and 3-*butylpyridine* were produced. These can be separated by fractional distillation or by crystallisation of the hydrochloride of the latter.

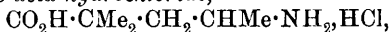
Dihydrometanicotine,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_5\text{H}_4\text{N}$ , is a stable oil, b. p. 260—262°,  $D_4^{25}$  0.9590, which exhibits but slight tendency to polymerisation; it has an ammoniacal odour; *dihydrochloride*, a very hygroscopic oil; *platinichloride*, a crystalline powder, m. p. 197°; *aurichloride*, a crystalline solid, m. p. 138°. Reduction of dihydrometanicotine by sodium and alcohol yielded octahydrometanicotine (compare Maass and Hildebrandt, A., 1906, i, 980).

3-*Butylpyridine*,  $\text{CH}\begin{smallmatrix} \text{CH} \\ \text{N}=\text{CH} \end{smallmatrix}\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\text{Et}$ , is a stable oil, b. p. 205—208°,  $D_4^{20}$  0.9797, which resembles collidine in odour; its properties generally recall those of 2-butylpyridine (Löffler and Plöcker, A., 1907, i, 437). It forms a *hydrochloride*, hygroscopic, feathery crystals, m. p. 126°; a *platinichloride*, crystals, m. p. 187—188° (decomp.); *aurichloride*, crystals, m. p. 95°; *picrate*, crystals, m. p. 89—90°.

By reducing with sodium and alcohol, 3-butylpyridine was converted into 3-*butylpiperidine*,  $\text{CH}_2\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{NH}-\text{CH}_2 \end{smallmatrix}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Et}$ , an oil, b. p. 196—197°, resembling piperidine in odour; *hydrochloride*, colourless crystals, m. p. 102°; *picrate*, crystals, m. p. 124°. D. F. T.

Action of Sodamide on the Dialkylallylacetophenones. General Method of Synthesis of Trialkylpyrrolidones. A. HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1914, 158, 1086—1092).—Under the ordinary conditions dimethylallylacetophenone undergoes no decomposition with sodamide in benzene solution (compare A., 1909, i, 108). If the solvent is reduced in amount to be equal in volume to the ketone, and one-fourth of the theoretical amount of sodamide is used, decomposition occurs and a product is obtained having m. p. 92° and b. p. 123—124°/16 mm. This substance is not the expected  $\alpha$ -methyl- $\alpha$ -allylpropionamide, since it does not decolorise bromine water, does not give off ammonia on boiling with alcoholic potassium hydroxide, and is not reduced by sodium in alcohol. By its properties and its synthesis from mesityl oxide the compound is shown to be 2:4:4-trimethyl-5-pyrrolidone. On heating with concentrated hydro-

chloric acid for twelve hours at  $120^{\circ}$  in a sealed tube, it yields  $\gamma$ -amino- $\alpha$ -dimethylvaleric acid hydrochloride,



which gives a *platinichloride*, small, orange needles. In aqueous solutions with alkalis the hydrochloride gives the original pyrrolidone, and in alcoholic solution on saturating with hydrogen chloride it yields *ethyl  $\gamma$ -amino- $\alpha$ -dimethylvalerate hydrochloride*, a yellow oil, giving a *platinichloride*, and regenerating the pyrrolidone on treatment with moist silver oxide.

2:4:4-Trimethyl-5-pyrrolidone, on methylating with sodamide and methyl iodide, gives 1:2:4:4-tetramethyl-5-pyrrolidone, a mobile liquid, b. p.  $92-96^{\circ}/15$  mm. On oxidation with 4% aqueous potassium permanganate the original pyrrolidone is converted into 2-hydroxy-2:4:4-trimethyl-5-pyrrolidone, m. p.  $165^{\circ}$ , which on heating with hydrochloric acid in sealed tubes at  $110^{\circ}$  for six hours gives mesitonic acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , m. p.  $74^{\circ}$ .

On oxidation with nitric acid (D 1.25), trimethylpyrrolidone gives dimethylmalonic acid.

2:4:4-Trimethylpyrrolidone can be synthesised by the following series of reactions. Mesityl oxide on treatment with potassium cyanide (compare Lapworth, T., 1904, 85, 1214) gives a nitrile which on hydrolysis gives a mixture of mesitonic and mesitylic acids, separable by fractionation of their ethyl esters. Mesitonic acid gives a phenyl-hydrazone, which, on reduction in alcoholic solution with sodium amalgam in the presence of acetic acid at  $5^{\circ}$  and filtering off the sodium acetate, gives an oil, on distillation under reduced pressure; this can be crystallised from a mixture of ether and light petroleum, yielding the 2:4:4-trimethylpyrrolidone.

W. G.

**New Reactions in the Pyrrole Series.** KURT HESS and FRIEDRICH WISSING (*Ber.*, 1914, 47, 1416—1428).—The action of the Grignard reagent on pyrrole has often been supposed to lead to salts in which the magnesium is attached to nitrogen, although subsequent decomposition furnishes 2- or 2:5-substituted derivatives. Since the same reactions occur with 1-methylpyrrole, the conclusion is drawn that this assumption is unjustified and that it is unnecessary to assume a rearrangement of a substituent from nitrogen to carbon. The magnesium salt gives no *N*-substituted derivatives at all, and in other respects differs from potassio-pyrrole, which is undoubtedly an imide.

The magnesium pyrrol salts have been made to react with a number of agents, and acyl and alkyl groups have been introduced with ease into the pyrrole nucleus (compare A., 1913, i, 1379). The alkylation of substituted pyrroles is of especial interest, but, in the case of the action of ethyl bromide on magnesium 2:3:5-trimethylpyrrol bromide an oil was obtained which is probably a trimethyldihydropyridine and not the expected phyllopyrrole.

The action of halogens on pyrrole and its derivatives is so vigorous that poly-substitution usually takes place. By treating magnesium pyrrol salts with halogens at very low temperatures, however, mono-haloid derivatives have been obtained. They are unstable, and the

pure 2-bromopyrrole exploded spontaneously with great violence within a day or two. The ammonium haloid is one of the products of decomposition.

A better yield of 1-methylpyrrole than has hitherto been described (compare Ciamician and Dennstedt, A., 1885, 378) is obtained by boiling potassipyrrole and methyl iodide in pure ether for five hours under reflux and using a fractionating column in the subsequent distillation of the solvent, since the product is very volatile. 1-Methylpyrrole, b. p. 114—117°/749 mm., was added to magnesium ethyl bromide, when ethane was liberated, and acetyl chloride was then added to the mixture, under cooling. The product was decomposed by ice and steam distilled. 2-Acetyl-1-methylpyrrole, b. p. 75—76°/15 mm., was thus obtained (*ibid.*). Similarly prepared, 2-propionyl-1-methylpyrrole is a very pleasant smelling, colourless oil, b. p. 90—91°/12 mm., and 2-benzoyl-1-methylpyrrole is a colourless, viscous, aromatic oil, b. p. 159—160°/20 mm. The 2-magnesium-1-methylpyrrol bromide was also treated with ethyl chlorocarbonate, but the product could not be purified by fractionation.

2-Magnesium pyrrol bromide and ethyl bromide were boiled in ether for seven and a-half hours, and subsequently, after distillation in steam, two fractions were obtained. They consisted of 2-ethylpyrrole, b. p. 59—60°/15 mm. (Ciamician and Zanetti, A., 1889, i, 729), and 2:5-diethylpyrrole, b. p. 82—85°/16 mm. The constitution of the latter was shown by the action of hydroxylamine (compare Ciamician and Zanetti, A., 1890, i, 264), when  $\gamma\zeta$ -dioximino-octane was obtained in indefinite crystals, m. p. 169° (corr.). The same diethylpyrrole was obtained by heating 1-methylpyrrole with sodium ethoxide and alcohol in a sealed tube (compare Fischer and Bartholomäus, A., 1912, i, 384, 901).

Magnesium 2:3:5-trimethylpyrrol bromide was treated with ethyl bromide, when a base and certain pyrrole derivatives were obtained. The latter were coupled with diazobenzenesulphonic acid, and the former was then removed by distillation in steam from an alkaline solution. The base,  $C_8H_{13}N$ , is a colourless oil, b. p. 184—185°/737 mm., which forms a *picrate*, m. p. 138°, but does not respond to the pin-shaving test.

An ethereal solution of 2-magnesium pyrrol bromide was treated with chlorine dissolved in ether, at  $-50^\circ$  to  $-20^\circ$ , when 2-chloropyrrole was obtained as a colourless, heavy, unstable oil. J. C. W.

**Pyrrole Derivatives from Diethyl Ketone.** EZIO VECCHI (*Gazzetta*, 1914, 44, i, 473—479).—4-Acetyl-2:5-dimethyl-3-ethylpyrrole,  $NH < \begin{matrix} CMe:CEt \\ CMe:CAc \end{matrix}$ , prepared by the condensation of nitroso-

diethyl ketone and acetylacetone in acetic acid solution and in presence of zinc dust, forms shining needles, m. p. 170—171°, and gives the usual reaction with a pine splinter; it acts as a feeble base and its acetic acid solution is slightly opalescent. Treatment with hydroxylamine or phenylhydrazine did not give definite products, but by benzaldehyde it is converted into the corresponding *cinnamoyl* deriva-

tive,  $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{CEt} \\ \text{CMe} \cdot \text{C} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh} \end{smallmatrix}$ , which forms straw-yellow prisms, m. p. 149—150°.

*Ethyl 2:5-dimethyl-3-ethylpyrrole-4-carboxylate*,  $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{CEt} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$  obtained by the reduction of nitrosodiethyl ketone and ethyl acetoacetate by means of zinc dust and acetic acid, forms shining, white needles, m. p. 106—107°, and is isomeric with the compound obtained by Knorr and Hess from nitrosomethyl propyl ketone and ethyl acetoacetate (A., 1911, i, 1019; 1912, i, 900). The corresponding acid forms a microcrystalline powder, which softens and decomposes at 110—120°; the silver salt readily undergoes reduction in the air, and the lead, ferric, copper, and zinc salts are insoluble. T. H. P.

**Some Derivatives of Two Isomeric Acetyldimethylpyrroles.** EZIO VECCHI (*Gazzetta*, 1914, 44, i, 468—473).—The action of hydroxylamine on 2-acetyl-3:5-dimethylpyrrole yields the corresponding oxime,  $\text{C}_8\text{H}_{12}\text{ON}_2$ , which forms bluish-white needles, m. p. 139—140°. With 3-acetyl-2:4-dimethylpyrrole, only a very small quantity of oxime is formed.

2-Acetyl-3:5-dimethylpyrrole readily yields the phenylhydrazone,  $\text{C}_{14}\text{H}_{17}\text{N}_3$ , in yellow needles, m. p. 115—116°, but 3-acetyl-2:4-dimethylpyrrole yields only a tarry mass.

With benzaldehyde, the two compounds give the corresponding cinnamoyl derivatives,  $\text{C}_4\text{H}_2\text{NMe}_2 \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$ , m. p. 189—190° and 164—165° respectively for the 2-acetyl and 3-acetyl compounds.

T. H. P.

**Electrolytic Oxidation of Cyclic Ammonium Bases. II.** K. NEUNDLINGER and M. CHUR (*J. pr. Chem.*, 1914, [ii], 89, 466—480).—In an earlier paper (A., 1913, i, 1226) Fischer and Neundlinger have shown that 1-methyl-2-pyridone is readily obtained in good yield by the electrolytic oxidation of 1-methylpyridinium methosulphate, between iron electrodes, with a catholyte and anolyte of aqueous sodium hydroxide, the latter containing potassium ferricyanide as catalyst.

Full details of the method of working and the condition necessary to obtain a good yield are now given

The method has been extended to the preparation of 1:6- and 1:8-dimethyl-2-quinolone, 1-methylnaphthaquinolone, and 10-methyl-acridone from 6- and 8-methylquinoline, naphthaquinoline, and acridine respectively, the latter bases being first converted into the methosulphates of their *N*-methyl derivatives by heating on the water-bath with the calculated amount of methyl sulphate and then submitted to electrolytic oxidation.

1-Methyl-2-pyridone forms a hydrochloride, white, prismatic needles, m. p. 166°, a platinichloride, orange needles, m. p. 141°, hydrobromide, white, prismatic needles, m. p. 174°, picronolate, brownish-yellow needles, m. p. 120°, styphnate,  $\text{C}_6\text{H}_7\text{ON} \cdot \text{C}_6\text{H}(\text{NO}_2)_3(\text{OH})_2$ , yellow needles, m. p. 162°. It combines with quinol in alcoholic solution, yielding an

*additive* compound,  $2C_6H_7ON, C_6H_4(OH)_2$ , which separates in prismatic crystals, m. p.  $118^\circ$ .

Similar *additive compounds* are formed with resorcinol and catechol. On treatment with bromine in glacial acetic acid solution it yields  *dibromo-1-methyl-2-pyridone*, which crystallises in white needles, m. p.  $181^\circ$ , and is accompanied by an unstable, orange-yellow *bromo-compound*, m. p.  $142^\circ$ .

1:8-Dimethyltetrahydro-2-quinolone,  $\begin{array}{c} \text{CH:CH} \text{---} \text{C} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \\ | \quad | \\ \text{CH:CHMe} \cdot \text{C} \cdot \text{NMe} \cdot \text{CO} \end{array}$ , prepared from 8-methylquinoline, as described previously, has b. p. about  $300^\circ$ , m. p.  $100^\circ$ , and crystallises in pale yellow leaflets.

On treatment with aqueous potassium hydroxide, 1:8-dimethyl-quinolone methosulphate yields 1:8-dimethylquinolinium hydroxide, which forms colourless needles and readily passes into the corresponding carbinol.

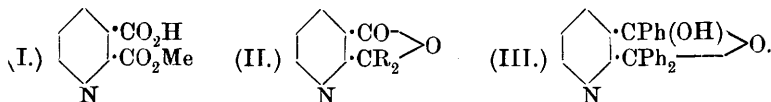
1:6-Dimethyltetrahydro-2-quinolone crystallises in pale yellow needles, m. p.  $90^\circ$ .

1-Methyl- $\alpha$ -naphthaquinolone (annexed formula) separates from alcohol in lustrous, pale brown needles, m. p.  $178^\circ$ .

10-Methylacridone,  $C_6H_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} C_6H_4$ , crystallises in lustrous, citron-yellow needles, m. p.  $203^\circ$ , and gives yellow solution having a sky-blue fluorescence. F. B.

### Alkylated Pyridophthalides and Hydroxypyridophthalans.

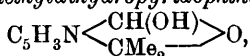
H. SIMONIS and HENRYK COHN (*Ber.*, 1914, **47**, 1238—1245).—The action of magnesium alkyl haloids under ordinary conditions in ethereal solution on  $\alpha$ -methyl hydrogen quinolinate (I) results in the formation of compounds of the type (II), for which the author suggests the term dialkylpyridophthalides; if magnesium phenyl bromide is employed and the temperature at which the reaction is carried out is raised by the addition of anisole, hydroxytriphenylpyridophthalan (III) is produced.



*Dimethylpyridophthalide*, obtained together with  $\alpha$ -propenylnicotinic acid, m. p.  $107\text{--}108^\circ$ ,  $\begin{array}{c} \text{CH:CH:C} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH-N:C} \cdot \text{CMe:CH}_2 \end{array}$ , by the action of magnesium methyl iodide on  $\alpha$ -methyl hydrogen quinolinate, has b. p.  $124^\circ/25\text{ mm.}$ , and solidifies to a white, crystalline mass, m. p.  $83\text{--}84^\circ$ ; the *picrate* forms large, yellow prisms, m. p.  $92^\circ$ ; the *platinichloride* crystallises with  $2H_2O$  in orange leaflets, which do not fuse below  $280^\circ$ ; the *aurichloride* crystallises with  $1H_2O$  and has m. p.  $231\text{--}238^\circ$  with previous softening; the *methiodide* forms slender, colourless needles, m. p.  $189^\circ$  (decomp.).

It is reduced by sodium amalgam and sulphuric acid in aqueous

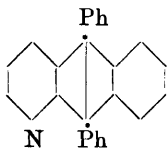
alcoholic solution to *dimethyldihydropyridophthalide*,



which forms a yellow powder, m. p. 107—109°.

*Diethylpyridophthalide*,  $\text{C}_5\text{H}_3\text{N} \begin{array}{c} \text{CO} \\ \text{CEt}_2 \end{array} \text{O}$ , is a pale yellow liquid, b. p. 140°/15 mm., D 1.067, and forms an oily *hydrochloride*, a *picrate* (orange-red prisms, m. p. 114—115°), *platinichloride*, m. p. 119° (decomp.), and *aurichloride*, m. p. 201—207°. When heated with aniline it yields the *anil*,  $\text{C}_5\text{H}_3\text{N} \begin{array}{c} \text{CO} \\ \text{CEt}_2 \end{array} \text{NPh}$ , as a yellow oil, b. p. 115—118°/30 mm.; the corresponding *p-tolil* has b. p. 131°/12 mm.

*Hydroxytriphenylpyridophthalan* (formula III) crystallises in white prisms, m. p. 230—231°; the *acetyl* derivative has m. p. 220—222°, the *picrate* (yellow, felted needles), m. p. 124—126°, the *bromo*-compound,  $\text{C}_{25}\text{H}_{18}\text{ONBr}$ , m. p. 171°. On reduction with sodium amalgam in alcoholic solution, it yields a *substance*,  $\text{OH}\cdot\text{CHPh}\cdot\text{C}_5\text{H}_3\text{N}\cdot\text{CPh}_2\cdot\text{OH}$  (?), which crystallises in light yellow, microscopic needles, m. p. 80—82°, and when warmed with sulphuric acid is converted into *diphenylanthrapyridine* (annexed formula). This sublimes in small, slender, light yellow needles, and forms a sparingly soluble *sulphate*, m. p. 246° (decomp.). F. B.



**Indirect Formation of Double Salts. V. Double Platinic, Cupric, and Silver Iodides of Substituted Ammonium Bases.** RASIK LAL DATTA and TARAPADA GHOSH (*J. Amer. Chem. Soc.*, 1914, 36, 1017—1022).—The experiments described were carried out in continuation of earlier work (Datta, T., 1913, 103, 426; A., 1913, i, 1046, 1047; and Datta and Mukherjea, P., 1913, 29, 185). Platini-iodides of substituted ammonium bases have been prepared by precipitation from solutions of the ammonium iodides by means of chloroplatinic acid. Double salts of silver iodide have been obtained by adding silver nitrate solution to a saturated solution of the substituted ammonium salt, and double salts of cupric iodide have been prepared by the method used previously (T., 1913, 103, 430).

The following compounds are described: *platini-iodides* of piperidinium, isoquinolinium, guanidinium, quinoline ethiodide, quinaldine ethiodide, and phenylmethylethylpropylammonium; double *cupric iodides* of tripropylammonium, *p*-tolyltrimethylammonium, isoquinolinium, and triethylsulphonium; double *silver iodides* of tetramethylammonium, *p*-tolyltrimethylammonium, pyridinium, quinolinium, and tetrapropylammonium. E. G.

**Preparation of Amino-ketones of the Quinoline Series.** ADOLF KAUFMANN (D.R.-P. 268931).—4-Quinolyl ketones of the general formula  $\text{C}_9\text{H}_6\text{N}\cdot\text{COR}$ , where R = Me, Et, etc., in which the carbonyl group is next to a methyl or methylene group, are easily brominated or chlorinated, and the halogen derivatives obtained in this way are converted into the corresponding amines by treatment with primary or secondary aliphatic amines. 6-Ethoxy-4-quinolyl methyl



ketone (A., 1913, i, 294) on bromination in hydrochloric acid solution gives 6-ethoxy-4-quinolyl bromomethyl ketone, m. p. 104—105°; the hydrochloride forms sulphur-yellow needles, decomp. 190°. The hydrobromide, obtained by brominating the ketone in hydrobromic acid solution with potassium bromate and bromide, decomposes at 204°. On treatment with piperidine the bromo-ketone yields 6-ethoxy-4-quinolyl piperidylmethyl ketone, m. p. 156—157°, and the hydrobromide of the bromo-ketone, with diethylamine, furnishes 6-ethoxy-4-quinolyl diethylaminomethyl ketone, yellow needles, m. p. 130—131°, of which the hydrobromide forms yellow needles, decomp. 187°. In a similar way are obtained 6-ethoxy-4-quinolyl methylaminomethyl ketone, yellow needles, m. p. 180°, and 6-ethoxy-4-quinolyl piperidylethyl ketone, m. p. 162°; 6-ethoxy-4-quinolyl bromoethyl ketone hydrobromide, from which the preceding amino-ketone is obtained, forms yellow crystals; decomp. 208°. 4-Quinolyl bromomethyl ketone has m. p. 200—210°, and 6-ethoxy-4-quinolyl chloromethyl ketone hydrochloride is a white, crystalline powder. J. C. C.

**The Constitution of Kynurenic Acid.** ANNIE HOMER (*J. Biol. Chem.*, 1914, 17, 509—518. Compare A., 1913, i, 646).—The identity of kynurenic acid with Camps' synthetic 4-hydroxyquinoline-2-carboxylic acid was established. It melts at 289° (uncorr.). Attempts to synthesise Camps' 4-hydroxyquinoline-3-carboxylic acid were made, and an acid isolated which gave the reactions of a 4-hydroxyquinolinecarboxylic acid, but whether it is the same acid as that isolated by Camps is uncertain; it, however, is not kynurenic acid. W. D. H.

**Stereoisomerism of Ammonium Salts containing Asymmetric Nitrogen and Two Asymmetric Carbon Atoms.** E. WEDEKIND and K. BANDAU (*Annalen*, 1914, 404, 322—333).—It has been shown (this vol., i, 81) that inactive ammonium salts of the tetrahydroisoquinolinium series containing asymmetric nitrogen and asymmetric carbon fulfil the demands of the stereochemical theory in yielding four stereoisomerides. The present paper deals with the stereoisomerism of the additive compounds of asymmetric tertiary tetrahydroisoquinoline bases,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CHR}' \cdot \text{NR} \end{smallmatrix}$ , and optically active alkyl iodides (for example, *l*-menthyl iodoacetate). In consequence of the addition, the nitrogen atom becomes asymmetric, and there are, therefore, three centres of optical activity in the tetrahydroisoquinolinium derivative,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CHR}' \cdot \text{NR} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot C_{10}H_{19} \end{smallmatrix}$ . Theory predicts the formation of four stereoisomerides, which can be represented by the schemes (I)  $(C + \dots N +)C -$ , (II)  $(C - \dots N -)C -$ , (III)  $(C + \dots N -)C -$ , and (IV)  $(C - \dots N +)C -$ , where the symbols in the brackets denote the centres of activity in the heterocyclic ring, and C - the centre in the menthyl group. No two of these substances are enantiostereoisomerides, consequently it should be possible to isolate all four by suitable fractional crystallisation.

The best results have been obtained with *l*-menthyl 1:2-diethyl-

1 : 2 : 3 : 4-*tetrahydroisquinolinium-iodide-2-acetate*, which, by fractional crystallisation from absolute alcohol, yields three distinct, well-characterised isomerides; evidence of the existence of the fourth isomeride required by theory has also been obtained. The four salts, in the order of increasing solubility, are designated by the letters  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . The  $\alpha$ -*iodide-acetate* has decomp.  $201-203^\circ$ ,  $[\alpha]_D - 35.9^\circ$  in ethyl alcohol and in chloroform,  $[\alpha]_D - 34.6^\circ$  in methyl alcohol, and forms rhombic crystals  $[a:b:c = 0.22406:1:0.87904]$ . The  $\beta$ -*salt* has decomp.  $195^\circ$ ,  $[\alpha]_D - 31.0^\circ$ ,  $-30.5^\circ$ , and  $-29.6^\circ$  in ethyl alcohol, methyl alcohol and chloroform respectively, and forms holohedral rhombic crystals  $[a:b:c = 0.6023:1:1.0664]$ . The  $\gamma$ -*salt* (finally purified by crystallisation from water) has decomp.  $162^\circ$ ,  $[\alpha]_D - 27.2^\circ$ ,  $-29.4^\circ$ , and  $-25.0^\circ$  in ethyl alcohol, methyl alcohol and chloroform respectively, and crystallises from alcohol in monoclinic plates  $[a:b:c = 2.013:1:2.1377; \beta = 70^\circ]$ . From the mother liquor of the  $\gamma$ -*salt* an oil is obtained; this by repeated treatment with different solvents yields a *substance*,  $C_{25}H_{40}O_2NI$ , decomp.  $194-195^\circ$ , which does not crystallise well and is possibly the fourth ( $\delta$ -) isomeride.

Naturally, it is a very difficult problem to ascertain which of these four salts corresponds with each of the schemes, I, II, III, and IV. From the sign of the rotations of the following betaine derivatives, however (compare Wedekind, A., 1908, i, 258), the authors are inclined to associate the  $\alpha$ -salt with I or III, the  $\beta$ -salt with II, and the  $\gamma$ -salt with IV.

By treating a methyl-alcoholic solution of each of the preceding salts with moist silver oxide, the iodine and the menthyl group are eliminated and betaines are produced. These are very hygroscopic and have not been isolated in a pure state, but there is no doubt that the betaine from the  $\alpha$ -salt is dextrorotatory, whilst those from the  $\beta$ - and  $\gamma$ -salts are lævorotatory; the rotations do not change with time.

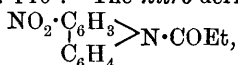
1-*Menthyl 2-ethyl-1-propyl-1 : 2 : 3 : 4-tetrahydroisquinolinium-iodide-2-acetate* crystallises well, but its solubility is great and only two of the four possible stereoisomerides have been isolated. The  $\alpha$ -*salt*,  $C_{26}H_{42}O_2NI$ , has decomp.  $182-183^\circ$ ,  $[\alpha]_D - 25.15^\circ$  in ethyl alcohol, and yields a dextrorotatory betaine, whilst the  $\beta$ -salt has decomp.  $163-165^\circ$ ,  $[\alpha]_D - 33.02^\circ$  in ethyl alcohol, and yields a slightly lævorotatory betaine.

C. S.

**Modified Method of Preparing Magnesium Compounds of Certain Heterocyclic Substances.** BERNARDO ODDO (*Gazzetta*, 1914, 44, i, 482-486).—Organo-magnesium derivatives containing the pyrrole, indole, scatole, or carbazole residue may be prepared in a single operation by bringing the base, the alkyl haloid, and the magnesium into contact in presence of anhydrous ether. The products obtained are identical with those formed when the magnesium ethyl haloid is first separated and then treated with the pyrrole, etc.

9-*Propionylcarbazole*,  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > N \cdot COEt$ , prepared by the action of propionyl chloride on the magnesium carbazole compound, forms white needles m. p.  $90^\circ$ , and yields a *picrate*,  $C_{15}H_{13}ON, C_6H_5O_7N_3$ , in tufts of

orange-red needles, m. p. 140°. The *nitro*-derivative,



forms soapy, white, prismatic needles, m. p. 233°.

T. H. P.

**New Method of Preparing Cyclic Ketones.** ALFRED SCHAARSCHMIDT (*Annalen*, 1914, **405**, 95—127).—2-Bromo-1-cyanoanthraquinone (Ullmann and van der Schalk, A., 1912, i, 387), an improved method of preparing which from 2-bromo-1-aminoanthraquinone is described, is converted into 2-amino-1-cyanoanthraquinone, brownish-yellow needles, m. p. above 310° (blue vat), by aqueous-alcoholic ammonia at 170—180°, into 2-aminoanthraquinone-1-carboxylamide, m. p. above 300°, brownish-orange crystals (red vat), by *p*-toluenesulphonylamide and potassium carbonate in boiling nitrobenzene and subsequent hydrolysis, into 2-methylamino-1-cyanoanthraquinone, m. p. above 305°, orange-brown needles (blue vat), by methylamine hydrochloride, potassium carbonate, and potassium hydroxide in amyl alcohol at 180—200°, and into 2-*p*-chloroanilino-1-cyanoanthraquinone, m. p. 265°, brownish-red, crystalline powder (greenish-blue vat), by *p*-chloroaniline in alcohol at 180—190°.

Quinones of the preceding type, containing amino- (or substituted amino-) and cyano-groups in the ortho-position to each other, are smoothly converted into quinoneacridones by concentrated sulphuric acid. Thus 2-*p*-chloroanilino-1-cyanoanthraquinone is converted by 95% sulphuric acid at 120—140° into *chloroanthraquinone-1:2-acridone*,  $\text{C}_6\text{H}_4:(\text{CO})_2:\text{C}_6\text{H}_2 < \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Cl}$ , orange-brown, crystalline powder, (red vat), whilst 1-*o*-cyanoanilinoanthraquinone,

$\text{C}_6\text{H}_4:(\text{CO})_2:\text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CN}$ , m. p. 276—277°, violet-red powder (red vat), prepared from *o*-chlorobenzonitrile, 1-aminoanthraquinone, potassium carbonate, and a little copper oxide in boiling nitrobenzene, is converted into anthraquinone-2:1-acridone (Ullmann and Ochsner, A., 1911, i, 489) in a similar manner.

2(1')-Anthraquinonylamino-1-cyanoanthraquinone,  $\text{C}_6\text{H}_4:(\text{CO})_2:\text{C}_6\text{H}_2(\text{CN}) \cdot \text{NH} \cdot \text{C}_6\text{H}_3:(\text{CO})_2:\text{C}_6\text{H}_4$ , m. p. above 300°, brownish-orange needles (reddish-brown vat), prepared from 2-bromo-1-cyanoanthraquinone, 1-aminoanthraquinone, and anhydrous sodium acetate in boiling nitrobenzene, is unchanged by 50% sulphuric acid or by concentrated hydrochloric acid at 150°, and by aqueous alcoholic potassium carbonate at 160—190°, probably owing to its slight solubility and to steric influences. It is converted by 96% sulphuric acid at 160—170° into 1:2:2':1'-*dianthraquinone-acridone*,  $\text{C}_6\text{H}_4:(\text{CO})_2:\text{C}_6\text{H}_2 < \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_2:(\text{CO})_2:\text{C}_6\text{H}_4$ , dark red crystals (bluish-violet vat).

2(2')-Anthraquinonylamino-1-cyanoanthraquinone, m. p. above 310°, brownish-yellow leaflets, prepared from 2-aminoanthraquinone in the same manner as the preceding isomeric, is converted by 96% sulphuric

acid at 160—170° into 1:2:2':3'-*dianthraquinoneacridone*, brownish-yellow powder (red vat).

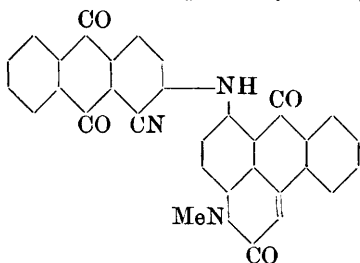
1:5-Diaminoanthraquinone, 2-bromo-1-cyanoanthraquinone, and sodium acetate in boiling nitrobenzene yield 1:5-di-1'-*cyanoanthraquinonylaminoanthraquinone*,

$C_6H_4 \cdot C_2O_2 \cdot C_6H_2(CN) \cdot NH \cdot C_6H_3 \cdot C_2O_2 \cdot C_6H_3 \cdot NH \cdot C_6H_2(CN) \cdot C_2O_2 \cdot C_6H_4$ , m. p. above 315°, reddish-brown, crystalline powder (olive vat), which is changed by 96% sulphuric acid at 170—180° to the *trianthraquinone*

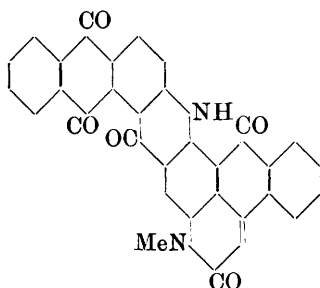
*diacridone*,  $C_{14}H_6O_2 \begin{smallmatrix} CO \\ < \\ NH \end{smallmatrix} C_{14}H_4O_2 \begin{smallmatrix} CO \\ < \\ NH \end{smallmatrix} C_{14}H_6O_2$ , reddish-brown

powder (violet-blue vat). By methods similar to the preceding, 1:8-diaminoanthraquinone is converted successively into 1:8-di-1'-*cyanoanthraquinonylaminoanthraquinone*, m. p. above 315°, reddish-brown powder (olive vat), and the corresponding *trianthraquinonediacridone*,  $C_{44}H_{18}O_8N_2$ , reddish-brown powder (violet-blue vat), and 1:4-diaminoanthraquinone into 1:4-di-1'-*cyanoanthraquinonylaminoanthraquinone*, brownish-violet, crystalline powder (violet vat), and the corresponding *trianthraquinonediacridone*, blackish-blue powder (violet vat).

2-Bromo-1-cyanoanthraquinone, 4-amino-1-methylanthrapyridone, and sodium acetate react in boiling nitrobenzene to form 4:1'-*cyanoanthraquinonylamino-1-methylanthrapyridone* (formula I), m. p. above 315°, brown leaflets (brownish-red vat), which is converted by sulphuric acid at 170—190° into *anthraquinonemethylanthrapyridoneacridone* (formula II), red powder (red vat).



(I.)

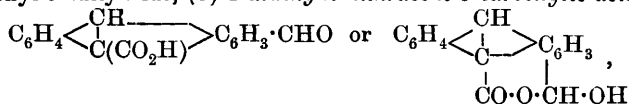


(II.)

The colours and dyeing properties of the preceding acridones and of their vats (alkaline hyposulphite) are discussed. C. S.

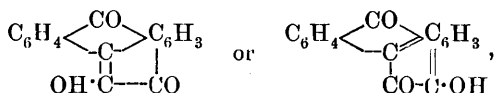
#### Behaviour of Aceanthrenequinone Towards Dilute Alkali.

C. LIEBERMANN and M. KARDOS (*Ber.*, 1914, 47, 1203—1210. Compare A., 1911, i, 387; 1913, i, 883).—When boiled with 10% aqueous potassium hydroxide, aceanthrenequinone yields the following substances: (1) anthraquinone-1-carboxylic acid, (2) anthracene-1:9-dicarboxylic anhydride, (3) 1-aldehydoanthracene-9-carboxylic acid,



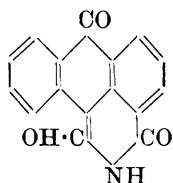
which crystallises with  $1\text{H}_2\text{O}$  in yellow needles, m. p.  $98-100^\circ$ ; the anhydrous acid is orange-red, and has m. p.  $133-134^\circ$ . On oxidation with chromic acid in glacial acetic acid solution it is converted into anthraquinone-1-carboxylic acid. The *sodium* salt (golden-yellow leaflets), *silver* salt and *phenylhydrazone*, yellowish-brown leaflets (decomp.  $200^\circ$ ), are described.

(4) *Hydroxyaceanthrenedione*,

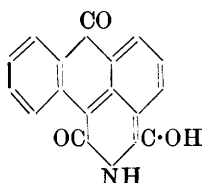


which crystallises in bordeaux-red needles, m. p.  $283^\circ$  (decomp.), and forms a reddish-brown silver salt; the *potassium* and *ammonium* salts are also mentioned. The *methyl ether*, prepared by heating the dione with 3% methyl-alcoholic hydrogen chloride, crystallises in lustrous, silky, red needles, m. p.  $233^\circ$ , and gives bluish-violet solutions in sulphuric acid.

The *phenylhydrazone*,  $\text{C}_{16}\text{H}_8\text{O}_2 \cdot \text{N} \cdot \text{NHPh}$ , forms orange-red needles, m. p.  $244^\circ$  (decomp.). The *oxime* crystallises in small, brown rods (decomp.  $234^\circ$ ), and when warmed with sulphuric acid yields *anthrone-hydroxypyridone* (formula I. or II.). This crystallises in red

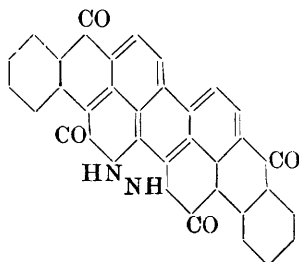
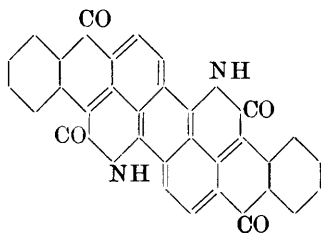


(I.)



(II.)

needles and does not melt below  $300^\circ$ . When fused with potassium hydroxide, it is converted into a green dye (*isoaceanthrene-green*), for which the following formulæ are suggested:



The dye is probably isomeric with the aceanthrene-green described previously. It is reduced by hyposulphite to a cherry-red vat, which colours cotton violet, passing into green on exposure to air.

On reduction with zinc dust and acetic acid or ammonia, hydroxy-aceanthrenedione is converted into a substance, which crystallises in

brownish-yellow needles, and yields solutions in alkalis, having an intense green fluorescence.

*Aceanthrenequinonephenylhydrazone*,  $C_{14}H_{18} \begin{smallmatrix} \diagup CO \\ C:N \cdot N\dot{H}Ph \end{smallmatrix}$ , separates from benzene in orange needles, m. p.  $203^{\circ}$ . F. B.

**Derivatives of Phenylisooxazolone.** A. MEYER (*Ann. Chim.*, 1914, [ix], 1, 252—331).—A résumé of work already published (compare A., 1910, i, 593; 1911, i, 341, 420, 687; 1912, i, 582, 1019; 1913, i, 393, 913, 1383, 1390; and Wahl and Meyer, A., 1908, i, 368). W. G.

**Quinonoid Salts of the Thiazine Group.** II. RUDOLF PUMMERER, FRITZ ECKERT, and SEBASTIAN GASSNER (*Ber.*, 1914, 47, 1494—1507).—In a previous communication, Pummerer and Gassner (A., 1913, i, 991) have proposed *p*-quinonoid formulæ for certain of the simpler thiazine derivatives, and similar formulæ have since been brought forward by Kehrmann, Havas, and Grandmougin (A., 1913, i, 908, 1241). The exact optical results on which their conclusions are based are given in the present communication.

An error in the previous paper has been pointed out by Kehrmann (A., 1913, i, 1320). The change of colour in solutions of thiazone and thiazim hydrochloride in concentrated hydrochloric acid does not depend on a *para*  $\rightarrow$  *ortho*-quinonoid isomerisation, but on reduction and quinhydrone formation. This point has now been more completely investigated.

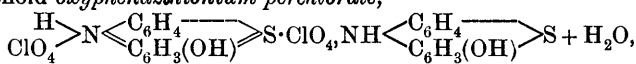
An aqueous solution of phenazthione shows a very broad absorption band, whilst the curve of 3-hydroxyphenazthionium chloride shows the sharp band in the violet which is characteristic of the simple phenazthionium salts. Hence the former has the *p*-quinonoid constitution,  $C_6H_4 \begin{smallmatrix} \diagup S \\ N \end{smallmatrix} \diagdown C_6H_3 \cdot O$ . Further, the absorption curves of the bluish-red thiazone, the violet thiazim hydrochloride, and the green phenylthiazim hydrochloride show these substances to be closely related, whilst differing markedly from the *o*-quinonoid curve of the reddish-brown acetaminophenazthionium chloride, which gives a sharply-defined band in the visible violet. The salts therefore have the formulæ  $C_6H_4 \begin{smallmatrix} \diagup S \\ N \end{smallmatrix} \diagdown C_6H_3 : NH, HCl$  and  $C_6H_4 \begin{smallmatrix} \diagup S \\ N \end{smallmatrix} \diagdown C_6H_3 : NPh, HCl$  respectively.

The information which has been accumulated up to the present is insufficient in amount to warrant conclusions being drawn with certainty as to the constitution of derivatives of thiodiphenylamine containing two auxochrome groups. The violet-blue thionin and the reddish-violet diacetylthionin (3:9-diacetylaminophenothiazonium chloride) have been investigated. The latter substance has been prepared by Kehrmann, who attributes to it an *o*-quinonoid structure (A., 1906, i, 307). The absorption curves show, at first sight, great similarity with those of the corresponding mono-substituted derivatives,

but closer investigation proves that the curve of thionin is less symmetrically formed than that of the diacetyl derivative, whilst the former substance is completely transparent between  $\lambda$  500  $\mu\mu$  and  $\lambda$  430  $\mu\mu$ , whereas the latter appears to show a second band within the given limits.

Re-investigation of the violet salt previously described as the hydrochloride of phenazthione shows it to be a semi-quinonoid compound. Titration with titanium trichloride in the presence of oxalic acid gives results in agreement with those required for a *holo*-quinonoid salt, whilst in presence of hydrofluoric acid (Piccard, A., 1910, i, 67) the lower values required for a semi-quinonoid salt are obtained. The hydrochloric acid functions as a reducing agent and yields a mixture of chlorine-free quinhydrone salt and of nucleus-substituted chloro-products. Optical investigation of the change indicates a unimolecular reaction which in reality is composed of two parts: (1) the unimolecular change of oxyphenazthiazonium chloride into chloro-oxythiodiphenylamine which is measured, and (2) the immeasurably rapid quinhydrone formation from the new leuco-compound and unchanged oxyphenazthionium chloride.

When an aqueous solution of perchloric acid is added to a solution of thiazone in glacial acetic acid, the brown *holo*-quinonoid oxyphenazthionium perchlorate,  $\text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{ClO}_4$  is obtained which is readily hydrolysed by water. When, however, quinol is added to a solution of thiazone and perchloric acid in glacial acetic acid, *meri*-quinonoid oxyphenazthionium perchlorate,



is formed in violet needles with black metallic glance. Inversely, the similarly constituted semi-quinonoid methoxyphenazthionium perchlorate (previously classed as *holo*-quinonoid) is prepared by the addition of benzoquinone ( $\frac{1}{2}$  mol.) to methoxythiodiphenylamine. This gives a brown solution in water due to hydrolysis into the *holo*-quinonoid salt and free leuco-base; the violet colour is, however, restored by addition of perchloric acid in excess. The violet solution in nitrobenzene similarly becomes brownish-red when strongly diluted, but violet on addition of perchloric acid; it is notable, however, that the dissociation of the quinhydrone salts is scarcely affected by heat, so that a solution of *meri*-oxyphenazthionium chloride in nitrobenzene can be boiled without a marked alteration of the violet colour taking place. The quinhydrone salts are optically interesting, since they scarcely show the well-defined absorption band in the violet which is characteristic of *holo*-quinonoid phenazthionium salts, whilst the band in the orange, which is ill-defined with *holo*-quinonoid salts, is sharply marked.

A third series of quinhydrone salts of the thiazine group, which have a greenish-orange colour, has been described by Kehrmann; their spectra greatly resemble those of the violet quinhydrone salts (a sharp band at  $\lambda$  515—25  $\mu\mu$ ), so that the two series must be closely related.

A solution of thiazine hydrochloride in fuming hydrochloric acid which has been preserved for some time (or immediately after addition of a reducing agent) has the same colour (and also a sharp band at  $\lambda$  415—25  $\mu\mu$ ) as phenazthionium chloride in hydrochloric acid; contrary to the previous assumption, therefore, it must be a *meri*-quinonoid, poly-acid salt of the ortho-series. H. W.

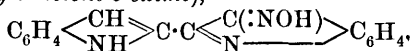
**Some Chlorine Derivatives of the Diphenyl- and Triphenyl-methane Bases.** MARIO MAYER (*Ber.*, 1914, 47, 1161—1163).—A further examination of the reaction between *o*-chloroaniline and formaldehyde (Bischoff and Reinfeld, A., 1903, i, 247) shows that in addition to the substance  $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl})_2$ , a nitrogenous, crystalline compound, m. p.  $210^\circ$ , is produced. The former substance, when treated with *o*-chloroaniline and excess of hydrochloric acid, is converted into the *hydrochloride* of 1:1'-dichloro-2:2'-diaminodiphenyl-methane, the free base,  $\text{CH}_2(\text{C}_6\text{H}_3\text{Cl}\cdot\text{NH}_2)_2$  forming scales, m. p.  $110^\circ$ . On heating with *o*-chloroaniline hydrochloride, together with a little nitrotoluene and ferrous chloride at  $170^\circ$  for 3—5 hours, the base gives rise to *o*-trichloromagenta; this dissolves in acetic or hydrochloric acid to a solution of strong reddish-violet colour, the absorption curve of which shows a band with a maximum at 533  $\mu\mu$ .

The above compound, m. p.  $210^\circ$ , also gave rise to trichloromagenta, although with difficulty, when treated in the above manner, but the anhydro-compound  $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{CH}_2)_x$ , m. p.  $154^\circ$ , obtained by Bischoff and Reinfeld (*loc. cit.*) from *m*-chloroaniline and formaldehyde, as well as another substance, m. p.  $228^\circ$ , obtained by the author, failed to yield magenta derivatives in this way. D. F. T.

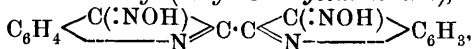
**New Syntheses of Indigotin.** W. MADELUNG (*Annalen*, 1914, 405, 58—95).—2:2'-Di-indyl (A., 1912, i, 499) cannot be directly oxidised to indigotin. An improved method of preparing 2:2'-indyl, in 26% yield, is described. The substance forms additive compounds with acids (an unstable *hydrochloride*,  $\text{C}_{16}\text{H}_{12}\text{N}_2\cdot\text{HCl}$ , orange-yellow prisms, and more stable *perchlorate*,  $\text{C}_{16}\text{H}_{12}\text{N}_2\cdot\text{HClO}_4$ , orange-yellow needles, are described), yields a *tetrachloro*-derivative,



yellow crystals, and condenses with diazonium salts. It is extremely sensitive to nitrous acid. By treatment with sodium ethoxide and amyl nitrite, it yields the *sodium* derivative, and by the action of concentrated aqueous sodium nitrite, hydrochloric acid, and glacial acetic acid, the *hydrochloride*, violet crystals, of 3-oximino-2:2'-indyl (2-[2']-indylindolone-3-oxime),



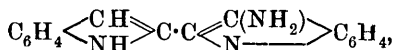
m. p.  $253^\circ$  (decomp.), reddish-brown crystals, whilst in the absence of alkali or mineral acid, for example, by the action of sodium nitrite and glacial acetic acid, it (or, better, 3-oximino-2:2'-di-indyl) yields 3:3'-dioximino-2:2'-di-indyl (*dehydroindigotindioxime*),



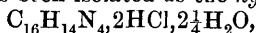


faintly yellow powder, the *potassium* salt, orange yellow plates, of which is almost completely hydrolysed by an excess of water.

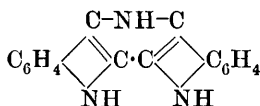
By reduction with alkaline sodium hyposulphite on the water-bath, 3-oximino-2 : 2'-di-indyl yields 3-amino-2 : 2'-di-indyl,



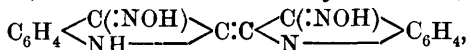
m. p. 115—119° (decomp.), colourless prisms, which rapidly becomes blue in the air and forms a *hydrochloride*,  $\text{C}_{16}\text{H}_{13}\text{N}_3 \cdot 2\text{HCl}$ , canary-yellow, microscopic needles, and *acetyl* derivative,  $\text{C}_{16}\text{H}_{12}\text{N}_3\text{Ac}$ , m. p. 259—260° (decomp.), colourless plates containing  $\frac{1}{2}\text{EtOH}$  (from alcohol and benzene). The same reducing agent, acting on 3 : 3'-dioximino-2 : 2'-di-indyl in aqueous alcohol, produces 3 : 3'-diamino-2 : 2'-di-indyl, which has been isolated as the *hydrochloride*,



greenish-yellow leaflets, on account of its great sensitiveness to atmospheric oxidation; the *stannochloride*, yellow prisms, and *diurethane*,  $\text{C}_{22}\text{H}_{22}\text{O}_4\text{N}_4$ , needles, are mentioned. The reduction of 3-oximino-2 : 2'-di-indyl by stannous chloride and alcoholic hydrochloric acid on the water-bath produces the stannichloride of a *substance* (*acetyl* derivative,  $\text{C}_{16}\text{H}_{10}\text{N}_3\text{Ac}$ , decomp. above 350°, prisms), which is extremely readily oxidised and is probably 3 : 3'-imino-2 : 2'-di-indyl (annexed formula).



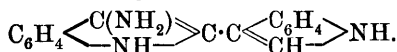
The oxidation of 3 : 3'-diamino-2 : 2'-di-indyl hydrochloride by alcoholic ferric chloride on the water-bath yields the *hydrochloride*,  $\text{C}_{16}\text{H}_{12}\text{N}_4 \cdot \text{HCl} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , violet needles, of di-iminoindigotin (A., 1913, i, 903), m. p. 215°, blue needles; the *acetate*,  $\text{C}_{16}\text{H}_{12}\text{N}_4 \cdot \text{CH}_3 \cdot \text{CO}_2\text{H}$ , m. p. 175°, dark blue needles or prisms, is described. Di-iminoindigotin is oxidised to *di-iminohydroindigotin*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{NH}) \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{C}(\text{NH}) \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{C}_6\text{H}_4$ , m. p. 193° (decomp.), orange-yellow needles, by warming with lead peroxide in benzene, yields indigotin by boiling its hydrochloride with water or by heating it with fused oxalic acid, and is converted into *indigotindioxime*,



(*hydrochloride*,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4 \cdot \text{HCl}$ ; *acetate*,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4 \cdot \text{CH}_3 \cdot \text{CO}_2\text{H}$ , m. p. 167—168°, brownish-violet needles), by treatment with hydroxylamine hydrochloride in boiling alcohol.

The reaction between indole, alcoholic sodium ethoxide, and amyl nitrite at 0° yields an orange-yellow solution of the sodium derivative of 3-oximinoindole (indolone 3-oxime) (Angeli and Marchetti, A., 1907, i, 551), which is converted into the *sodium hydrogen sulphite* compound,  $\text{C}_8\text{H}_6\text{ON}_2 \cdot \text{NaHSO}_3$ , yellow leaflets, by sulphur dioxide, and into 3-aminoindole, m. p. 117° (decomp.), colourless leaflets (*hydrochloride*, yellow leaflets; *acetyl* derivative, m. p. 162—163° [decomp.]), by reduction with alkaline sodium hyposulphite. 3-Aminoindole hydrochloride is oxidised to di-iminoindigotin hydrochloride by ferric chloride, whilst the base itself is converted by boiling sodium hyposulphite into a *substance*,  $\text{C}_{16}\text{H}_{13}\text{N}_3$  (*acetyl* derivative, decomp. 244—

245°, colourless plates), which oxidises readily in the air, and is probably 3-amino-2 : 3'-*di-indyl*,



C. S.

**Pyrimidines. LXIX. Colour Test for 5-Aminopyrimidines.** TREAT B. JOHNSON and CARL O. JOHNS (*J. Amer. Chem. Soc.*, 1914, **36**, 970—980).—In an earlier paper (this vol., i, 579) it has been shown that 4 : 5-diaminotetrahydropyrimid-2 : 6-dione and the corresponding 2 : 5-diamino-compound both give an intense blue coloration with solution of phosphomolybdic acid. The present work supports the view that this reaction depends on the presence of the 5-amino-group in the pyrimidine ring.

Folin and Denis (A., 1912, ii, 1011) have described two reagents : (1) the uric acid reagent, consisting of a solution of phosphotungstic acid, which does not react with monohydric phenols or their derivatives, and (2) the phenol reagent, a solution of phosphotungstic and phosphomolybdic acids, which is exceeding sensitive to phenol groups. Both these reagents and a 2% solution of phosphomolybdic acid have been applied, in neutral, acid, and alkaline solutions, to twenty-nine different pyrimidines and the results are tabulated.

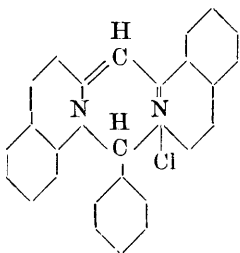
These tests have shown that the 5-amino-group is the functioning group when phosphotungstic acid (uric acid reagent) produces a blue coloration in an ammoniacal solution. If both the hydrogen atoms of this group are replaced by other groups or if the amino-group is in any other position in the ring or in a side-chain, the reaction always fails to take place in alkaline solution.

E. G.

**Pyrimidine-sugar. [Preliminary Notice.]** S. J. THANNHAUSER and G. DORFMÜLLER (*Ber.*, 1914, **47**, 1304—1308).—Johnson (this vol., i, 366) expressed the opinion that pyrimidine compounds are the precursors of purine derivatives in the plant, and announced that he was engaged on the combination of pyrimidines with sugars. The authors have already obtained results in this field. They have evaporated aqueous solutions of equivalent quantities of a diamino-pyrimidine and an aldehydic sugar or a hexoic acid and purified the condensation products by crystallisation.

4 : 5-Diamino-2 : 6-dioxo-1 : 3-dimethylpyrimidine forms with mucic acid the compound,  $\text{CO} \begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{CO}_2\text{H} \\ \text{NMe} \text{---} \text{C} \cdot \text{NH}_2 \end{array}$ , in colourless needles, m. p. 284—285° (decomp.), and with galactonic acid the compound,  $\text{C}_{12}\text{H}_{20}\text{O}_8\text{N}_4$ , which crystallises from boiling water in long, colourless needles, m. p. 253—254°. The same base yields with dextrose the white, crystalline compound,  $\text{C}_{12}\text{H}_{20}\text{O}_7\text{N}_4$ , m. p. 206—207°, and with lactose the compound,  $\text{C}_{18}\text{H}_{20}\text{O}_{12}\text{N}_4$ , m. p. 218—219° (decomp.), and also condenses with galactose and maltose. Dextrose combines with 4 : 5-diamino-2 : 6-dioxypyrimidine, yielding the pale yellow compound,  $\text{C}_{10}\text{H}_{16}\text{O}_7\text{N}_4$ , m. p. decomp. 186—187° (slow heating), 205—206° (quickly heated). The substance was crystallised from a boiling 30% solution of dextrose and washed with alcohol and ether. It decomposes in boiling water.

J. C. W.



**Structure of Quinoline-Red.** L. P. KRANTZ (*Chem. Weekblad*, 1914, **11**, 364—367).—A review of investigations of the constitution of quinoline-red, the author assigning to it the annexed formula (compare A., 1910, i, 201). A. J. W.

**4:4-Diphenylsemicarbazide and some of its Derivatives.** B. TOSCHI (*Gazzetta*, 1914, **44**, i, 443—447).— $\delta\delta$ -Diphenylsemicarbazide,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}_2$ , prepared by heating *as*-diphenylcarbamide (1 mol.) and hydrazine hydrate (1 mol.) in a sealed tube at  $100^\circ$ , or by the interaction of the chloride,  $\text{NPh}_2\cdot\text{COCl}$ , and hydrazine hydrate in alcoholic solution, forms long, prismatic crystals, m. p.  $154^\circ$ . It has feebly basic properties and reduces Fehling's solution and ammoniacal silver nitrate solution; with aldehydes it gives the corresponding 4:4-diphenylsemicarbazones, which are easily obtained pure. With nitrous acid its behaviour is that typical of compounds of the type  $\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , the corresponding *azide*,  $\text{NPh}_2\cdot\text{CO}\cdot\text{N}\cdot\text{N}:\text{N}$ , m. p.  $78\text{--}79^\circ$ , being formed. With concentrated sulphuric acid and a small quantity of an oxidising agent such as ferric chloride,  $\delta\delta$ -diphenylsemicarbazide and its derivatives give blue or violet colorations.

*Tetraphenylhydrazodicarbonamide*,  $\text{NPh}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}_2$ , formed in small proportion in the above preparation, forms colourless needles, m. p.  $214\text{--}215^\circ$ , reduces Fehling's solution and ammoniacal silver nitrate solution, and yields an indigo coloration with concentrated sulphuric acid and ferric chloride.

$\delta\delta$ -Diphenylsemicarbazide hydrochloride,  $\text{C}_{13}\text{H}_{13}\text{ON}_3\cdot\text{HCl}$ , has m. p.  $218\text{--}220^\circ$ , and the *picrate*,  $\text{C}_{13}\text{H}_{13}\text{ON}_3\cdot\text{C}_6\text{H}_8\text{O}_7\text{N}_3$ , m. p.  $164\text{--}167^\circ$  (decomp.).

$\delta\delta$ -Diphenyl- $\alpha$ -benzylidenesemicarbazide,  $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}_2$ , forms colourless needles, m. p.  $177^\circ$ , and  $\delta\delta$ -diphenyl- $\alpha$ -anisylidenesemicarbazide,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}_2$ , colourless needles, m. p.  $162\text{--}163$ . T. H. P.

**Some Ethers of 2-Hydroxyphenylnaphthatriazoles.** G. FERRERI (*Atti R. Accad. Sci. Torino*, 1914, **49**, 497—507).—When the *o*-aminoazo-compounds obtained by the reaction of *o*- and *p*-methoxybenzene- and *o*- and *p*-ethoxybenzene-diazonium chlorides with  $\beta$ -naphthylamine are heated to about  $300^\circ$  they decompose according to the equation  $3\text{C}_{10}\text{H}_6\begin{smallmatrix} \text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OR}(\alpha) \\ \text{NH}_2 \end{smallmatrix} = 2\text{C}_{10}\text{H}_6\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OR} + \text{C}_{10}\text{H}_6\begin{smallmatrix} \text{NH}_2(1) \\ \text{NH}_2(2) \end{smallmatrix} + \text{C}_6\text{H}_4\begin{smallmatrix} \text{OR} \\ \text{NH}_2 \end{smallmatrix}$ , and this forms a good method of preparation for the methyl and ethyl ethers of *o*- and *p*-naphthylene-*N*-hydroxyphenyltriazole.

2-*o*-Anisylnaphthatriazole,  $\text{C}_{17}\text{H}_{13}\text{ON}_3$ , forms colourless, prismatic tablets, m. p.  $113^\circ$ . It gives a green coloration with sulphuric acid. It does not react with dilute nitric acid, the mononitro-derivative being prepared by oxidation of 4-nitro-2-methoxybenzeneazo- $\beta$ -naphthyl-

amine with aqueous chromic acid. 4-Nitro-2-methoxybenzeneazo- $\beta$ -naphthylamine,  $C_{17}H_{14}O_5N_4$  (from 4-nitro-2-methoxybenzenediazonium chloride and an alcoholic solution of  $\beta$ -naphthylamine), forms red needles, m. p.  $206^\circ$ . 2-p-Nitro-o-anisyl-naphthatriazole,

$C_{17}H_{12}O_3N_4$ ,  
crystallises in colourless needles, m. p.  $203^\circ$ .

2-o-Phenetyl-naphthatriazole,  $C_{18}H_{15}ON_3$ , crystallises in prismatic tablets, m.p.  $85^\circ$ .

N-p-Anisyl-naphthatriazole,  $C_{17}H_{13}ON_3$ , forms colourless needles, m. p.  $129^\circ$ . It dissolves in concentrated sulphuric acid with production of a green coloration. It yields a mononitro-derivative,  $C_{17}H_{12}O_3N_4$ , when boiled with dilute nitric acid (2*N*); this substance forms pale yellow needles, m. p.  $220-221^\circ$ .

2-Nitro-4-methoxybenzeneazo- $\beta$ -naphthylamine,  $C_{17}H_{14}O_3N_4$ , forms red needles, m. p.  $186^\circ$ , and yields the above mononitro-compound when oxidised with aqueous chromic acid.

N-p-Phenetyl-naphthatriazole,  $C_{18}H_{15}ON_3$ , forms colourless needles, m. p.  $141^\circ$ . It yields 2-o-nitro-p-phenetyl-naphthatriazole,

$C_{18}H_{14}O_3N_4$ ,  
which crystallises in pale yellow needles, m. p.  $177^\circ$ .

R. V. S.

**Theophyllinerhamnoside.** EMIL FISCHER and KÁLMÁN VON FODOR (*Ber.*, 1914, 47, 1058—1061).—In continuation of the work on the synthesis of glucosides of the purines (compare Fischer and Helferich, this vol., i, 333), the authors have investigated the formation of the rhamnosides of theophylline and theobromine. The former is readily obtained; on the other hand, the condensation of acetobromorhamnose with theobromine takes place with considerable difficulty, and the yields of the acetyl derivatives are so poor that the isolation of the free glucoside has not been effected. Acetobromorhamnose is obtained by the action of a solution of hydrogen bromide in glacial acetic acid on syrupy acetyl-rhamnose.

Triacetyltheophyllinerhamnoside,  $C_7H_7O_2N_4 \cdot C_6H_8O_4Ac_3$ , m. p.  $135-136^\circ$  (corr.), after softening at about  $133^\circ$ ,  $[\alpha]_D^{20} - 48.87^\circ$  in *s*-tetrachloroethane solution, is obtained by boiling the silver salt of theophylline with a solution of acetobromorhamnose in xylene. When dissolved in methyl alcohol and treated with a saturated methyl alcoholic solution of ammonia, it yields theophyllinerhamnoside (compare Fischer and Helferich, *loc. cit.*), m. p.  $169-170^\circ$  (corr.),  $[\alpha]_D^{22} - 78.6^\circ$  in aqueous solution. The latter is fairly readily hydrolysed by warm 5% hydrochloric acid; it does not reduce boiling Fehling's solution, and gives a precipitate with phosphotungstic acid in not too dilute solution. The rhamnose residue is in the position 7 or 9, but the exact place is not yet decided.

Triacetyltheobrominerhamnoside,  $C_7H_7O_2N_4 \cdot C_6H_8O_4Ac_3$ , is obtained by the action of the silver salt of theobromine on a boiling solution of acetobromorhamnose in xylene. It forms shining leaflets which melt at about  $222^\circ$  (corr.) to a brown cloudy liquid, which darkens when further heated and becomes clear at about  $250-260^\circ$ . It reduces boiling Fehling's solution strongly.

H. W.

**Polychromic Salts of Oximino-ketones. II. I. LIFSCHITZ** (*Ber.*, 1914, 47, 1068—1076).—It has been previously shown (A., 1913, i, 1361) that in the case of oximino-ketones the presence of the group,  $-\text{CO}\cdot\text{C}(\text{NOH})\text{X}$  (in which X is an unsaturated group), is of primary importance for the appearance of polychromism. According to the literature, negative groups appear to have a marked influence on the colour and stability of the polychromic forms. Thus, Traube found that the salts of oximinomalonylguanidine (A., 1894, i, 7) have a pale colour which, in contrast to the violurates, deepens with decreasing atomic weight of the alkali metal, whilst, according to Whiteley and Mountain (P., 1909, 25, 121), diphenylthiovioluric acid not only yields polychromic salts, but itself exists in three chromoisomeric forms.

The author finds these data to be incorrect, since the replacement of the  $:\text{CO}:$  group of violuric acid by the group  $:\text{C}:\text{NH}$  causes a deepening in colour of the corresponding salts. This action is much more marked in the case of the replacement of  $:\text{CO}$  by  $:\text{CS}$  and, in addition to the red or blue salts, dark green inner complex salts are also formed.

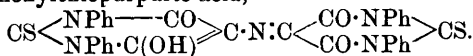
In the case of cyclic oximino-ketones, the nature of the ring system is of far greater importance. Whilst isomerisation and polychromism are exhibited by oximino-oxazolone and oximinotriazolone, in the case of oximinopyrazolone a nitroso-band is not observed on salt formation; this can possibly be explained by the assumption of a *trans*-configuration,

$$\begin{array}{c} \text{N}:\text{CR}\cdot\text{C}\cdot\text{CO}' \\ \text{HO}\cdot\text{N} \end{array}$$
, for the substance which inhibits isomerisation to the nitroso-enol form.

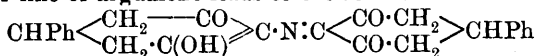
The neutral ammonium salt of oximinomalonylguanidine (Traube, *loc. cit.*) is converted by cold concentrated solutions of alkali hydroxide into dimetallic salts which dissolve in water with carmine-red colour. Carbon dioxide converts them into the sparingly soluble normal salts. The bluish-violet *disodium* and the carmine-red *dipotassium* salts were analysed. The normal salts are best obtained by boiling the green silver salt with solutions of the chlorides of the alkaline metals. The *monopotassium* salt,  $\text{C}_4\text{H}_3\text{O}_3\text{N}_4\text{K}\cdot\text{H}_2\text{O}$ , pure blue, micro-crystalline powder, and the *monosodium* salt,  $\text{C}_4\text{H}_3\text{O}_3\text{N}_4\text{Na}\cdot\text{NaCl}$ , reddish-violet, micro-crystalline substance, were analysed. The *lithium* and *copper* salts are red and green respectively.

Yellow  $\beta$ -diphenylthiovioluric acid has been described by Isherwood (P., 1909, 25, 120) and by Whiteley and Mountain (*loc. cit.*), whilst, according to the latter authors, the acid also exists in a purple  $\alpha$ -form and as a violet hydrated isomeride. The author finds that the yellow  $\beta$ -acid is the true diphenylthiovioluric acid, and yields with the alkali-metals red, violet, blue and deep green salts, the spectroscopic changes during salt formation being precisely similar to those observed with diphenylvioluric acid and dimethylviolanic acid. On the other hand, the chromoisomerism of the so-called  $\alpha$ -acid is shown to be doubtful, since it cannot be converted into the  $\beta$ -acid. Determination of molecular weight in ethylene bromide solution gives values nearly twice as great as those required for diphenylthiovioluric acid. Since, also, spectroscopic investigation shows the acid to be closely analogous

to murexide, the author is led to the conclusion that the  $\alpha$ -acid is, in reality, tetraphenylthiopurpuric acid,

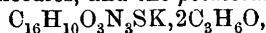


A similar line of argument leads to the formula



for the brown product obtained by the action of hot water on phenyl-violanic acid (A., 1913, i, 1362).

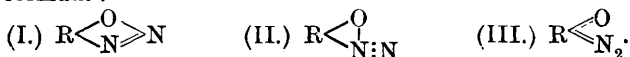
Diphenylthiovioluric acid is best obtained by slowly adding mixed solutions of sodium nitrite and alkaline diphenylthiobarbituric acid to cold dilute hydrochloric acid, and is conveniently purified through the green pyridine salt, which, when heated at  $100^\circ$ , yields the pure  $\beta$ -acid, yellow powder, m. p.  $224^\circ$  (decomp.). The alkali salts are obtained by warming a solution of the acid in acetone with alkali carbonates. In this manner, the *lithium* salt,  $\text{C}_{16}\text{H}_{10}\text{O}_3\text{N}_3\text{SLi} \cdot 2\text{C}_3\text{H}_6\text{O}$ , wine-red needles, the *sodium* salt, violet needles, and the *potassium* salt,



dark green needles, have been prepared. These salts yield bluish-green solutions in methyl alcohol; in acetone, the solutions have the colour of the solid salts.

Tetraphenylthiopurpuric acid is prepared by the addition of ethyl nitrite to a suspension of diphenylthiobarbituric acid in cold methyl or ethyl alcohol, and is separated from the small amount of diphenylthiovioluric acid, simultaneously formed, by means of boiling chloroform. It is a dark purple, microcrystalline powder, which decomposes above  $210^\circ$ . It dissolves in the usual organic media, yielding dark purple solutions. When water is added to the alcoholic solution, the colour changes to violet, owing to the formation of the dihydrate; the same substance is occasionally obtained by the action of atmospheric moisture on the finely-divided red acid. In accordance with the data of Whiteley and Mountain, the salts of tetraphenylthiopurpuric acid are invariably monochromic, the anhydrous compounds being purple-red, the hydrated substances violet. The *pyridine* salt,  $\text{C}_{37}\text{H}_{26}\text{O}_4\text{N}_6\text{S}_2$ , was analysed.  
H. W.

**The Formation of *o*-Nitro-*p*-diazoniumphenol.** The Constitution of "Diazophenols." A. KLEMENC (*Ber.*, 1914, 47, 1407—1416).—The so-called diazophenols can be represented by the three constitutional formulæ:

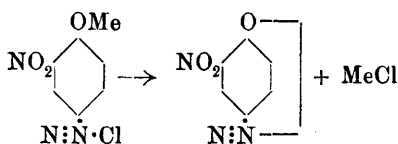


Wolff's researches have rendered formula (I.) improbable, and he, with Hantzsch, favours the third constitution. The author now seeks to show that the latter structure is as improbable as the first and that formula (II.) is correct.

The explosive character of these compounds would agree with either constitution, but the fact that the substances dissolve in concentrated acids and can be recovered on dilution would not be expected of quinonediazides (III.). The latter might also be expected

to be more freely soluble than are the "diazophenols," only a few of which dissolve in organic media. In most respects the diazophenols share the characteristics of "anhydrodiazocarboxylic acids" and "anhydrodiazosulphonic acids" to which Hantzsch and Gerilowski assigned the constitution of diazonium salts, and it is expected that the absorption spectra of these three classes of compounds will prove to be similar. It is, indeed, contended that the absorption curves for "*p*-quinonediazide" and benzenediazonium chloride, as measured by Hantzsch and Lifschitz (A., 1912, ii, 1116) show the same features (compare Cain, A., 1913, ii, 169).

*o*-Nitro-*p*-diazoniumphenol may be prepared in acid solution and exhibits the usual properties of such compounds with the exception that it has not been possible to replace the diazo-group by hydroxyl.



It is obtained quantitatively by heating the diazonium chloride of *o*-nitro-*p*-anisidine with acetic anhydride at 80°, according to the annexed scheme. This reaction is remarkable in that the removal of the methoxyl group by

hydriodic acid, from the diazonium chloride as well as from the free base, is unusually difficult, and confirms the author's view that the "diazophenol" is an inner diazonium salt.

The constitution of *o*-nitro-*p*-anisidine, m. p. 56—57°, which is obtained from the commercial sulphate, has been confirmed by boiling the diazonium chloride with methyl alcohol, when an almost quantitative yield of *o*-nitroanisole was obtained. *o*-Nitro-*p*-acetanisidide forms yellow needles, m. p. 153°. Many attempts were made to decompose the diazonium salt so as to introduce the hydroxyl group, but an amorphous powder was the chief product. When the *o*-nitro-*p*-anisidine salt is diazotised at 70—80°, however, the main product is *o*-nitro-*p*-diazoniumphenol, which crystallises either at once or after some hours, mixed with the amorphous substance. The dried material is shaken with cold acetone, which dissolves the amorphous product and is then recrystallised from boiling acetone. *o*-Nitro-*p*-diazoniumphenol forms yellow leaflets which explode with violence at 168°, or when struck, but dissolve in concentrated sulphuric acid or fuming nitric acid, only to be recovered on dilution. It dissolves in hot water, but the solution decomposes on prolonged boiling, with evolution of nitrogen. On boiling with alcohol for some days, it decomposes into *o*-nitrophenol and a non-volatile, amorphous substance, which gives a blood-red solution in potassium hydroxide. *o*-Nitro-*p*-diazoniumphenol may also be obtained by diazotising *o*-nitro-*p*-anisidine by amyl nitrite, precipitating the diazonium salt with ether, and warming the aqueous solution. The diazo-nitrogen was estimated by decomposing the substance by dilute potassium hydroxide, and the remaining nitrogen was estimated in the evaporated solution by combustion.

J. C. W.

**The Formation of Mono- and Bisazo-compounds of Phenols and Phenolic Ethers.** K. VON AUWERS and F. MICHAELIS (*Ber.*, 1914, 47, 1275—1297).—An accidental discovery that *p*-xylenol

condenses with benzenediazonium chloride in alkaline solution to form a bisazo-compound has led the authors to study the conditions under which the formation of bisazo-derivatives of substituted phenols is possible. It was already known that phenol, *o*- and *m*-cresol form such compounds in concentrated, but not in dilute, solutions, and bisazo-derivatives of thymol and carvacrol were prepared by Mazzara and Pozzetto in 1885. A rough examination of the new material shows that the tendency to the formation of bisazo-compounds rises with the number of alkyl groups in the phenol molecule, whereas the presence of other substituents, such as the nitro-, carboxyl and carboxylic ester groups, destroys, not merely the tendency to, but frequently the possibility of, such condensation. Many of the observations on the influence of substituents on the coupling of phenols which are scattered throughout the literature are reviewed in this paper, and it is pointed out that, as a rule, negative substituents diminish the reactivity of the phenol. However, the formation of a bisazo-compound is controlled, not so much by the speed of coupling of the phenol as of the mono-azo-derivative. The experimental conditions are also of influence. Bisazo-compounds are best formed in alkali hydroxide solutions, not so well in the presence of alkali carbonates, and scarcely at all in acetic acid. The yield is also increased by raising the concentration of the alkali, but only within limits, for the mono-azo-compound frequently separates as a salt from very alkaline solutions.

Inspired by the discovery that the ethers of many phenols are also capable of forming azo-compounds (Meyer and Lenhardt, A., 1913, i, 723), the authors have also studied the influence of alkyl groups in this field, using azophor-red as the diazo-reagent. The differences are still more marked than in the case of the free phenols. It has been found that only those monocyclic ethers are capable of condensation which contain an alkyl group meta to the ether group, and, in addition, a free para-position. Furthermore, the speed of reaction is increased when there is a second alkyl group in the ortho-position, and is at its maximum when the two alkyl groups are both meta to the ether group. The theory of the formation of azo-derivatives of phenols and ethers is discussed at some length.

The derivatives described below were prepared by the following general methods. The benzene- and xylene-diazonium chloride solutions employed contained 1 mol. of the base, 1 mol. of sodium nitrite, and 2.5 mols. of hydrochloric acid per litre. In some cases the phenol was dissolved in sodium hydroxide (3 mols.) and diluted so that 1 gram of the alkali was contained in 50 or 100 c.c. of water, or equally strong solutions of the phenol and sodium carbonate or sodium acetate were made with the assistance of alcohol. Mono-azo-derivatives were extracted from the bisazo-compounds by warming with dilute sodium hydroxide, and reprecipitated by acetic acid or carbon dioxide. Benzoyl derivatives were prepared by heating the mono-azo-compounds with a slight excess of benzoyl chloride at 110–160°, and were reduced by means of zinc dust in a mixture of acetic acid with alcohol or ethyl acetate. For the condensation of the ethers with azophor-red, a solution of the ether (1/40 mol.) in 60 c.c. of glacial acetic acid was



left with a solution of sodium acetate (1/40 mol.) and the equivalent quantity of the diazonium salt in 60 c.c. of water, and the dye was washed with 50% acetic acid and finally with water.

The condensation of the components in acetic acid solution results in the formation of *p*-benzeneazo-*p*-xylenol, in orange-yellow, sparkling prisms, m. p. 92°. The benzoate of this forms slender, orange-yellow needles, m. p. 136·5—137·5°, and yields a *hydrazo*-derivative,  $C_{21}H_{20}O_2N_2$ , in the form of white crystals, m. p. 122—123°. *o*-*p*-Bisbenzeneazo-*p*-xylenol,  $C_{20}H_{18}ON_4$ , is prepared by coupling in alkaline solution. It crystallises in brownish-violet, glistening needles, m. p. 179°, and yields a pale red acetate, m. p. 138—139°. *p*-p-Nitrobenzeneazo-*p*-xylenol methyl ether,  $C_{15}H_{15}O_3N_3$ , forms slender, bluish-red needles, m. p. 163—164°.

*p*-Benzeneazo-*m*-5-xylenol forms bright orange, flat needles, m. p. 104—105°, and yields a benzoate in pink, silky needles, m. p. 94—95°, whilst the white *hydrazo*-derivative obtained from the latter has m. p. 126—128°. *o*-*p*-Bisbenzeneazo-*m*-5-xylenol crystallises in masses of dark bronze-coloured needles, m. p. 146°. *p*-*m*-4-Xyleneazo-*m*-5-xylenol,  $C_{16}H_{18}ON_2$ , and the corresponding bisazo-compound,  $C_{26}H_{26}ON_4$ , are both formed by condensation in alkaline solution. The former crystallises in moss-like masses of orange-yellow needles, m. p. 124—125°, and the latter in silky, brown needles, m. p. 189—190°. *p*-Nitrobenzeneazo-*m*-5-xylenyl methyl ether,  $C_{15}H_{15}O_3N_3$ , forms violet needles, m. p. 119—120°.

*p*-Benzeneazo-*o*-3-xylenol can be obtained from dilute alkaline solutions, since the bisazo-compound is less quickly formed. It crystallises from dilute methyl alcohol, or when a solution in light petroleum is allowed to cool slowly, in orange-red, glistening prisms, m. p. 125—126°, but a pure yellow powder, m. p. 129—130°, separates when the latter solution is quickly cooled. The benzoate forms silky needles, m. p. 151—152°, and yields a *hydrazo*-derivative, m. p. 151—153°. *o*-*p*-Bisbenzeneazo-*o*-3-xylenol forms golden-brown, silky needles, m. p. 165—166°. *p*-p-Nitrobenzeneazo-*o*-3-xylenyl methyl ether crystallises in dark brick-red masses of slender needles, m. p. 142°.

*p*-Benzeneazothymol forms pure yellow needles, m. p. 95·5—96·5°, and *o*-*p*-bisbenzeneazothymol has m. p. 181°. Mazzara and Pozzetto (A., 1885, 893) described less pure products. Similarly, *p*-benzeneazocarvacrol forms orange-red leaflets, m. p. 99·5—100·5°, and the bisazo-compound dark brown plates, m. p. 158°, whereas Mazzara (A., 1885, 1132) quoted other constants.

*p*-Nitrobenzeneazo-*m*-tolyl methyl ether,  $C_{14}H_{13}O_3N_3$ , crystallises in sparkling, orange-red, flat needles and leaflets, m. p. 138°. *p*-Benzeneazo-*o*-nitro-*m*-cresol,  $C_{13}H_{11}O_3N_3$ , forms small, yellowish-brown crystals, m. p. 83—85°. Ethyl *p*-benzeneazo-*m*-cresotate,  $C_{16}H_{16}O_3N_2$ , forms orange-yellow needles.

*p*-Xylenol was nitrated in acetic acid solution by the fuming acid, and the product was distilled in steam, when the para-derivative remained behind and *o*-nitro-*p*-xylenol and *p*-xyloquinone passed over. The former was removed from the ethereal extract of the distillate by shaking with sodium carbonate solution and obtained, for the first

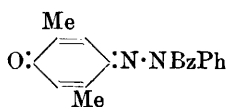
time, in the form of flat, golden yellow needles, m. p. 34—35°, b. p. 150°/15 mm. J. C. W.

**The Migration of Acid Residues in Hydrazo-compounds and Hydrazones.** K. VON AUWERS and F. MICHAELIS (*Ber.*, 1914, 47, 1297—1304).—It has already been shown that, during the reduction of acetylated benzeneazo-*p*-cresol, the acetyl group wanders from oxygen to nitrogen, whereas no rearrangement takes place in the case of the benzoyl derivative (A., 1908, i, 480). In a later paper (A., 1909, i, 436) it was demonstrated that the presence of a substituent in either nucleus prevented this transformation, except in the one instance of a methyl group in the para-position of the benzene, but not of the cresol nucleus. It is now shown that the ethyl group also permits the migration of the acetyl group. It has also been tested whether the benzoylphenylhydrazone of *p*-xyloquinone suffers the same rearrangement as the benzoylphenylhydrazone of benzoquinone, which changes into *p*-benzoxazobenzene by the action of alkalis (Willstätter and Veraguth, A., 1907, i, 453; Auwers and Eisenlohr, A., 1909, i. 915). In this case, however, the transformation is not complete after some weeks. The benzoylphenylhydrazones of the two quinones are both dimorphic.

The coupling of *p*-ethylphenol and benzenediazonium chloride proceeds smoothly in alkaline solution. *o*-Benzeneazo-*p*-ethylphenol,  $C_{14}H_{14}ON_2$ , forms lustrous, yellowish-red, silky needles, m. p. 48°, and the benzoyl derivative crystallises in orange, quadratic prisms, m. p. 86°. When this is carefully reduced in alcoholic solution by zinc dust and acetic acid, it yields *O*-benzoyl-*o*-benzenehydrazo-*p*-ethylphenol,  $C_{21}H_{20}O_2N_2$ , which forms white, slender, silky needles, m. p. 154—156°. When warmed with the reducing agents, however, hydrolysis succeeds reduction and, three of the four products, namely, aniline, benzanilide and *o*-benzanilido-*p*-ethylphenol,  $C_{15}H_{15}O_2N$ , have been isolated. The latter forms pearly leaflets, m. p. 153—154°. The acetyl derivative of the above azo-compound is liquid, but the product of reduction by sodium amalgam, namely, *N*<sup>β</sup>-acetyl-*o*-benzenehydrazo-*p*-ethylphenol,  $OH \cdot C_6H_4Et \cdot NH \cdot NAcPh$ , forms minute, white needles, m. p. 105—107°. This compound dissolves in dilute sodium hydroxide, and is, therefore, a free phenol. The position of the acetyl group is also proved by the fact that acetanilide, but not a trace of aniline, is obtained when the compound is boiled with zinc dust and dilute ammonium chloride.

*o*-*p*-Ethylbenzeneazo-*p*-ethylphenol,  $C_{16}H_{18}ON_2$ , forms flat, glistening, orange needles, m. p. 44—45°. The crude, oily acetate may be reduced by sodium amalgam to *N*<sup>β</sup>-acetyl-*o*-*p*-ethylbenzenehydrazo-*p*-ethylphenol,  $OH \cdot C_6H_4Et \cdot NH \cdot NAc \cdot C_6H_4Et$ , which forms small, white, branched needles, m. p. 94—96°, and dissolves in dilute alkali hydroxides.

A solution of *as*-benzoylphenylhydrazine in sufficient hydrochloric



acid was left with an aqueous solution of *p*-xyloquinone, when pure *p*-xyloquinonebenzoylphenylhydrazone (annexed formula) separated as a yellow compound, m. p. 122—124°, which crystallises from light petroleum in the same

form and remains unchanged during some weeks. It re-solidifies as an orange modification after melting, and this stable variety, m. p. 154—155°, crystallises when ether or dilute methyl alcohol is the solvent.

J. C. W.

**Nitrates of Hydroxyazo-compounds.** G. CHARRIER and G. FERRERI (*Gazzetta*, 1914, 44, i, 405—410).—It has been previously shown (A., 1913, i, 535, 1111, 1112, 1113) that ethers of arylazo- $\beta$ -naphthols combine with nitric acid to form nitrates which contain 2 mols. of acid and undergo diazo-decomposition, the nitro-group replacing the azo-group in the  $\beta$ -naphthol residue with formation of an aryl-diazonium nitrate and a 1-nitro-2-naphthol ether. It is now found that nitrates exhibiting analogous decomposition are given by *o*- and *p*-hydroxyazo-compounds. These nitrates usually form unstable garnet-red or brownish-red crystals with metallic lustre, and decompose violently when heated rapidly or even explode spontaneously; they are hygroscopic, and are decomposed into nitric acid and the original hydroxyazo-compounds by the action of atmospheric moisture. Alcohol, ether and, in general, organic solvents capable of dissolving nitric acid cause similar decomposition.

*p*-Benzeneazophenol nitrate,  $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot 2\text{HNO}_3$ , forms dark garnet-red leaflets, decomposing at about 75° into benzenediazonium nitrate and *p*-nitrophenol.

*p*-Toluene-*p*-azophenol nitrate,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot 2\text{HNO}_3$ , forms bright red needles or leaflets, becoming dark garnet-red when dried in a vacuum, m. p. 54—55°, and undergoes decomposition into *p*-toluenediazonium nitrate and *p*-nitrophenol at about 71°.

Benzeneazo- $\alpha$ -naphthol nitrate,  $\text{NPh}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot 2\text{HNO}_3$ , forms cantharides-green leaflets, m. p. 58—59°, and decomposes into benzenediazonium nitrate and 4-nitro-1-naphthol at about 60°.

Benzeneazo- $\beta$ -naphthol nitrate,  $\text{C}_{10}\text{H}_7\text{ON}_2\cdot 2\text{HNO}_3$ , forms reddish-brown needles, with green or golden-metallic lustre, m. p. about 40° (decomp.).

*p*-Tolueneazo- $\beta$ -naphthol nitrate,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot 2\text{HNO}_3$ , forms red needles with golden lustre, m. p. 85° (decomp.), and turns yellow at about 70° owing to the formation of 1-nitro-2-naphthol in consequence of diazo-decomposition.

T. H. P.

***o*-Hydroxyazo-compounds Derived from  $\alpha$ -Naphthol.** G. CHARRIER and L. CASALE (*Atti R. Accad. Sci. Torino*, 1914, 49, 477—496).—When benzenediazonium chloride acts on an alcoholic solution of  $\alpha$ -naphthol, a mixture of 2-benzeneazo-1-naphthol and 4-benzeneazo-1-naphthol is obtained, from which the former can be separated by reason of its insolubility in 4% sodium hydroxide. 2-*p*-Tolueneazo-1-naphthol can be prepared similarly.

2-*o*-Methoxybenzeneazo-1-naphthol,  $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$ , forms red leaflets of golden lustre, m. p. 180—181° (softening at 178°). It gives a reddish-violet coloration with concentrated sulphuric acid. Its methyl ether,  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$ , forms bright red prisms, m. p. 90—91°, and gives a red coloration with sulphuric acid. Its acetyl derivative,  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{N}_2$ , crystallises in red needles, m. p. 106°.

4-*o*-Methoxybenzeneazo-1-naphthol,  $C_{17}H_{14}O_2N_2$ , forms garnet-red leaflets of green or golden lustre, and has m. p.  $173^\circ$  (decomp.). It gives an indigo-blue coloration with concentrated sulphuric acid, and dissolves even in dilute acids (giving violet solutions) and alkalis (giving red solutions). Its *methyl ether*,  $C_{18}H_{16}O_2N_2$ , forms orange-yellow leaflets, m. p.  $121-122^\circ$ . The *ethyl ether*,  $C_{19}H_{18}O_2N_2$ , crystallises in orange-yellow needles, m. p.  $84^\circ$ . The *acetyl* derivative,  $C_{19}H_{16}O_3N_2$ , forms red needles, m. p.  $92^\circ$ . The *benzoyl* derivative,  $C_{24}H_{18}O_3N_2$ , crystallises in yellowish-brown needles, m. p.  $140^\circ$ .

2-*o*-Methoxybenzeneazo-1-naphthol can be obtained also from  $\beta$ -naphthaquinone and *o*-anisilhydrazine.

2-*p*-Methoxybenzeneazo-1-naphthol crystallises in garnet-red leaflets, m. p.  $127-128^\circ$  (softening at  $113^\circ$ ). It dissolves in concentrated sulphuric acid, giving a red coloration. On reduction it yields *p*-anisidine and 2-amino-1-naphthol. Its *sodium* salt forms red leaflets. The *acetyl* derivative,  $C_{19}H_{16}O_3N_2$ , forms orange-yellow needles, m. p.  $178^\circ$ .

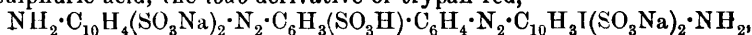
4-*p*-Methoxybenzeneazo-1-naphthol,  $C_{17}H_{14}O_2N_2$ , forms cantharides-green needles or golden leaflets, m. p.  $168^\circ$  (decomp.; softening at  $165^\circ$ ). It gives a blue coloration with concentrated sulphuric acid. The *sodium* salt forms golden leaflets. The *methyl ether*,  $C_{18}H_{16}O_2N_2$ , crystallises in reddish-yellow needles, m. p.  $134^\circ$ . The *ethyl ether*,  $C_{19}H_{18}O_2N_2$ , forms orange-yellow needles, m. p.  $128^\circ$ . The *acetyl* derivative,  $C_{19}H_{16}O_3N_2$ , forms yellow needles, m. p.  $119^\circ$ .

2-*o*-Ethoxybenzeneazo-1-naphthol,  $C_{15}H_{16}O_2N_2$ , crystallises in red needles, which have a green lustre, and have m. p.  $162^\circ$  (softening slightly about  $159^\circ$ ). Concentrated sulphuric acid dissolves it with production of a red coloration tinged with violet. The *acetyl* derivative,  $C_{20}H_{18}O_3N_2$ , forms red needles, m. p.  $77-78^\circ$ .

4-*o*-Ethoxybenzeneazo-1-naphthol,  $C_{18}H_{16}O_2N_2$ , crystallises in dark garnet-red needles, m. p.  $160-161^\circ$ . It gives an indigo-blue coloration with concentrated sulphuric acid. The *methyl ether*,  $C_{19}H_{18}O_2N_2$ , forms bright red, prismatic crystals, m. p.  $91^\circ$ . The *ethyl ether*,  $C_{20}H_{20}O_2N_2$ , forms red needles, m. p.  $98^\circ$ . The *acetyl* derivative,  $C_{20}H_{18}O_3N_2$ , crystallises in red needles, m. p.  $101^\circ$ . The *benzoyl* derivative,  $C_{25}H_{20}O_3N_2$ , forms red needles, m. p.  $111^\circ$ . R. V. S.

**Preparation of Compounds of Trypan-red with Iodine and Other Substances.** ROBERT B. KRAUSS (*J. Amer. Chem. Soc.*, 1914, 36, 961-970).—Lewis (*Arch. Intern. Med.*, 1912, 10, 68) has found that trypan-red and certain other dyes have a more or less selective affinity for different portions of the tuberculous tissue produced experimentally in the rabbit. It was considered that owing to this fact it might be possible to distribute various physiologically active substances, such as iodine, to the diseased tissue. Compounds of trypan-red containing iodine in the molecule have therefore been prepared.

On treating trypan-red with potassium iodide and water and adding sulphuric acid, the *iodo*-derivative of trypan-red,



is produced as a crimson powder. *Di-iodo-trypan-red*,

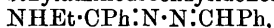
$\text{NH}_2 \cdot \text{C}_{10}\text{H}_3\text{I}(\text{SO}_3\text{Na})_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_3\text{I}(\text{SO}_3\text{Na})_2 \cdot \text{NH}_2$ , obtained by the action of an alcoholic solution of iodine on trypan-red in presence of mercuric oxide, is a red dye. A compound of trypan-red with iodoform was obtained as a dark brown substance. *Tetraiodo-trypan-red*,  $\text{C}_{32}\text{H}_{16}\text{N}_4\text{O}_{15}\text{S}_5\text{Na}_4\text{I}_4$ , obtained by the Sandmeyer reaction is also dark brown; when dissolved in 20% sodium hydroxide and treated with chlorine, it is converted into *di-iodo-di-iodoso-trypan-red*,

$\text{IO} \cdot \text{C}_{10}\text{H}_3\text{I}(\text{SO}_3\text{Na})_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_3\text{I}(\text{SO}_3\text{Na})_2 \cdot \text{IO}$ . Condensation products of trypan-red were obtained with phenol, *o*-, *m*- and *p*-cresols, thymol, guaiacol, pyrrole, and cineole, and their iodine derivatives were prepared. *Dicinnamoyldi-o*-, *-m*-, and *-p-cresol-trypan-reds*, and the corresponding *dicinnamoyldi-tri-iodo-cresol-trypan-reds* are also described. E. G.

**The Reactions of Benzoylbenzylidenehydrazide Chloride and of Dibenzoylhydrazide Dichloride.** R. STOLLÉ and FR. HELWERTH (*Ber.*, 1914, 47, 1132—1141).—Dibenzoylhydrazide dichloride has already been shown to condense with bases producing cyclic compounds (Stollé and Thomä, A., 1906, i, 461; Stollé and Weindel, *ibid.*, 707), and it is now shown that benzoylbenzylidenehydrazide chloride also reacts similarly with bases forming open-chain compounds which can undergo transformation into cyclic substances.

Benzoylbenzylidenehydrazide chloride,  $\text{CPhCl}:\text{N}:\text{N}:\text{CHPh}$  (compare Stollé, A., 1912, i, 504), was prepared by passing chlorine into a cold solution of benzaldazine in carbon tetrachloride; the liquid, after the removal of the separated benzaldazine hydrochloride, was evaporated in a vacuum, when pure benzoylbenzylidenehydrazide chloride, m. p. 57°, remained. When a boiling alcoholic solution of this substance was treated with dry ammonia, ammonium chloride separated, whilst *benzoylbenzylidenehydrazidine*,  $\text{NH}_2 \cdot \text{CPh}:\text{N}:\text{N}:\text{CHPh}$ , yellow needles, m. p. 134°, together with some diphenyltetrazine was formed in the solution. If the separation and treatment of the soluble portion of the products is protracted, 2:5-diphenyl-1:3:4-triazole is almost alone obtained.

Interaction of benzoylbenzylidenehydrazide chloride and ethylamine in the presence of benzene in a sealed tube at the ordinary temperature gave rise to *a-ethylaminodibenzylidenehydrazine*,

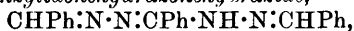


as an oil; *hydrochloride*, m. p. 106°. This was accompanied by some 2:5-diphenyl-1-ethyl-1:3:4-triazole, needles, m. p. 159°, which becomes the main product at 100°, and a little diphenyltetrazine.

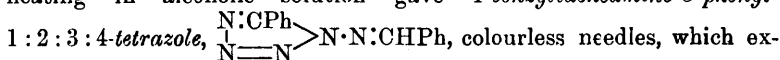
With an ethereal solution of aniline at the ordinary temperature, benzoylbenzylidenehydrazide chloride slowly reacted, giving *a-anilino-dibenzylidenehydrazine*,  $\text{NHPh}:\text{CPh}:\text{N}:\text{N}:\text{CHPh}$ , a yellow, crystalline powder, m. p. 126°. In boiling benzene solution the only product of the reaction was 1:2:5-triphenyl-1:3:4-triazole, which also appeared to a small extent as a by-product at the ordinary temperature.

On shaking an ethereal solution of benzoylbenzylidenehydrazide chloride with hydrazine hydrate there was obtained *a-hydrazino-dibenzylidenehydrazine*,  $\text{NH}_2 \cdot \text{NH}:\text{CPh}:\text{N}:\text{N}:\text{CHPh}$ , silvery leaflets,

m. p. 175—185° (decomp.), according to the rate of heating. When an alcoholic suspension of this substance was heated with benzaldehyde, *benzoyldibenzylidenehydrazonohydrazide*,



greyish-yellow needles, m. p. 113°, was formed; the *hydrochloride*, canary-yellow crystals, m. p. indistinct near 145°, was also obtainable by the action of hydrochloric acid on *α*-hydrazinodibenzylidenehydrazine in the cold. The action of an aqueous solution of sodium nitrite and dilute hydrochloric acid on an alcoholic-ethereal suspension of this last-named hydrazine base converted it into *α*-azoiminodibenzylidenehydrazine,  $\text{CPhN}_3\text{:N:N:CHPh}$ , yellow needles, m. p. 72°, which on treatment in the cold with an alcoholic solution of sodium ethoxide lost the azoimide group with formation of sodium azoimide and *α*-hydroxydibenzylidenehydrazine,  $\text{OH}\cdot\text{CPh:N:N:CHPh}$ , and on heating in alcoholic solution gave 1-benzylideneamino-5-phenyl-

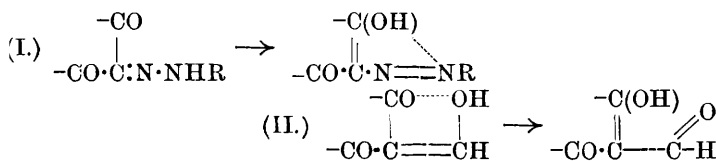


plodes feebly on rapid heating above its m. p., 105°. The benzylidene radicle can be removed from this product by heating with hydrochloric acid, the structure of the resulting 1-amino-5-phenyl-1:2:3:4-tetrazole,  $\begin{array}{c} \text{N:CPh} \\ | \\ \text{N}=\text{N} \end{array} > \text{N}\cdot\text{NH}_2$ , m. p. 155°, being confirmed by treatment with nitrous acid, which gave rise to 5-phenyltetrazole, m. p. 213°, and nitrous oxide.

The only products obtained from the interaction of benzoylbenzylidenehydrazide chloride and phenylhydrazine whether in cold ethereal solution or without a solvent were benzaldehydephenylhydrazone and 3:6-diphenyl-1:2:4:5-tetrazine, the latter being also formed in the action with ammonia and ethylamine.

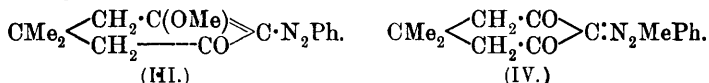
When an ethereal solution of dibenzoylhydrazide dichloride was heated with an excess of ethyl sodiomalonate for 20 hours under reflux, there was produced the *azine* of *ethyl benzoylmalonate*,  $\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{CPh:N:N:CPh}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , yellow, prismatic crystals, m. p. 103°. D. F. T.

**Rearrangement of, and Salt Formation by, Hydrazoketones.** I. LIFSCHITZ (*Ber.*, 1914, 47, 1401—1407).—By reason of enolisation and the activity of partial valencies, hydrazodiketones should exhibit polychromism, like the oximino-ketones (A., 1913, i, 1361), the rearrangement into coloured azo-enols being represented by the scheme (I).



An analogous rearrangement of hydroxymethylenediketones (II), however, would cause no important changes in the chromophoric

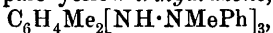
groups. It has indeed been found that the yellow hydroxymethyleneindanedione (Errera, A., 1903, i, 854) and its sodium salt are optically identical, whereas the yellow condensation product of dimethyldihydroresorcin with benzenediazonium chloride forms orange-yellow to red salts. In the latter case it has also been possible to prepare the methyl derivatives of both forms. The red methyl ether of the condensation product is easily degraded by reduction into aniline and a primary base and is therefore of the azo-enol type (III), whereas the isomeric phenylmethylhydrazone (IV) obtained by the action of phenylmethylhydrazine on dibromodimethyldihydroresorcin is white.



The absorption spectrum shows that the yellow condensation product with diazonium chloride is itself an azo-enol, whereas Baly, Tuck and Marsden (T., 1907, 91, 1572) were of the opinion that only the salts of such compounds are azo-enolic.

*Benzeneazodimethyldihydroresorcin*,  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$ , crystallises from alcohol in sulphur-yellow, thick prisms, m. p.  $146^\circ$ . It decomposes alkali carbonates, and forms yellow *ammonium* and *pyridine* salts, yellowish-orange to reddish-orange *sodium* and *potassium* salts, and a dark red *silver* salt. The *methyl ether* (III.) is best prepared by the action of methyl sulphate, and forms red prisms, m. p.  $143^\circ$ .

2:2-Dibromodimethyldihydroresorcin (Haas, T., 1906, 89, 189) reacts vigorously with *as*-phenylmethylhydrazine in cold, alcoholic solution, yielding the pale yellow *trihydrazone*,



m. p.  $224^\circ$ , together with much red resin. The hydrochloride of the base gives rise only to resin. In pyridine, a mixture of the mono- and tri-hydrazone is obtained, but the *hydrazodiketone* (IV.) is best prepared by the action of the base in alcoholic solution in presence of potassium ethoxide. It is more soluble than the trihydrazone in benzene, and forms soft, snow-white leaflets, m. p.  $179^\circ$ .

J. C. W.

**Protein Precipitation by Protein.** BETH AF UGGLAS (*Biochem. Zeitsch.*, 1914, 61, 469—505).—The author has carried out a detailed study of the precipitation of proteins by caseinogen and hæmoglobin. These particular proteins have been chosen as it is possible to readily determine the composition of the precipitates, in the former case by phosphorus estimations, and in the latter case colorimetrically, by a method described fully. As a result of examinations of precipitates produced by very varied methods of precipitation, the author draws the following conclusions. The precipitates, within certain narrow limits, have a constant composition when produced (a) by hæmoglobin when in excess, or when in such quantity as is just necessary to precipitate the basic protein; (b) by caseinogen by excess both of this and the basic protein; by choosing in this case the correct proportions, both proteins are precipitated quantitatively. The composition in these cases is independent of the method of precipitation. An excess of non-

basic protein dissolves the precipitate. The components of the precipitate cannot be precipitated from a solution separately by precipitating reagents. The hæmoglobin-caseinogen precipitate forms, however, an exception to this rule. The author discusses in detail the nature of the protein precipitates, and inclines to the view that they are chemical compounds of proteins with one another, rather than adsorption complexes. S. B. S.

**The Methylation of Proteins.** J. HERZIG and K. LANDSTEINER (*Biochem. Zeitsch.*, 1914, 61, 458—463).—By methylation of proteins by diazomethane, products containing both NMe and OMe groups could be obtained. The reaction is specially marked in the case of Witte's peptone. S. B. S.

**Separation of Carbon Dioxide from Proteins.** FRITZ LIPPICH (*Zeitsch. physiol. Chem.*, 1914, 90, 441—488).—Estimations of the amounts of carbon dioxide liberated from various proteins when boiled with acid and with alkali. Whilst the results cannot be said to prove that the carbamide group is present in the protein molecule, they are consistent with the view of the presence of carbamide.

N. H. J. M.

**Protein Hydrolysis.** WILLIAM WYNN PRATT PITOM (*Biochem. J.*, 1914, 8, 157—169).—Many of the simpler polypeptides are not precipitated by phosphotungstic acid, and a definite point in hydrolysis occurs at which complex polypeptides are broken down into simpler ones, most of which are not precipitable by phosphotungstic acid. It is advantageous to stop the hydrolysis here in order to isolate complex polypeptides. The results on nitrogen distribution and yield of amino-acids emphasise the difference between caseinogen and egg-albumin, which were the two proteins employed. W. D. H.

**Changes in the Physical Conditions of Colloids. XVIII. The Protein Salts of Different Acids.** WOLFGANG PAULI and MAX HIRSCHFELD (*Biochem. Zeitsch.*, 1914, 62, 245—265).—The combination of serum albumin and dialysed euglobulin-free serum of horse, gelatin, and deamino-gelatin with hydrochloric, sulphuric, and acetic acids has been studied by the electrometric method. The amount of combination for strong acids can be calculated from the equation  $n' = n - C_H/a$ , where  $n'$  denotes the combined and  $n$  the original acid concentration,  $C_H$  the measured hydrion concentration, and  $a$  the dissociation grade in concentration  $n$ . For a weaker acid (acetic acid) the following formula was deduced:  $C_{CH_3COO} = k(n - C_H) - C_H^2/k + C_H$ , where  $k$  is the dissociation constant of acetic acid. In addition, the hydrolytic dissociation of the acid salts was determined. Information on this point was obtained by the measurement of bound acid in varying dilutions of the same mixture. A measurement of hydrolytic dissociation was also possible by a graphical method. As acid is added to the protein solution a point is attained where a maximum of combination occurs, which takes place only in presence of excess of acids. If the added acid is plotted on the abscissa and combined acid on the



ordinate, the difference between the length of the ordinate at any point on the curve, when sufficient acid for maximum combination has been added, and the ordinate representing maximal combination, will give a measure of the amount of hydrolytic dissociation. If  $k_b$  is the constant of the mean basic dissociation of the protein (the protein being considered as a substance with several basic valencies) then  $k_b = k\omega(1-x).v/x^2$ , where  $x$  is the grade of hydrolysis, and  $v$  the concentration in volumes. If the molecular weight of the protein be taken to be between 1000 and 10,000, a number is obtained experimentally for  $k_b$ , which is about the order of that of the basic dissociation constant to be expected for the basic dissociation constant of the higher polypeptides. The dynamics of the protein-acetate (considered as a buffer mixture) are also treated by the authors. S. B. S.

**Precipitation of Protein by Zinc Sulphate. II.** F. LIPPICH (*Zeitsch. physiol. Chem.*, 1914, 90, 236—249. Compare A., 1911, i, 934).—Another series of experiments with horse-serum and zinc sulphate, similar to those formerly described but with a greater concentration of protein, confirms the conclusions then arrived at in regard to the stoicheiometric as opposed to the adsorptive character of the compounds formed: in this case, however, the compounds are of the type  $\text{ZnO-protein-ZnSO}_4$ , which, like the simpler type (protein- $\text{ZnSO}_4$ ) revealed in the earlier experiments, has been found also in the case of the amino-acids and of the polypeptides.

Precipitates obtained under different conditions in the neighbourhood of the other maximum referred to in the former paper can be analysed directly and are found to have a constant composition, thus affording further support of the views advanced thereon.

The author replies to the criticism of Pauli and Flecker (A., 1912, i, 668). R. V. S.

**Fibrin in its Relation to Problems of Biology and Colloidal Chemistry. The Problem of Blood Coagulation.** E. HEKMA (*Biochem. Zeitsch.*, 1914, 62, 161—179).—A number of experiments are described by means of which clots can be obtained from fibrin. If the latter is dissolved in either alkali or acid, acid or alkali, on addition to the solutions until they are neutral, produce precipitation, and the precipitates thus produced are gradually converted into fibrous gels resembling the ordinary blood-clot. The original precipitate is soluble in excess of acid or alkali, and these solutions on neutralisation produce phenomena similar to the original fibrin solutions. The author is of the opinion that the solution in acid or alkali does not produce a degradation product of the fibrin; he is rather of the opinion the acid or alkali converts this substance into the form of a sol, which in certain circumstances can be converted into a gel, and that fibrin itself is to be regarded as a reversible gel. S. B. S.

**Production of Casein from Caseinogen.** SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1914, 8, 152—153).—Harden and Macallum state that cleavage of nitrogen, phosphorus, and calcium occurs in the conversion of caseinogen into casein. This does not accord with the

author's results, nor with those of Bosworth. The discrepancy can be explained by the fact that they used a solution of the basic calcium caseinogenate, whereas the author employed a saturated solution of caseinogen in lime water. The author still holds, although he admits he does not prove, that casein is a compound of caseinogen and rennin, but agrees with Harden and Macallum that casein formation is irreversible.

W. D. H.

**Constitution of the Colouring Matter of Blood. Coloured Dipyrromethane Derivatives.** II. O. PILOTY, J. STOCK, and E. DORMANN (*Ber.*, 1914, **47**, 1124—1230).—In a previous communication (this vol., i, 327) the formation of coloured substances closely related to bilirubin by the condensation of hæmopyrrole-*b* and phorpholecarboxylic acid-*a* with chloroform has been described. By the use of perchloroethane, the authors have attempted to prepare substances of the type  $\begin{matrix} \text{A} > \text{C} - \text{C} < \text{B} \end{matrix}$  (where A is  $\text{N} \begin{matrix} \text{CR} \cdot \text{CR} \\ \text{=C} - \text{CR} \end{matrix}$

and B is  $\text{NH} \begin{matrix} \text{CR} \cdot \text{CR} \\ \text{=C} - \text{CR} \end{matrix}$ ). Under suitable conditions, hæmopyrrole-*b* and perchloroethane yield a crystalline dye which is identical with di(4:5-dimethyl-3-ethylpyrrol)methane previously obtained by use of chloroform. Simultaneously amorphous dyes are obtained, the spectra of which approximate closely to those of certain chlorophyll derivatives, notably phytochlorin-*a*. These dyes probably belong to the type indicated above, but attempts to purify them have been unsuccessful.

Preliminary attempts have also been made to condense 4:5-dimethylpyrrole-3-carboxylic acid with formaldehyde with the object of obtaining a dye by the oxidation of the condensation product. The latter process, however, does not take place in a simple manner.

2:5- and 2:4-Dimethylpyrrole condense with chloroform in the same manner as hæmopyrrole-*b*, whilst their monocarboxylic acid yields products with formaldehyde which can be oxidised to similar dyes.

Dyes similar to the above type are directly obtainable from the pyrroles by the action of chloral and glyoxal.

Di(4:5-dimethyl-3-ethylpyrrol)methane hydrochloride is obtained when hæmopyrrole is heated with perchloroethane and aqueous alcoholic potassium hydroxide at 185—200°, and the product acidified with hydrochloric acid. The course of the reaction depends greatly on the temperature employed; below 185° and about 200°, the crystalline hydrochloride is not formed, and the nature of the amorphous dye obtained at 185—190° differs from that obtained between 190° and 200°. In two experiments, one at 185—190°, the other at 200°, two dyes similar in appearance but differing in spectrum were obtained, neither of which, however, could be obtained in the crystalline state.

When 4:5-dimethylpyrrole-3-carboxylic acid is condensed with formaldehyde (40%) in the presence of concentrated hydrochloric acid, a substance,  $\text{C}_{15}\text{H}_{18}\text{O}_3\text{N}_2$ , colourless, prismatic rods, m. p. 247° (decomp.), is obtained, which appears to be the anhydride of the expected dicarboxylic acid. Oxidation with potassium ferricyanide yields an amorphous, dark violet dye, the hydrochloride of which is a dark violet,

microcrystalline powder with a faintly green lustre. The latter has not been obtained in the pure state, but appears to have the composition,  $C_{13}H_{15}N_2Cl$ .

The ester of 3:5-dimethylpyrrole-4-carboxylic acid yields a similar condensation *product*, m. p.  $224.5^\circ$ , which can be oxidised by ferric chloride or alkaline potassium ferricyanide to a dye, red needles, m. p.  $212^\circ$ .

H. W.

**The Action of Hydrazine Hydrate on Methæmoglobin.** GEORGE A. BUCKMASTER (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, 48, xxv—xxvi).—The hydrazine method for estimating the oxygen of blood gives values identical with those obtained by the ferricyanide method of Haldane and Barcroft. It may also be used to determine the amount of oxygen liberated from methæmoglobin when this is converted into reduced hæmoglobin; but the nitrogen evolved (from which the oxygen present is deduced) is only about one-half of that yielded by oxyhæmoglobin. It would, therefore, appear that methæmoglobin contains a smaller quantity of oxygen than oxyhæmoglobin, as originally stated by Hoppe-Seyler (1877), and more recently by Küster and Letsche.

W. D. H.

**Preparation of Nucleic Acid from the Thymus of the Calf.** R. FEULGEN (*Zeitsch. physiol. Chem.*, 1914, 90, 261—270).—In the preparation of nucleic acid by the usual method, due to Neumann (A., 1900, i, 319), the evaporation in presence of sodium acetate is an essential part of the process, leading, in fact, to the removal of the remaining protein, for if the evaporation is omitted the final product gives the biuret reaction.

The author describes in detail a more rapid method (for which the original must be consulted) for the preparation of nucleic acid.

R. V. S.

**Nucleohistone. II.** H. STEUDEL (*Zeitsch. physiol. Chem.*, 1914, 90, 291—300. Compare A., 1913, i, 1116).—Different preparations of nucleohistone differ in composition. When the substance is precipitated, the nucleic acid carries with it various proteins in varying amounts. The author's experiments on the estimation of the histone in nucleohistone show that even histone cannot always be obtained in satisfactorily pure condition.

R. V. S.

**Preparation of the Therapeutically Active Constituent of the Pituitary Body in a Crystalline Form.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 268841).—The extract is completely freed from albumin, precipitated with alkaloidal precipitants such as phosphotungstic acid, phosphomolybdic acid, tannin, picric acid or a solution of iodine in potassium iodide, freed from the precipitant (for example, phosphotungstic acid) by means of barium hydroxide, and the filtrate treated with sulphuric acid. The sulphate thus obtained gives, on evaporation of the solution, pale yellow crystals, and when freed from sulphuric acid by means of barium hydroxide gives the active principle in a crystalline form when the solution is evaporated in a vacuum.

J. C. C.

**Preparation of Alkaline Albumose-Silver Compounds.**

CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 268968).

—A solution of a silver salt in ammonia is treated with albumose and the solution is evaporated to dryness in a vacuum. The products are brown and contain about 7% of silver which is not precipitated when the compounds are treated with ammonium sulphide or sodium chloride. Hydrochloric acid gives a precipitate which is dissolved when excess of the acid is added.

J. C. C.

**The Formation of a Peptone from Caseinogen by the Prolonged Action of Dilute Hydrochloric Acid in the Cold.** CASIMIR FUNK and JAMES WALTER McLEOD (*Biochem. J.*, 1914, 8, 107—109).—One kilo. of commercial caseinogen was left in contact with 5 litres of a 1% solution of hydrochloric acid for three months; the filtrate was found to contain a substance which proved to be a peptone; the yield of product obtained was 14 grams. It contained 13.35% of nitrogen, and some of the amino-acids in it were estimated. The only diamino-acid in it was lysine; the nature of the monoamino-acids is still unknown.

W. D. H.

**Pepsinglutinpeptone.** M. SIEGFRIED (*Zeitsch. physiol. Chem.*, 1914, 90, 271—285. Compare Siegfried and Schmitz, A., 1910, i, 448).—The author has applied to this substance the treatment with silver sulphate and barium hydroxide suggested by Kossel. A detailed examination of the product, by the methods formerly employed (*loc. cit.*) as well as by others, shows it to be identical with the untreated substance in all respects except rotatory power; this is less than before treatment, but the diminution may be due to racemisation by the barium hydroxide used.

R. V. S.

**Action of Pepsin and Trypsin on one Another.** EDWARD STAFFORD EDIE (*Biochem. J.*, 1914, 8, 193—203).—Excess of trypsin inhibits the action of pepsin in acid solution, but does not destroy it. The inhibition is not due to the protein associated with trypsin. This power is lost to some extent if the trypsin is previously boiled. The trypsin may combine with the protein without digesting it, and thus the pepsin cannot act on the protein. The converse action of pepsin on trypsin is not so marked, and its inhibiting power is largely destroyed by heat. The action is explained in the same way.

W. D. H.

**Mutual Action of Certain Digestive Ferments.** J. H. LONG and G. W. MUHLEMAN (*Arch. Internat. Med.*, 1914, 13, 314—318).—It is shown that whilst pepsin has some action on amylopsin, the action is not always as distinct with commercial specimens owing to the varying amounts of inorganic salts present. The salts may neutralise the small amount of acid and so prevent the pepsin being activated. In the normal action in the body no action of the pepsin on amylopsin is likely to occur, owing to neutralisation; some destruction of amylopsin may, however, occur in the stomach.

The destructive action of acid on trypsin is accelerated by the presence of pepsin, the action being modified, to some extent, by the

presence of protein. The results seem to support the view that pepsin is antagonistic to the tryptic ferment under practical conditions.

N. H. J. M.

**A Thermo-stable Form of Invertase.** O. DURIEUX (*Bull. Soc. chim. Belg.*, 1914, 28, 99—101).—A series of extracts has been prepared from dried yeast, baker's yeast, brewer's yeast, and hefanol. Portions of the extracts have been heated at 50°, 70°, 80°, 90°, and at the boiling point for a minute and also under 1, 2, and 3 atmospheres' pressure, then cooled and filtered. The behaviour of the filtrates towards sucrose solution has been investigated, when it is found that the inverting power of the filtered extract is suppressed when it is heated to 80°, whilst the liquid separated from an extract which has been heated to the boiling point still shows an appreciable activity greater than that of an extract heated at 70°. The cause of the phenomenon is found in the absorption of the invertase by the coagulated protein substances, since when this coagulum is boiled with water and filtered, the filtrate is found to have inverting power.

H. W.

**The Reversibility of Invertase Action.** A. BLAGOVESTSCHENSKI (*Biochem. Zeitsch.*, 1914, 61, 446—457).—As a result of experiments on the action of the ferment on inverted sugar in various concentrations, the author draws the conclusion that there is no evidence of synthetic formation of sucrose. There is no object in attempting to discover such a synthesis in solutions weaker than 50—60% as this would be contrary to the second law of thermodynamics. The changes of the reaction rates during hydrolysis can be expressed by the equation of a unimolecular reaction, the deviations from constancy found being due to experimental errors, whilst the deviations at the end of the reaction are due to the combination of the ferment with the hydrolysis products. There is, however, a possibility of a synthesis of maltose.

S. B. S.

**Examination of the Amylolytic Diastase of the Pancreas.** P. MACQUAIRE (*Compt. rend.*, 1914, 158, 1289—1291).—An examination of the hydrolysing power of fresh pig's pancreas on potato starch during one hour under the official conditions. The amounts of pancreatic pulp were varied, as were also the amounts of starch on which they acted. The amount of starch converted into reducing sugar in one hour at 55° never exceeded 45% of the total and dropped to 38·4% when the amount of starch used was increased. Similar results were obtained with dry pancreatin. The results are drawn up in a table for use in determining the strength of amylolytic ferments, and in particular of pancreatic amylase.

W. G.

**The Behaviour of Emulsin in the Presence of Collodion.** ROY E. CLAUSEN (*J. Biol. Chem.*, 1914, 17, 413—441).—The time course for the absorption of emulsin by collodion films gives decreasing values for the unimolecular constant, and yields a curve like that for processes determined by capillary forces; fixation may be a surface condensation phenomenon. Between 25° and 45°, the temperature-

coefficient is 1.17. The absorbed enzyme can be largely regained by placing the films in solutions of the substrate, or by dissolving the collodion. The absorptive power of the films decreases with repeated use. There is no evidence that the enzyme is converted into inhibitory substances.

W. D. H.

**Action of Ricinus Lipase on Fats.** N. V. TANCOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 333—343).—The lipase used in the author's experiments was prepared by the following method, which yields the enzyme in a convenient form. The *Ricinus* seeds, freed from shell, were pounded and mixed with castor oil in the proportion 1:1 to a thick paste, which was centrifuged until the precipitate no longer separated into an upper powdery and a lower clotted layer. The upper part was then separated by means of ether, washed with water and dried over calcium chloride. Its emulsion in ether was next filtered by means of a pump, and the residue washed with ether and dried to a fine, white powder. This preparation loses its activity after about a fortnight.

A number of experiments were made on the action of the lipase on olive oil, the proportions of enzyme, oil and acid present being varied. The results show that the substrate and the products formed from it alter the behaviour of the lipase towards the activating acid, and hence form compounds with the enzyme. These compounds must be regarded as intermediate, since in presence of the products and of comparatively large proportions of substrate, the scission of fat by the lipase proceeds with concentrations of acid considerably exceeding those which arrest the reaction when the products are absent and the proportions of substrate comparatively small. The action takes place, therefore, not by means of "free" lipase, but by way of intermediate compounds of the lipase with the substrate and its products. The intermediate compounds of lipase with the products of its action are decomposed more readily by low than by high concentrations of acid, their stability diminishing with the latter to a minimum, which is found to correspond with the optimal activity of the enzyme. With high concentration of acid, the substrate and its products in the system undergo an irreversible change.

T. H. P.

**Enzyme Action. X. Lipolytic Properties of Human Duodenal Contents.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1914, 36, 1047—1057).—A study has been made of the lipolytic activity of human duodenal contents under varying conditions. Two lipases were detected, one of which, formed as a rule after the ingestion of food, was under certain conditions more active towards glyceryl triacetate than towards ethyl butyrate, whilst the other, present when food had not been taken, was more active towards ethyl butyrate than towards glyceryl triacetate. The occurrence of lipases showing similar variation in their activity towards esters has been observed by the author in the castor bean (this vol., i, 98), and by Loevenhart in extracts of the pancreas and liver of various animals (*A.*, 1907, ii, 281). The influence of several salts and alcohols on the activity of the duodenal contents towards glyceryl triacetate and ethyl butyrate was investigated.

E. G.

**The Fermentative Decomposition of Hydrogen Peroxide.** L. MICHAELIS and H. PECHSTEIN (*Biochem. Zeitsch.*, 1914, 62, 295—298).—A reply to Waentig and Steche (this vol., i, 605).

S. B. S.

**Reduction of 3:5-Dinitro-4-aminophenylarsinic Acid.** L. BENDA (*Ber.*, 1914, 47, 1316—1318).—The above acid (A., 1912, i, 328) has been reduced by the addition of ferrous chloride to an alkaline solution. The product, 3:4:5-triaminophenylarsinic acid,  $C_6H_{10}O_3N_3AsH_2O$ , crystallises from boiling water in colourless needles, decomp. 170—175°, and dissolves in dilute mineral acids, alkali hydroxides or carbonates and ammonia. The compound may be transformed into 3:4:5:3':4':5'-hexaminoarsenobenzene, which is the product when the reduction of the nitro-compound is performed in acid solution (compare Boehringer & Söhne, P.-A.B. 66891).

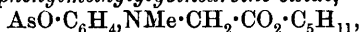
J. C. W.

**Action of Arsenic Trichloride on Monoalkylaromatic Bases and on Phenylalkylglycine Esters.** KARL ÖCHSLIN (*Ann. Chim.*, 1914, [ix], 1, 239—251).—The author has prepared a number of new phenyl- and tolyl-alkylaminoacetic esters and studied their reactions with arsenic chloride, and also the reactions of monoalkylaromatic amines with the latter substance (compare Michaelis, 1902, i, 411, 515).

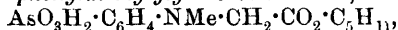
On warming dimethylaniline with propyl chloroacetate at 150—225°, *propyl phenylmethyldaminoacetate*,  $NMePh \cdot CH_2 \cdot CO_2Pr$ , b. p. 175°/24 mm., is obtained. Other esters have been similarly prepared as under: *amyl phenylmethyldaminoacetate*, b. p. 179—181°/17 mm. and 300—302°/760 mm.; *amyl phenylethyldaminoacetate*, b. p. 187°/18 mm.; *amyl phenylamylaminoacetate*, b. p. 215—216°/20 mm.; *ethyl o-tolylmethyldaminoacetate*, b. p. 146—150°/16 mm.; *amyl o-tolylmethyldaminoacetate*, b. p. 180—182°/17 mm. and 298°/760 mm.

*Phenylmethyldaminoacetic acid* is obtained as a crystalline mass, m. p. 95—100°, on hydrolysing any of its esters with fuming hydrochloric acid, dissolving the hydrochloride formed in water, and extracting with ether, which solvent is then allowed to evaporate, leaving the free acid.

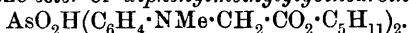
In condensing these substances with arsenic trichloride the presence of some dry pyridine is found materially to favour the action. Arsenic trichloride (150 grams), amyl phenylmethyldaminoacetate (200 grams), and pyridine (70 grams) are heated for two and a-half hours at 100—112°. The product is poured on to ice before it solidifies, and washed with water. The oily layer is dissolved in ether and shaken with a solution of sodium carbonate and some hydrogen peroxide. The amyl ester of *phenylmethyldaminoarsinic acid*,



separates in a crystalline form, m. p. 133—134°. On adding hydrochloric acid to the sodium carbonate solution an oil separates, which slowly crystallises, and is separable by means of warm acetic acid into the amyl ester of *phenylmethyldaminoarsinic acid*,

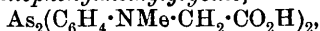


m. p. 118°, and the ester of *diphenylmethylglycinearsinic acid*,



Similarly there have been prepared the *ethyl* ester, m. p. 169°, and the *propyl* ester, m. p. 154°, of phenylmethylglycinearsinic acid, and the *amyl* ester, m. p. 107°, of the corresponding *o*-tolyl acid.

*Phenylmethylglycinearsinic acid* is obtained by saponifying one of its esters with sodium hydroxide and acidifying the solution with acetic acid. It decomposes at 180°. On warming for three hours at 50–55° with *N*-sodium hydroxide and sodium hyposulphite solution, this acid is converted into *arsenophenylmethylglycine*,



a yellow powder, moderately stable in air, soluble in alkali carbonates, from which solutions alcohol precipitates the alkali salt as a pale yellow powder stable in air and soluble in water.

*Diphenylmethylglycinearsinic acid*,  $\text{AsO}_2\text{H}(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , is prepared by saponifying its esters, and it decomposes at 180–190°. Two other acids have been similarly prepared: *phenylethylglycinearsinic acid*, decomposing at 178°, and *phenylamylglycinearsinic acid*, decomposing at 180°.

The monoalkylanilines react similarly with arsenic trichloride in the presence of pyridine, giving the corresponding alkylaminophenylarsinic acids and small quantities of dialkylaminodiphenylarsinic acids, which are removed by precipitating the solutions of the sodium salts with alcohol. *Ethylaminophenylarsinic acid* decomposes at 190°, and *amylaminophenylarsinic acid* decomposes at 182°.

From experiments performed it appears that *arsenophenylmethylglycine* has a remarkable activity in the cases of infection of mice by *Tryp. Evansii* and *Tryp. Rhodesiense*. The drug applied by hypodermic injections has apparently no detrimental effect on mice and guinea-pigs.

W. G.

**Preparation of Reduction Products of Organic Arsenic Compounds.** HEINRICH BART (D.R.-P. 270568).—Organic derivatives of arsenic or arsenious acids can be electrolytically reduced in alkaline, neutral or acid solution.

J. C. C.

**Preparation of 3:3'-Dinitro-4:4'-dihydroxyarsenobenzene.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269886, 269887. Compare D.R.-P. 206456, A., 1909, i, 347).—3:3'-Dinitro-4:4'-dihydroxyarsenobenzene is obtained by reducing 3-nitro-4-hydroxyphenylarsinic acid or the corresponding arsenoxide by means of stannous chloride (1st patent), or hypophosphorous acid (2nd patent). The compound is a bright yellow powder which inflames when dry.

J. C. C.

**Preparation of Arseno-metallic Derivatives.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270253, 270256, 270257. Compare this vol., i, 345).—(I) Compounds similar to those described in the chief patent (268220, *loc. cit.*) are obtained by treating 3:3'-diamino-4:4'-dihydroxyarsenobenzene with salts of mercury, silver, or copper.



(II) The polyarseno-compounds obtained by reducing a mixture of an arsenic acid and an inorganic arsenic compound (D.R.-P. 270254, this vol., i, 609) may be used instead of 3 : 3'-diamino-4 : 4'-dihydroxy-arsenobenzene in the above reaction.

(III) Similar compounds to the above are obtained from arsenophenylglycine and gold chloride, the sodium derivative of 4 : 4'-dihydroxyarsenobenzene and gold chloride, arsenobenzene and silver nitrate, and sodium 3 : 4 : 3' : 4'-tetra-aminoarsenobenzeneformaldehydesulphoxylate.  
J. C. C.

**Preparation of Amino-derivatives of Primary Aromatic Antimony Compounds.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 270488).—The compounds are prepared by reducing the corresponding nitro-derivatives or by hydrolysing the acylamino-derivatives.

*p*-Aminophenylstibinic acid is obtained by hydrolysing the acetyl compound with 5% sodium hydroxide. On heating it decomposes without melting. It decomposes gradually on keeping, but the sodium salt is more stable. *m*-Aminophenylstibine chloride hydrochloride, prepared by treating *m*-nitrophenylstibinic acid with stannous chloride and hydrochloric acid, forms white leaflets, m. p. 215°. On oxidising its alkaline solution with hydrogen peroxide, *m*-aminophenylstibinic acid is obtained.

3-Amino-4-hydroxyphenylstibinic acid is obtained by reducing the nitro-acid with sodium hyposulphite. It is unstable and decomposes on heating. The sodium salt is also mentioned.  
J. C. C.

**Preparation of Derivatives of Bismethylaminotetra-aminoarsenobenzene which are Readily Soluble in Water with a Neutral Reaction.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 269660).—The substance dissolves readily in aqueous alkali or ammonium hydrogen carbonate solutions to form compounds (probably carbamates), which can be isolated by precipitation with alcohol or acetone, and are readily soluble in water.  
J. C. C.

**Mechanism of the Grignard Reaction.** LAMBERT THORP and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1914, 36, 1022—1028).—In accordance with Stadnikov's oxonium theory of the constitution of organo-magnesium compounds (*A.*, 1911, i, 435; 1912, i, 109, 971, 972; 1913, i, 1183, 1335), it should be possible to obtain an oxonium compound of the type  $\begin{matrix} R^1 \\ R^2 \end{matrix} > O < \begin{matrix} R^1 \\ MgX \end{matrix}$  in two different ways: (1) from  $R^1 \cdot O \cdot R^1$  and  $R^2X$ , and (2) from  $R^1 \cdot O \cdot R^2$  and  $R^1X$ .

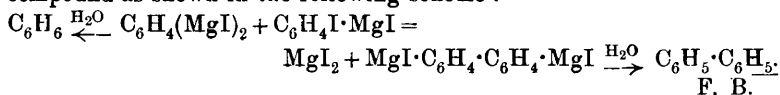
In order to test this question, experiments have been made on the action of magnesium on (1) a mixture of diethyl ether and bromobenzene, and (2) a mixture of phenetole and ethyl bromide. The product resulting from the former reaction when decomposed with dilute sulphuric acid yielded benzene (61% of the theoretical), diphenyl, ether, hydrogen, and a small quantity of hydrocarbon insoluble in fuming sulphuric acid, and when decomposed with carbon dioxide it furnished benzoic acid, but no propionic acid.

In the second case, the product on decomposition with dilute

sulphuric acid yielded ethane (97% of the theoretical), and on decomposition with carbon dioxide gave propionic acid. These results indicate that the compounds formed in the two cases are not identical, and they are therefore at variance with Stadnikov's theory. It is not necessary to assume an oxonium structure to account for the decomposition products obtained in these experiments, but if the assumption of such a structure is desired, the Baeyer-Villiger formula is preferable to Stadnikov's.

E. G.

**The Grignard Reaction with Aromatic Polyhalogen Derivatives.** E. VOROČEK and J. KÖHLER (*Ber.*, 1914, **47**, 1219—1221. Compare Bodroux A., 1904, i, 216. Gomberg and Cone, A., 1906, i, 822).—The authors have investigated the behaviour of a number of polyhalogenobenzenes towards magnesium in ethereal solution in order to determine to what extent the ability to form magnesium compounds depends on the nature of the halogen atoms in the molecule and whether it is possible for more than one halogen atom to enter into reaction with the magnesium. They find that whilst *o*-bromiodobenzene, the three di-iodobenzenes, and 2:4-dichloro-1-iodobenzene yield magnesium compounds, 2:4-dichloro-1-bromobenzene and 1:2:4-tribromobenzene do not react with magnesium, and hence draw the conclusion that the presence of more negative halogen atoms in the molecule diminishes, and finally suppresses the ability of the less negative halogen atom to enter into reaction with the magnesium. The possibility of more than one halogen atom reacting with magnesium has been investigated in the case of *p*-di-iodobenzene. When heated for twelve hours in ethereal solution and the resulting magnesium compound decomposed by water, the di-iodobenzene yields *p*-iododiphenyl, benzene and diphenyl, the formation of the two last-named substances being due to the decomposition of a dimagnesium compound as shown in the following scheme:



### Physiological Chemistry.

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**A Microrespiration Apparatus and Some Investigations therewith on the Temperature-metabolism Curve of Chrysalides.** AUGUST KROGH (*Biochem. Zeitsch.*, 1914, 62, 266—279).—The apparatus is constructed on the principle of that used by Barcroft for blood-gas analysis by the differential method. It consists of a capillary manometer fixed to a millimetre scale. Both limbs of the manometer are connected to pressure tubing at the upper end, which can be closed by the same screw-clip. Behind each limb below the rubber is a branched tube, which connects with flasks,

in one of which is placed the animal under observation, whilst the other serves as a control. These are immersed in a constant temperature bath. Dilute sodium hydroxide is used to absorb the carbon dioxide expired by the animal, and by the rise of the liquid (light petroleum or any other convenient substance) in one limb, the oxygen consumption can be calculated by a formula given by the author. The apparatus has been applied to measure the effect of temperature on the respiratory exchanges of *Tenebrio chysalides*.  
S. B. S.

**The Photo-activity of the Blood.** V. SCHLAEPFER (*Zeitsch. Biol.*, 1914, **63**, 521—530).—The blood of pigmented and albino rabbits affects a sensitive photographic plate in from sixteen to twenty hours. This is due to the red corpuscles, and especially to those rich in oxyhæmoglobin; oxygen increases and carbon dioxide lessens the effect; putrefaction abolishes it. This effect is not attributed to emission of rays of light from the blood, and so is not true photo-activity, but probably depends on the production of hydrogen peroxide. Further work on the conditions which lead to and influence the formation of hydrogen peroxide is contemplated.  
W. D. H.

**Constricting Action of Adrenaline on Cerebral Vessels.** CARL J. WIGGERS (*J. Physiol.*, 1914, **48**, 109—112).—The present experiments on the completely isolated brain perfused with Locke's solution show that in eight experiments out of thirteen a diminution of outflow amounting to a few millimetres occurred when adrenaline was added to the fluid. The paper is a reply to criticisms made by Dixon and Halliburton on the author's previous work (*A.*, 1905, ii, 846).  
W. D. H.

**The Different Circumstances of Adrenaline Action on Peripheral Vessels.** W. A. SVETSHNIKOV (*Pflüger's Archiv*, 1914, **157**, 471—485).—The constriction of blood vessels by adrenaline occurs at high pressures in the same degree as at normal blood pressure. No signs of immunity were noticed. Adrenaline is rapidly destroyed when dissolved in Locke's solution, especially when warmed; this is lessened by the addition of blood serum. At 36—39° the pressor action of adrenaline is less marked than at room temperature; at 41—46° vaso-dilatation may be produced; 4- $\beta$ -aminoethylglyoxaline is more resistant in solution than adrenaline, and its action on the vessels is more marked and lasts longer.  
W. D. H.

**The Creatinine and Creatine Content of Blood.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.* 1914, **17**, 487—491).—In 200 patients no case of creatinine retention (analogous to uric acid retention in gout) occurred. The kidneys remove creatinine from the blood with remarkable ease and certainty, except in conditions approaching anuria. The figure in normal human blood is about 1 mg. of creatinine, and 6—8 mg. of creatine + creatinine per 100 grams of

blood. In the common domestic animals the figures are approximately the same; in birds the creatinine figure is 0.1 mg., and the creatine + creatinine higher, namely, 11. W. D. H.

**Factors Affecting the Coagulation Time of Blood.** W. B. CANNON, W. L. MENDENHALL, and HORACE GRAY (*Amer. J. Physiol.*, 1914, **34**, 225—261).—Coagulation was observed under constant conditions, and its onset marked by a recorder attached to a weight, which ceased to fall when coagulation set in. The coagulation time is lessened by small doses of adrenaline given intravenously, provided the blood passes through the liver and intestines, which are stimulated to throw into the circulation some agent which hastens clotting. Stimulation of the splanchnic nerve produces the same effect, provided the adrenals are intact. Pain and emotional excitement similarly, via the adrenal nerves in the splanchnic, cause an increased output of adrenaline into the circulation, which hastens the coagulation time. In fear and rage, with the possibilities of wounds and hæmorrhage, this is protective. W. D. H.

**The Behaviour of Blood-serum towards Dextrose, Lævulose, and Galactose before and after Parenteral Administration of these Sugars.** EMIL ABDERHALDEN and E. BASSANI (*Zeitsch. physiol. Chem.*, 1914, **90**, 369—387).—Normal blood-serum has no action on the sugars enumerated in the title; this was determined by the polarisation test. After parenteral administration of the monosaccharides, the same was true in twenty-two out of twenty-four experiments. In the remaining two, in both of which dextrose was the sugar employed, a change was noted. These experiments were on rabbits. In dogs similar negative results were obtained. W. D. H.

**The Behaviour of Blood-serum towards Sucrose before and after Parenteral Administration of this Sugar.** EMIL ABDERHALDEN and F. WILDERMUTH (*Zeitsch. physiol. Chem.*, 1914, **90**, 388—418).—Normal blood-serum (rabbit) does not contain invertase. After parenteral administration of sucrose, the serum contains invertase and splits sucrose (twenty-three out of twenty-four experiments), but it has no action on lactose, dextrose, lævulose, or galactose. After the invertase containing serum is inactivated by heat, efforts to reactivate it failed. W. D. H.

**The Behaviour of Blood-serum towards Sucrose before and after Parenteral Administration of this Sugar. Experiments on Dogs.** EMIL ABDERHALDEN and L. GRIGORESCU (*Zeitsch. physiol. Chem.*, 1914, **90**, 419—436).—In dogs the results are very variable; in some cases invertase can be detected in the serum after parenteral administration of sucrose in varying quantities, especially if the animal receives much sucrose in the food as well; in other cases the results are negative. W. D. H.

**The Formation of Lactose from Lævulose by means of Serum Derived from Animals which have Received a Parenteral Administration of Sucrose.** F. RÖHMANN and T. KUMAGAI (*Biochem. Zeitsch.*, 1914, 61, 464—468).—Evidence is now produced to show that the polysaccharide produced by the action on lævulose of sera of animals immunised against sugars is lactose (compare Kumagai, A., 1914, i, 112). S. B. S.

**Glycolysis.** IV. P. RONA and G. G. WILENKO (*Biochem. Zeitsch.*, 1914, 62, 1—10).—Higher concentrations of the hydrogen ion have an unfavourable influence on the sugar destruction by the blood, just as they have on glycolysis by the isolated rabbit's heart. When this concentration reaches  $4-6 \cdot 10^{-7}$ , the sugar destruction ceases, and is considerably weakened even at  $H=2-3 \cdot 10^{-7}$ . On bringing the concentration again to that normal to the blood, glycolysis begins again in its original intensity. Attention is called to the importance of these facts in connexion with acidosis in diabetes. High concentrations of sugar (up to 0.5%) produce, in accordance with the reaction as a unimolecular one, an increase in the absolute amount of sugar destroyed; in still higher concentrations (about 1%), glycolysis is strongly inhibited. These facts are also of importance when considered in connexion with diabetes. S. B. S.

**The Preparation of Pancreatic Extracts.** J. MELLANBY and V. J. WOOLLEY (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, 48, xx—xxi).—The various pancreatic enzymes are best extracted with different reagents; trypsinogen is recommended to be extracted with 0.5% hydrochloric acid; this is neutralised with sodium carbonate, filtered, preserved with toluene, and activated when wanted with a filtered aqueous extract of duodenal mucosa. Trypsin is also soluble in glycerol, but the presence of glycerol inhibits activation subsequently unless the glycerol extract is diluted with water. The inhibitory action of glycerol on enterokinase favours extraction of lipase with this reagent, since any trypsin rapidly destroys lipase. Glycerol extracts are in the authors' experience unsatisfactory (the grounds for this are omitted), hence 0.5% sodium carbonate is recommended, as this reagent also prevents the formation of trypsin. Amylase is best extracted with glycerol, and the activity of this enzyme is increased by small quantities of hydrochloric acid or sodium chloride. W. D. H.

**The Physiological and Therapeutic Action of Pancreas Extracts.** FRANZ MÜLLER and S. N. PINKUS (*Biochem. Zeitsch.*, 1914, 61, 337—371).—Attention is directed to the variability of various commercial preparations as regards toxicity, and stress is laid on the possible presence of putrefactive products in them, due to defects in the process of preparation. The authors have carried out a series of investigations with Fairchild's "injectio trypsinii." They describe in detail a method for determining the tryptic value, using for this purpose a gelatin-plate method.

As digestive index, they designate that dilution, in which the preparation is just able to produce a visible indentation in the plate. They have investigated the effect of injection, and ascertained the amount necessary to produce the presence of trypsin in the blood, and to neutralise all the antitryptic substance present therein. For this purpose, relatively very strong doses are necessary, and only when this limit is reached are marked toxic effects produced. Injection of small doses, equivalent to those used for therapeutic purposes, produces a fall of blood pressure, which is not converted into a rise by subsequent injection of atropine. The fall is due to a dilatation of the peripheral vessels. When the pancreas extract is injected into a starving animal, it causes a diminution of tone of the intestinal muscular tissue during the sinking of the blood pressure, just as do the albumoses, whereas when injected into a fed animal it causes an increase in tone. It can also stop the peristaltic action produced by a previous injection of hormonal. The antagonistic action of hormonal and pancreatic extract could be repeated several times. The relations of the results obtained to the clinical observations made after administration of trypsin are discussed by the authors.

S. B. S.

[**Enteroamylase.**] L. J. TE GROEN (*Zeitsch. physiol. Chem.*, 1914, 90, 309—310).—Polemical. A reply to London (this vol., i, 451).

R. V. S.

**Glycogen Metabolism in Fish. I. The Glycogen Content of Fresh-Water Fish.** BERNHARD SCHÖNDORFF and KURT WACHHOLDER (*Pflüger's Archiv*, 1914, 157, 147—164).—In fresh-water fish the liver contains abundant glycogen (2.5 to 13%); in active animals this is lessened by inanition; it disappears usually post mortem. Fishes' muscle contains from 0 to 0.68% of glycogen, the ovary 0 to 0.6%, and the testes only traces. Fishes' glycogen is identical with that obtained from mammals, and its function appears to be the same.

W. D. H.

**Protein Metabolism from the Point of View of Blood and Tissue Analysis. VII. An Interpretation of Creatine and Creatinine in Relation to Animal Metabolism.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1914, 17, 493—502).—Varying views concerning creatine-creatinine metabolism are discussed, and the one supported, which holds that creatine is a part of living protoplasm, the liberation of the creatine from the protoplasmic complex being the result of post-mortem changes. Creatine is absorbed to an extraordinary extent by the muscles when it is injected into the blood stream; the accumulation in the blood is comparatively small; its absorption from the blood by living muscles is just as rapid and extensive as the corresponding absorption of urea, creatinine, or amino-acids. The compound of creatine formed in the muscular substance is very unstable, and creatine is liberated therefrom by mechanical injury or extraction with water or saline

solution. During metabolism, however, the substance liberated from the muscle is creatinine, except under abnormal conditions (fever, fasting), when creatine appears. Gottlieb and Stangassinger's hypothetical enzymes are believed to play no part in metabolism, but represent post-mortem conditions, and the view that the liver has any special work in this direction is not agreed with. It is admitted that many points still remain to be cleared up, and further work is promised. W. D. H.

**The Influence of Carbohydrate and Fat on Protein Metabolism. III. The Effect of Sodium Selenite.** E. P. CATHCART and J. B. ORR (*J. Physiol.*, 1914, **48**, 113—127).—In dogs an injection of sodium selenite produces salivation, vomiting, anorexia, and lethargy; the excretion of total nitrogen and urea is raised, especially on carbohydrate-poor diets; the ammonia output in normal animals is greatest on carbohydrate-rich diets, but after the injection it is highest on carbohydrate-poor diets. There is no marked acidosis, but an immediate rise, followed by a fall, occurs in creatinine elimination, and creatine is also found in the urine, especially on carbohydrate-poor diets. W. D. H.

**The Nitrogen-sparing Action of Sodium Acetate in the Case of Ruminants.** ERNST PESCHECK (*Biochem. Zeitsch.*, 1914, **62**, 186—218).—The author continues his investigations (compare A., 1913, i, 925) on the nitrogen-sparing action of sodium acetate. The present series of experiments refer to its action in sheep; the salt is added to a basal diet, and the nitrogenous metabolism is determined during a preliminary period on this diet without the salt, a period with added salt, and a final period with the basal diet alone. He draws the conclusion, again, that the acetate exerts a nitrogen-sparing action. S. B. S.

**Is Polished Rice plus Vitamine a Complete Food?** CASIMIR FUNK (*J. Physiol.*, 1914, **48**, 228).—Experiments on birds show that polished rice, plus vitamine prepared from yeast, constitutes a complete food. There is no necessity at present to accept the view that there is one vitamine with anti-neuritic properties and another which maintains body-weight. The vitamine fraction used was free from phosphorus, and the importance attributed by some to the part played by lipoids in "deficiency diseases" is therefore minimised. W. D. H.

**The Action of Certain Anions on the Isolated Frog's Ventricle.** TAKUZO SAKAI (*Zeitsch. Biol.*, 1914, **64**, 1—43).—The isolated ventricle of the frog's heart was perfused with Ringer's solution in which the sodium chloride was replaced by other sodium salts. The salts affect the amount of contraction in the following order of diminution: iodide, bromide, nitrate, chloride, acetate, sulphate, tartrate, citrate. The lactate is slightly weaker than the chloride at first, but this soon recovers. The order of the salts in their effect on frequency is somewhat different, and those that



increase frequency especially inhibit "extra-systoles." The difference in the action of these various anions is, however, after all a very small one.

W. D. H.

**Vaso-motor Nerves in the Lungs.** ENID M. TRIBE (*J. Physiol.*, 1914, **48**, 154—170).—The question has long been discussed whether the lung vessels possess an effective nervous control, and the matter has been investigated, as in the similar case of the cardiac and cerebral vessels, by experiments with adrenaline. The present experiments show that adrenaline produces some constriction, and therefore favours the view that the pulmonary arterioles possess vaso-constrictor nerves.

W. D. H.

**The Microscopic Detection of a Protein Storage Product in the Liver.** W. BERG (*Biochem. Zeitsch.*, 1914, **61**, 428—433).—Certain drops, stained by methylene-green-pyronin, are observable in the histological preparations of the livers of animals, after a diet of proteins, which are not found in those of animals in a state of starvation, or after a fat or carbohydrate diet. They consist, apparently, of protein, as they give a positive reaction with Millon's reagent.

S. B. S.

**The Microscopic Detection of Protein Storage Products in the Liver after Feeding with Amino-acids.** W. BERG and C. CAHN-BRONNER (*Biochem. Zeitsch.*, 1914, **61**, 434—445).—After ingestion of amino-acids produced by the complete degradation of proteins (ereptone), protein storage products (see preceding abstract) could be detected in the liver, which are not distinguishable from those produced by feeding with proteins; these results indicate the synthesis of proteins in the organism.

S. B. S.

**Intravital Protein Cleavage in the Liver of Sensibilised Animals and the Influence of the Spleen upon it.** MASAKADZU HASHIMOTO and ERNST P. PICK (*Arch. exp. Path. Pharm.*, 1914, **76**, 89—117).—In guinea-pigs sensibilised by an injection of horse-serum, the percentage of non-coagulable nitrogen in the liver rises from 8 to 22% of the total nitrogen; the latter remains unaltered. This is not due to the breakdown of the injected foreign protein, but of the proper proteins of the liver itself. In the kidney, spleen, brain, and blood the difference, if present at all, is very small. The effect on the liver is most marked about two weeks after the injection, and is lessened by subsequent injections. Removal of the spleen after sensibilising, or sensibilising after extirpation, of the spleen reduces the effect greatly; the spleen is therefore regarded as the source of the agent that leads to proteolysis in the liver. There does not appear to be a causal relationship between this protein cleavage and the occurrence of bronchial spasms and anaphylactic shock.

W. D. H.

**The Significance of Cholesterol in the Processes of Fatty Degeneration.** ERNST VON CZYHLARZ and ADOLF FUCHS (*Biochem. Zeitsch.*, 1914, **62**, 131—136).—The fatty acids (estimated by the

Kumagawa-Sato method) and the cholesterol (estimated colorimetrically) were determined in the liver and kidneys from a number of pathological cases (human). The authors were unable to discover any type of fatty liver where the pathological phenomenon was the result of a cholesterol accumulation in the organ, as opposed to a glyceride accumulation, the ratio of fatty acid to cholesterol not showing any very great fluctuations. S. B. S.

**The Action of Leucocytes and Kidney Tissue on Pyruvic Acid.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1914, 17, 443—449).—In glycolysis, lactic acid is formed as an intermediate product; pyruvic acid is probably another. How lactic acid is broken up into carbon dioxide and water is not known.

Aseptic kidney tissue and leucocytes are not able to bring about the oxidation of lactic acid; on the supposition that two enzymes are concerned, one leading to the formation of pyruvic acid and the other to carbon dioxide, the effect of aseptic tissues on pyruvic acid was tried, but in no case was any carbon dioxide formed, nor was there any change in the oxygen requirement. W. D. H.

**Adrenal Deficiency and the Sympathetic Nervous System.** R. G. HOSKINS and HOMER WHEELON (*Amer. J. Physiol.*, 1914, 34, 172—185).—After complete adrenal extirpation in dogs, there is marked asthenia, both in the heart and the skeletal muscles. There is, however, a compensating action of the vasomotor system; the vascular muscle is unimpaired, and it reacts to stimuli in the usual way. W. D. H.

**The Anterior Lobe of the Pituitary Body in its Relationship to the Early Period of Growth in Birds.** ROSALIND WULZEN (*Amer. J. Physiol.*, 1914, 34, 127—139).—The feeding of young fowls on the anterior lobe of ox-pituitary retards growth, and this is accompanied by involution of the thymus, which may bear a causal relationship to it. The effects are more marked in males than females. W. D. H.

**Abderhalden's Dialysis Method.** CARL LANGE (*Biochem. Zeitsch.*, 1914, 61, 193—255).—The author has submitted to a detailed critical investigation Abderhalden's dialysis method for diagnosis of pregnancy, etc. The placenta chosen for investigation were taken exclusively from sound individuals. In the mechanical preparation of the same, care was taken to shorten as much as possible the grinding process, which causes the specific substrate to be washed away, leaving only the connective tissue. To avoid this loss, the wash-waters were filtered. In separating the blood, tap-water is unsuitable, as this removes the hæmoglobin, but leaves the stromata, which degrade during the test in the same way as the whole corpuscle. The process of removal of the blood is best accomplished by treatment of the very finely disintegrated tissue with saline, and filtration of the washings through silk. On heating the organ with water, care must be taken to produce sufficient coagulation; prolonged heating of the same, however, causes a

certain amount of the protein to dissolve, and the solution on concentration will give a positive ninhydrin reaction. The testing of the dialysing membranes by Abderhalden's method was also found to lead to erroneous results. Their permeability is altered by repeated heating with water. It is not difficult to obtain membranes which are not permeable to proteins; their permeability to peptones, however, is very variable, and it is impossible to choose membranes with a standard permeability to a definite peptone, such as silk-peptone. The suggestion of Abderhalden's to test the membranes every four weeks can readily lead to false results. It was found, in fact, impossible to obtain concordant results in control experiments, when Abderhalden's technique was employed. It was found, furthermore, that a positive reaction of the placenta-serum mixture towards ninhydrin was not specific for a degradation, and could be produced by a summation of non-specific factors, such as the "autolysis" of the serum, or the extractions of the same, or bacterial degradation, which is difficult to exclude even with careful manipulation.

Attempts were also made to apply a microchemical estimation of non-protein nitrogen to determine degradation, and thus to abolish the use of dialysing membranes. Attention is called to various differences in the two processes.

As a result of prolonged experimentation, the author draws the conclusion that Abderhalden's process can lead to false results, and that the specificity of the serum ferments in pregnancy is not proved. In various cases of illness, false results were obtained in 30—65% of the cases. No placenta could be obtained, furthermore, which were in accordance with Abderhalden's requirements, namely, that they should not be degraded by sera from cases of carcinoma or salpingitis.

S. B. S.

**The Carbon Dioxide Production of Heat-rigor in Muscle and the Theory of Intramolecular Oxygen.** W. M. FLETCHER and G. M. BROWN (*J. Physiol.*, 1914, **48**, 177—204).—One hundred grams of muscle (excised from frog) yields at 40° (heat rigor) 35—40 c.c. of carbon dioxide; a further 15—20 c.c. at 75° when the proteins are completely coagulated, and a final 15—20 c.c. when the temperature is close on 100°. If scalded by sudden immersion in boiling salt solution, no lactic acid is formed, but carbon dioxide is evolved in amount about 10% less than that mentioned above. Previous exposure to an atmosphere of oxygen for hours, during which time the surviving muscle is giving off carbon dioxide, does not alter these figures, but previous survival in nitrogen abolishes the yield of carbon dioxide at 40°, but that at 100° remains normal; the total yield, however, that is, to the nitrogen atmosphere whilst the muscle is becoming acid, plus that at 100°, is about the normal; chloroform rigor acts like nitrogen. Addition of acid to muscles at or below room temperature causes a large output of carbon dioxide, and almost abolishes the yield on subsequent heating to 40°, but not that given off at 100°; at 40°, however, the lactic acid yield is increased.

The yield of carbon dioxide at 40° is regarded as pre-existent, and acid is expelled from carbonates by the acid set free in heat rigor; the gas expelled at higher temperatures is held by the muscle colloids or combined with amino-acid groups. The "Inogen theory," with its assumption of intramolecular oxygen, is therefore untenable; carbonic acid is the immediate product of respiratory oxidation, which has for its chief end the supply of energy for replacing the lactic acid in the molecular position from which stimulation of some kind has displaced it.

W. D. H.

**The Carbohydrate Metabolism of Isolated Amphibian Muscle and the Relationship between Disappearance of Carbohydrate and Formation of Lactic Acid in Muscle.**

J. PARNAS and RICHARD WAGNER (*Biochem. Zeitsch.*, 1914, 61, 387—427).—Both glycogen and simpler carbohydrates were estimated in the experiments, and the conditions observed by Fletcher and Hopkins to avoid formation of lactic acid by mechanical stimulation were observed. Such mechanical stimulation (purposely applied) of the isolated muscles of *Rana temporaria*, which causes a rapid increase in the lactic acid, does not influence the carbohydrate content in the tissues. In the muscle paste, the disappearance of the carbohydrate slowly follows the formation of lactic acid. In processes which cause a slow accumulation of lactic acid in isolated muscles, such as fatigue by stimulation, killing by heat or chloroform, or the natural onset of rigor, there is a disappearance of carbohydrate, which is of about the same magnitude as that of the lactic acid which is formed simultaneously. The processes leading to the recovery of fatigued muscle in oxygen are accompanied by no appreciable change in the carbohydrate content. No relationship could be established between formation of lactic acid and disappearance of carbohydrate, on the one hand, and formation of inorganic phosphoric acid on the other, nor was the formation of lactic acid accompanied by any scission of a substance containing amino-nitrogen. In most cases observed, disappearance of carbohydrate and formation of lactic acid run parallel, but there are cases in which the former process follows the latter. The general theory of the formation of lactic acid is discussed in some detail by the authors, who draw the conclusion that lactic acid is not derived directly from carbohydrates, but from a precursor, which stands in intimate genetic relationship with these substances.

S. B. S.

**The Prolonged Contraction of Striated Muscle Produced by Chemical Substances.** G. SCHWENKER (*Pflüger's Archiv*, 1914, 157, 371—452).—Contracture is produced by numerous acids, bases, bile, halogen salts, alcohols, certain substances formed in intermediary metabolism, chloroform, and ether. Carbon dioxide, mannitol, dextrose, glyceraldehyde, taurine, glycine, etc., do not produce contraction; increase in contraction is produced by a number of substances which are enumerated. In acids of the same hydrogen-ion concentration the contracture effect varies. Acids and bases readily pass into muscular fibres. Alcohols and higher fatty

acids produce a narcotic action also. When the substance producing contracture is removed, contraction also passes off, except in the case of chloroform.

W. D. H.

**The Creatine Content of Muscle.** OTTO FOLIN and T. E. BUCKMAN (*J. Biol. Chem.*, 1914, 17, 483—486).—Estimations made by the new method (this vol., ii, 505) indicate that the creatine content of the muscles of cats, rabbits, and hens vary substantially within the same limits. These are too large to permit the use of average figures in calculations as to the alleged relationship between creatinine elimination and total creatine in the tissues.

W. D. H.

**Occurrence of Fumaric Acid in Fresh Meat.** HANS EINBECK (*Zeitsch. physiol. Chem.*, 1914, 90, 301—308. Compare A., 1913, i, 1132).—Fumaric acid can be isolated from fresh beef. The chief product of the oxidation of succinic acid by tissues as carried out by Battelli and Stern (A., 1911, ii, 132) is not malic acid, but fumaric acid.

R. V. S.

**The Hydrion Concentration of Tissue Juices.** L. MICHAELIS and A. KRAMSZTYK (*Biochem. Zeitsch.*, 1914, 62, 180—185).—The reaction of the juices (determined electrometrically) is not alkaline like the blood, but very nearly neutral. The reaction becomes slightly acid as the result of post-mortal changes in the surviving organ, mostly so in striated muscle. If the post-mortal acidification is excluded by boiling the organs with water, an extract is obtained which is never alkaline. The most probably physiological value of the concentration of hydrogen ions in the living juice is  $1.5 \times 10^{-7}$ .

S. B. S.

**Preparation of Phosphatocalcium Chloride from the Ash of Bone and Teeth.** TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1914, 90, 250—253. Compare A., 1913, ii, 320).—The formula previously given for the phosphatocalcium salts derived from the ash of bones or teeth is confirmed by the fact that when the carbonate (the residue left after extracting the ash with acetic acid and water) is treated with barium chloride, the phosphatocalcium salt (and not a barium salt) is produced.

R. V. S.

**The Physiological Chemistry of Cholesterol and the Cholesteryl Esters. II. The Content in these Substances of Normal Organs.** TH. E. HESS THAYSEN (*Biochem. Zeitsch.*, 1914, 62, 115—130).—The author gives the results of a large number of analyses of organs, which show considerable variations in the content of cholesterol and cholesteryl esters. He is unable to suggest an explanation of these physiological variations.

S. B. S.

**The Content of Lipoids in *Rana temporaria* under the Influence of Various External Conditions and of Poisons.** D. M. LAVROV (*Biochem. Zeitsch.*, 1914, 62, 446—458).—In view of

the influence of lecithin on the toxicity of various poisons, to which attention has been already drawn by the author (compare A., 1913, i, 1135), an investigation was undertaken to determine the phosphatide content of animals kept under varying conditions, to ascertain whether the varying action of toxins could be accounted for by the varying lecithin content of the organism. The frogs were mixed with anhydrous sodium sulphate, and the dried mass was extracted repeatedly with alcohol at 60–65°. The residue from this extract was dissolved in ether, and the ethereal residue was then extracted with light petroleum. Phosphorus was estimated in an aliquot part of this last extract. It was found that there was a diminution of phosphorus content in the frogs which had been a long time in the laboratory, as compared with animals recently caught. The differences between the various animals do not appear to be sufficient, however, to account fully for their differences of behaviour towards administrations of lecithin with drugs.

S. B. S.

#### The Cerebro-spinal Fluid. II. Cerebro-spinal Pressure.

W. E. DIXON and W. D. HALLIBURTON (*J. Physiol.*, 1914, 48, 128–153).—The cerebro-spinal pressure is influenced passively, but only to a small extent, by changes in arterial and venous pressures. The cerebro-spinal pressure is, however, mainly an independent pressure, which varies with the rate and force of secretion, and often in the opposite direction to blood-pressure, especially when the secretion is increased by the introduction of substances which stimulate the choroid gland, such as extracts of the choroid gland itself, volatile anæsthetics, and any condition that leads to deficiency of oxygen or increase of carbon dioxide in the blood. The cranial contents can no longer be regarded as a fixed quantity without the power of expanding or contracting in volume.

W. D. H.

#### The Several Factors of Acid Excretion. LAWRENCE J.

HENDERSON and WALTER W. PALMER (*J. Biol. Chem.*, 1914, 17, 305–315. Compare A., 1913, i, 221, 558).—The average acidity of normal urine is 6, and the daily variation may range from 5.1 to 7. Relations can be observed between the total hydron concentration and the amount of titratable acid (due to acid phosphates) present. The average amount of ammonia found is practically constant. The volume of urine excreted increases as the acidity (both total and titratable) diminishes.

R. V. S.

#### The Synthesis of Hippuric Acid in the Animal Organism.

I. The Synthesis of Hippuric Acid in Rabbits on a Glycine-free Diet. HOWARD B. LEWIS (*J. Biol. Chem.*, 1914, 17, 503–508).—In rabbits fed on glycine-free food (milk) the ingestion of sodium benzoate causes no marked rise in the excretion of total nitrogen. The nitrogen eliminated as hippuric acid is derived at the expense of that normally present as urea. The glycine necessary is formed in katabolism of an unusual kind.

W. D. H.

**The Velocity of Hippuric Acid Formation and Elimination from the Animal Body.** A. M. RAIZISS, G. W. RAIZISS and A. I. RINGER (*J. Biol. Chem.*, 1914, **17**, 527—529).—Wiechowski, like others before him, found that more hippuric acid is excreted after benzoic acid feeding than can be accounted for by the preformed glycine of the body, and considers that higher amino-acids pass through a glycine stage before urea is finally formed. In the present experiments on rabbits the excretion of hippuric acid occurred rapidly in three cases during the nine hours following the ingestion of sodium benzoate. Slow elimination when observed is not due to difficulty of elimination, but either to slow absorption or slow synthesis. Wiechowski based his calculations on the assumption that eight hours was enough. This, however, is not justified; the percentage relationship must be calculated from an examination of the entire twenty-four hours' nitrogen. If this is done, Wiechowski's figures must be divided by three. W. D. H.

**The Nature of the Violet Sodium Nitroprusside Reaction in Urine.** HANAKICHI YANAGAWA (*Biochem. Zeitsch.*, 1914, **61**, 256—280).—The Arnold reaction in urine was investigated in various classes of animals, and was always found absent in fasting animals. It appears after ingestion of certain kinds of foods, especially of meat. The reaction is only weak after ingestion of most other kinds of foods. It is never found in the urine of birds. Extract of meat and various organs also give the nitroprusside reaction, due apparently to the same substance which gives the reaction in urine. The substance in the urine arises partly from the ingested food, and partly as an endogenous product of metabolism which owes its origin to the cell functions of the digestive organs. The chief food-stuffs, namely, proteins, carbohydrates, and fats, have little to do with its production, neither does it result from psychical excitation; nor is it found as a result of any pathological condition. The substance giving the reaction is precipitable by three precipitants of carbamide, namely, mercuric chloride + alkali hydroxide, mercuric oxynitrate, and ethereal solution of oxalic acid. None of the known urinary constituents gives the reaction; the substance in question appears to be an organic sulphur compound, possibly a thioamino-compound, as urines which give the reaction also give rise to thiocyanate and hydrogen sulphide on boiling with acids and alkali hydroxides. S. B. S.

**Detection and Estimation of Acetone. Physiological Acetonuria.** Influence of Certain Drugs on Hunger-acetonuria. II. C. CERVELLO and F. GIRGENTI (*Arch. expt. Path. Pharm.*, 1914, **76**, 118—124. Compare this vol., i, 354).—Caffeine and cocaine diminish the amount of acetone excreted in the urine during hunger. The experiments were made on dogs. W. D. H.

**The Theory of Diabetes. III. Glycollaldehyde in Phloridzinised Dogs.** W. D. SANSUM and R. D. WOODYATT (*J. Biol. Chem.*, 1914, **17**, 521—526).—Glycollaldehyde was prepared from Fenton

and Jackson's dihydroxyfumaric anhydride. In phloridzinised dogs given subcutaneously it causes a rise in urinary nitrogen and of dextrose, so that the G: N ratio remained constant; this initial rise is followed by a fall. Given slowly in dilute solutions the dextrose rises more than the nitrogen, which suggests a formation of sugar from the glycollaldehyde itself. W. D. H.

**"Emotional Glycosuria" in Man.** OTTO FOLIN, W. DENIS, and W. G. SMILLIE (*J. Biol. Chem.*, 1914, 17, 519—520).—Mita has stated that glycosuria is particularly frequent in insane persons subject to fear and depression; this is confirmed. More definite evidence of the existence of emotional glycosuria in man analogous to that produced by Cannon and his colleagues in cats was obtained in students after an examination; it was observed in about 18% of the cases examined. W. D. H.

**The Action of Opium Alkaloids in Certain Cases of Hyperglycæmia.** KJ. OTTO AF KLERCKER (*Biochem. Zeitsch.*, 1914, 62, 11—48).—No distinct action of opium alkaloids could be detected in cases of hyperglycæmia or glycosuria experimentally produced by injection of adrenaline or *piqure*. Alimentary glycosuria due to dextrose, on the other hand, can be distinctly affected by the alkaloids, being more or less inhibited by them. Tincture of opium produces the effect only in such doses as by themselves produce an increase of blood-sugar, so that it is apt to be masked. The inhibitory action can be best demonstrated when pantopon is used, and is administered to animals which are not too sensitive to opium, in repeated doses before and after a meal, in such quantities as, by themselves, are incapable of producing an increase of the blood-sugar. The inhibitory action is probably the result of the action of the alkaloids on slowing the rate of emptying of the ventricle. Bang's micro-method was employed in these investigations. S. B. S.

**The Chemical Rationale of the Benzene Treatment of Leucæmia.** H. BORUTTAU and E. STADELMANN (*Biochem. Zeitsch.*, 1914, 61, 372—386).—The free and conjugated sulphates, the volatile phenols, and the excreted purine substances were estimated in the case of leucæmic and other patients during the administration of benzene. Specially marked in the cases of the leucæmic patients was the change of the ratio of the free to the conjugated sulphates, the latter largely predominating shortly after the administration of the drug. The blood conditions were also investigated, and it was found that the large increase of erythrocytes and diminution of the leucocytes was specially marked when a large percentage of the benzene was oxidised to phenol. Attention is called to the probable connexion between the increased oxidative processes and the destructive processes in the lymphatic organs, and it is assumed that the solubility of benzene in lipoids is intimately connected with the therapeutic processes. A preliminary investigation of the lipoids and fats in the blood indicated that a



diminution of these substances was parallel with a diminution of leucocytosis. S. B. S.

**The Pathogenesis of Lipæmia.** S. SAKAI (*Biochem. Zeitsch.*, 1914, 62, 387—445).—The chief subject of investigation was the lipæmia, produced experimentally in rabbits, either by venesection or by poisons which cause anæmia. The chief points investigated were (1) the influence of the diet on the course of the phenomenon, (2) the chemical composition of the fats and lipoids in the serum, (3) the changes of the lipolytic power of the blood and organs accompanying lipæmia. It was found that normal rabbits, even after fat-rich diets, show but little tendency towards lipæmia. This indicates that the intensity of adsorption of fats from the alimentary tract is not greater than the rate of disappearance from the blood. In the case of anæmic rabbits, on the other hand, the diet has a considerable influence on the lipæmic condition, and the content of fat in the blood can be increased by fat-rich diets, or addition of fat to a fat-poor diet, especially in lactating animals. The lipæmia appears three hours after a single fat ingestion, and reaches its maximum in about twelve hours. The factor influencing the lipæmia is that which regulates the amount of fat in the blood; and it acts similarly towards fat derived from nutrition as well as depôt fat, as lipæmia also appears in animals made anæmic, which are receiving a fat-poor diet. The lipæmia is accompanied by a gradual disappearance of subcutaneous fat. The lipæmia is, however, less on a fat-free than a fat-rich diet. By means of the stalagmometric method of Michaelis and Rona, it could be shown that lipæmia is always accompanied by a diminution of the lipase or esterase content of the blood. It appears, therefore, that the diminution of this ferment is one of the main factors causing lipæmia.

In addition to the increase in the ordinary fats, the serum of lipæmic animals also contains an abnormally large quantity of the cholesterol substances. The relative increase of these, however, is never so large as that of the fats. It is probably due to the solution of cholesterol in the increased amount of fat, and is only of secondary importance. The main factors influencing lipæmia appear to be, therefore, (a) the presence of disposable fat, either in the food or fat depôts, (b) and the inhibition of the disappearance of the fat from the blood, due probably to the abnormally small amount of lipase. S. B. S.

**The Protective and Curative Properties of Certain Food-stuffs against Polyneuritis Induced in Birds by a Diet of Polished Rice.** E. A. COOPER (*J. Hygiene*, 1914, 14, 12—22. Compare A., 1913, i, 223).—The following tissues of the ox are arranged in descending order according to their anti-neuritic power:—Liver, heart-muscle, brain, voluntary muscle, and milk (cow). Alcoholic extracts of the excreta of a hen fed on unpolished rice, and of the fæces of a rabbit fed on bread and cabbage, cured polyneuritis in pigeons; the anti-neuritic substance in the food is

therefore not entirely absorbed, or else some is synthesised by the intestinal bacteria. Husked filberts are very efficient in preventing polyneuritis, being superior to lentils and husked barley. Cheddar cheese, on the other hand, has no preventive effect. Three samples of malt extract were examined: two only of these readily cured the disease. In the prevention of beri-beri, the poor value of voluntary muscle in vitamins should be remembered, and some of the other substances alluded to above should be employed instead.

W. D. H.

**The Action of Iodine on the Circulation.** ARNO LEHNDORFF (*Arch. expt. Path. Pharm.*, 1914, **76**, 224–238).—The main action of iodine on the circulation is a continued elevation of the volume beat of both heart chambers; this increases the velocity of the blood-flow, and explains the favourable influence of iodine therapy in arterial sclerosis. In cases of high blood pressure the use of iodine is contra-indicated. This action is independent of the specific use of iodine in certain infective diseases, such as syphilis, tuberculosis, and gland-swellings. Bromine salts have no special action on the circulation.

W. D. H.

**The [Pharmacological] Action of Colloidal Sulphur and of Carbon Prepared by a Chemical Method.** G. IZAR (*Biochem. Zeitsch.*, 1914, **61**, 332–335).—A reply to certain criticisms of the author's work by Sabbatani (this vol., i, 356, 357).

S. B. S.

**The [Pharmacological] Action of Colloidal Sulphur.** A. FAGINOLI (*Biochem. Zeitsch.*, 1914, **61**, 336).—A reply to certain criticisms of the author's results by Sabbatani (this vol., p. 356).

S. B. S.

**The Fate of *l*-Alanine in the Glycosuric Organism.** H. D. DAKIN and H. W. DUDLEY (*J. Biol. Chem.*, 1914, **17**, 451–454).—Inactive alanine, and inactive and *d*-lactic acid give rise in phloridzinised animals to a large increase in dextrose elimination. The same is true for *l*-lactic acid, and for methylglyoxal. The present experiments show that *l*-alanine causes an excretion of "extra dextrose," almost equal in amount to the theoretical yield. In the synthesis of dextrose from alanine and lactic acid the asymmetry of the central carbon atom must therefore be lost. Methylglyoxal is probably the symmetrical substance which is formed.

W. D. H.

**The Formation of Glycine in the Body.** III. ALBERT A. EPSTEIN and SAMUEL BOOKMAN (*J. Biol. Chem.*, 1914, **17**, 455–462).—Alanine, free or combined with a benzoyl radicle, fails to yield glycine; it is not conceivable that alanine can be directly converted into glycine; but it now appears that its cleavage product cannot behave in this way either. Alanine has no effect on hippuric acid metabolism. The increase of hippuric acid after the giving of benzoyl-leucine is probably not a function of the benzoyl radicle.

W. D. H.

The Degradation of Carboxylic Acids in the Animal Body. **XXI. The Formation of *l*- $\beta$ -Hydroxybutyric Acid from Crotonic Acid by Liver Emulsion.** E. FRIEDMANN (*Biochem. Zeitsch.*, 1914, 61, 281—285).—The above reaction will not take place in a current of hydrogen, carbon dioxide, or nitrogen, for oxygen is necessary. The exact rôle of oxygen has not yet been determined. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. **XXII. The Behaviour of Glycollic Acid when Perfused through the Liver.** KENSABURO HONJIO (*Biochem. Zeitsch.*, 1914, 61, 286—291).—By the perfusion of the liver of a fasting dog with the sodium and ammonium salts of glycollic acid, no increased production of acetoacetic acid was produced. The results are in accordance with those obtained by Mochizuki (A., 1913, i, 1277), but not in accordance with those of Embden and Loeb (A., 1913, i, 1411). S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. **XXIII. Influence of Propionic Acid on the Acetoacetic Acid Formation from Acetic Acid in the Surviving Liver.** KENSABURO HONJIO (*Biochem. Zeitsch.*, 1914, 61, 292—301).—Fatty acids with an uneven number of carbon atoms, such as valeric acid, should, on the principle of the  $\beta$ -oxidation, give rise to acetic acid, which is an acetoacetic acid producer when perfused through the liver. Acetoacetic acid is not, however, produced by the perfusion of valeric acid. This might be explained, according to Embden and Loeb (A., 1913, i, 1411), by the inhibitory action of the propionic acid on acetoacetic acid formation, as this acid is produced, together with acetic acid, on the  $\beta$ -oxidation of valeric acid. Experiments of the author show, however, that propionic acid, when it is not present in larger quantity than that equimolecular with acetic acid (as it should not be on the assumption of a  $\beta$ -oxidation), does not produce an inhibition of acetoacetic acid formation from acetic acid. From the results, the conclusion is drawn that the method of degradation of fatty acids with an uneven number of carbon atoms is not yet determined. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. **XXIV. The Behaviour of *iso*Valeric Acid and Acetaldehyde when Perfused through Glycogen-rich Livers.** K. IWAMURA (*Biochem. Zeitsch.*, 1914, 61, 302—311).—The author confirms the results of Mochizuki (A., 1913, i, 1277) that *isovaleric* acid gives rise to acetoacetic acid when perfused through the liver. The amount of the latter substance formed appears to be independent of the glycogen content of the liver. Acetaldehyde-ammonia, when perfused through a glycogen-rich liver, does not give rise to acetoacetic acid, and behaves in this respect like acetic acid. S. B. S.

**The Degradation of Carboxylic Acids in the Animal Body. XXV. Behaviour of Malonic Acid when Perfused through the Liver.** GORO MOMOSE (*Biochem. Zeitsch.*, 1914, **61**, 312—314).—Malonic acid gives rise to a volatile substance, which combines with iodine, but which is destroyed by silver oxide, and is therefore not acetone; its nature has not yet been determined. In two of the nine experiments carried out there was, in addition, an increase in the acetone.  
S. B. S.

**Carbon Dioxide Formation by the Organs.** PAUL MAYER (*Biochem. Zeitsch.*, 1914, **62**, 462—469).—Dilute oxalacetic acid solutions, on keeping in an incubator, only evolve about half the carbon dioxide which should be set free in the event of a total degradation of the acid into pyruvic acid. In the presence of animal organs, and a "buffer" mixture to keep the solutions neutral, at least the total amount to be expected in the complete degradation to pyruvic acid is evolved. The reaction takes place without the addition of oxygen.  
S. B. S.

**Choline Esters and Muscarine.** H. H. DALE and A. J. EWINS (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, **48**, xxiv—xxv).—Synthetic muscarine is not an aldehyde, but when prepared by heating choline with strong nitric acid is a choline ester of nitrous acid. It causes all the muscarine effects except constricting the mammalian pupil; it has potent actions of the nicotine-curare type, which are absent in natural muscarine, and are not annulled by atropine. The constitution of natural muscarine is once more an open question; on the idea that it might be the nitrous acid ester, it was found that the latter has all the actions of muscarine, except that the effect on the frog's heart is weaker; this can be remedied by adding a little acetylcholine; it differs, however, from muscarine in having a nicotine-curare-like action on the atropinised frog. The choline esters, and to some extent choline itself, show different actions according to dose. This double effect may account for the controversy whether pure choline is a pressor or depressor substance.

W. D. H.

**Synthesising Action of Endolipases.** ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1914, **90**, 489—494).—The results of experiments on the action of different organs on a mixture of oleic acid and glycerol (or amyl alcohol), both without and with *N*/10-sodium carbonate, showed that the reduction in acidity is greatest with pancreas, and next with the intestinal mucous membrane of pigs. With the remaining organs which gave definite results, the reduction in acidity diminishes in the following order: bullock's liver, intestinal mucous membrane of horses, and, last, dog's lungs.

N. H. J. M.

**Phenylurethane Derivatives as Local Anæsthetics.** K. FROMHERZ (*Arch. expt. Path. Pharm.*, 1914, **76**, 257—302).—The action, fatal dose, action on the cornea, and action on nerve trunks,

of seven derivatives, all of which contained a phenylurethane group, were investigated in comparison with novocaine; all work well with differences in detail, but not better than novocaine. The same sort of differences are noted in eight other preparations; the actions on nerve endings and nerve trunks are not always parallel. Certain physical properties, such as solubility in fat, influence the results.

W. D. H.

**The Physiological Action of Organ Extracts.** F. HAFNER and A. NAGAMACHI (*Biochem. Zeitsch.*, 1914, 62, 49—57).—Aqueous extracts from thyroids and ovaries of ox were precipitated by alcohol, and the parts soluble in ether and insoluble in ether, but soluble in water, were investigated either separately or together. The total extracts of both organs increase the tone and contraction of the isolated uterus of guinea-pigs and rats, which action is due to the ethereal extract alone; the aqueous extract, on the other hand, exhibits just the opposite action. The action of the ethereal extract is due to the fatty acids and soaps, and can be regarded as analogous to the cytolytic action on isolated cells. The ethereal extract is non-toxic to cats, but very toxic to rabbits, producing cessation of respiration. The combined extracts are without action, but the aqueous extract alone produces a transient fall in blood-pressure in cats, but no action on rabbits. The aqueous fraction produces a reversible contraction of the vessels when perfused through the rabbit's ear. Neither in case of ovary nor thyroid could any action specific for the organ be detected.

S. B. S.

**Constitution of the Hæmolysing Phosphatide (Lysocithin) formed by the Action of Cobra-venom on the Vitellus of Egg.** C. DELEZENNE and E. FOURNEAU (*Bull. Soc. chim.*, 1914, [iv], 15, 421—434).—A more detailed chemical investigation of the hæmolysin, now named *lysocithin*, obtained by Delezenne and Ledebt (compare A., 1913, i, 141) from the action of cobra venom on the vitellus of egg. The substance has been obtained **pure in a** crystalline form by repeated crystallisation from absolute alcohol. The substance so obtained gives none of the reactions of choline. Analyses of the purified substance give it the constitution of choline palmitoglycerophosphate. This is confirmed by molecular-weight determinations and by examination of the products of hydrolysis by Haller's method (compare Fourneau and Piettre, A., 1912, ii, 1109), which are methyl palmitate, choline hydrochloride, and calcium glycerophosphate. The oleic acid and the other non-saturated acids are thus entirely removed from the lecithin by the action of the cobra venom. If a solution of lysocithin in alcohol is treated with a chloroform solution of cholesterol, and the mixture warmed for several hours, the residue on evaporation yields the whole of the cholesterol to ether. If, however, the dry residue is first treated with water, an emulsion is formed, separating rapidly to an opalescent liquid and a fine precipitate, in which a portion of the cholesterol is retained even after repeated extrac-

tion with ether. One molecule of cholesterol is retained for each molecule of lysocithin, and the product has no hæmolysing power.  
W. G.

## Chemistry of Vegetable Physiology and Agriculture.

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**A Water Thermo-regulator for Incubators.** L. VON HEYDEN-REICH (*Centr. Bak. Par.*, 1914, i, 73, 444—448).—The apparatus is particularly suitable for use with oil lamps. It consists of two parts, *A*, for insertion into the incubator, and *B*, for attachment to the chimney of the lamp. The bulb of *A* is filled with air under pressure, methylene chloride (b. p. 41.6°), and mercury. The tube attached is forked at a height of 76 cm., and through the two limbs of the fork a current of water is allowed to flow from a constant-level reservoir. The water runs into the second part of the apparatus, and exerts a pressure on a column of mercury in a special U-tube sufficient to raise a float, which in turn raises a shutter in the chimney of the lamp and allows a current of hot air to play on the base of the incubator. The base of the part *B* is provided with a side-tube with screw clip or stop-cock, which is permanently slightly open; when the temperature of the incubator becomes too high, the mercury in the first part of the regulator shuts off the flow of water from *A* to *B*, the water in the tube of *B* trickles out, and the float in the U-tube drops and closes the chimney, thus diverting the heat from the incubator. The regulator is stated to operate within a fraction of a degree.

H. B. H.

[Chemistry of Bacteria.] TADEUSZ KOŹNIEWSKI (*Zeitsch. physiol. Chem.*, 1914, 90, 208—209).—The author considers that Tamura's publication on this subject (this vol., i, 461) is in part anticipated, and in part contradicted, by his papers previously published (Kožniewski, A., 1913, i, 428).

R. V. S.

[Chemistry of Bacteria.] SAKAE TAMURA (*Zeitsch. physiol. Chem.*, 1914, 90, 210).—Polemical. A reply to Koźniewski (preceding abstract). The author maintains the accuracy of his results.

R. V. S.

**Chemistry of Bacteria. V. Chemical Composition of a Water Bacillus.** SAKAE TAMURA (*Zeitsch. physiol. Chem.*, 1914, 90, 286—290. Compare this vol., i, 461).—The bacillus investigated was obtained from water, and forms short, Gram-negative, non-sporeing rods, which do not liquefy gelatin. Extraction of the dry bacteria with alcohol yields a phosphatide, possibly a mono-aminomonophosphatide. Lipoids showing the cholesterol reaction.

acid-fast mycol, or other Gram-positive lipoids were not present. A reducing substance giving the orcinol and hydrochloric acid reaction is present. The proteins found differ in solubility from those of tubercle and diphtheria bacilli. Among their products of hydrolysis are arginine, histidine, lysine, tyrosine, *l*-proline, and tryptophan.

R. V. S.

**The Action of Some Aniline Dyes on Bacteria.** M. ISABOLINSKI and L. SMOLJAN (*Centr. Bakt. Par.*, 1914, i, 73, 413—427).—Comparative experiments on the bactericidal action of various dyes, such as methylene-blue, gentian-violet, crystal-violet, thionine, malachite-green, magenta, etc., on *Staphylococcus pyogenes aureus*, *Pneumococcus*, *B. anthracis*, *B. coli*, *B. typhi*, and *Vibrio cholerae asiaticae*. The majority of the dyes, with the exception of magenta and eosin, were found to possess marked bactericidal properties in the laboratory and in animal inoculation experiments, the greatest action being exerted by crystal-violet, methyl-violet, and malachite-green. The resistance of the various species of organisms showed great differences, *B. typhi* and *B. coli* persisting up to high concentrations of the dyes, while *B. anthracis* was relatively non-resistant. This action does not appear to be due to aniline, since actual experiments showed this compound to have only slight bactericidal effect. A certain amount of acclimatisation of the cholera organism to the presence of some of the dyes was also observed.

H. B. H.

**Biochemistry of Micro-organisms. The Nutritive Value of Different Sugars and Amino-acids for *Bacillus prodigiosus*.** HARTWIG FRANZEN and F. EGGER (*Zeitsch. physiol. Chem.*, 1914, 90, 311—354).—In the case of moulds and yeasts, the suitability of various chemical compounds as nutrients may be ascertained by the determination of the dry weight of the cells within a certain period; with bacteria this is not practicable, and the formation of by-products or the fermentative activity only can be taken as an indication. The capacity of *Bacillus prodigiosus* to ferment formic acid or its salts was taken as a criterion, when the dextrose and asparagine of a normal solution were replaced by sucrose, lævulose, maltose, galactose and lactose, and glycine and alanine respectively. The functional activity of the organism was found to be practically the same whether supplied with dextrose or lævulose; sucrose gave a similar, but rather lower, intensity curve, while with maltose the fermentation did not take place within the first three days; galactose and lactose were without value. Of the three amino-acids tested, asparagine proved to be most suitable, and alanine was better than glycine.

H. B. H.

**The Behaviour of Betaines in Putrefaction.** D. ACKERMANN (*Zeitsch. Biol.*, 1914, 64, 44—50).—The action of saprophytes on four betaines (trimethylserine, trimethylglutamic acid, hexamethylornithine, and stachydrine) was investigated. After putrefaction had progressed for twelve to twenty-three days, 92.5% of trimethyl-



serine, 86.5% of trimethylglutamic acid, 94.8% of hexamethylornithine, and 95.7% of stachydrine (*dl*-dimethylproline) were recovered, and in no case was any trimethylamine liberated.

W. D. H.

**Yeast.** HORACE T. BROWN (*Ann. Bot.*, 1914, 28, 197—226).—In nutrient solutions containing oxygen and an excess of essential nutrients, the number of yeast-cells per unit volume tends to attain a maximum, which is mainly dependent on the initial amount of dissolved oxygen, when this is not renewed. Within certain limits of oxygen supply, the maximal reproduction is strictly proportional to the initial amount of oxygen, and the rate of reproduction is a linear function of the time. The oxygen is rapidly absorbed by the seed-yeast before cell-budding commences.

The apparent waste of energy under the usual artificial conditions is attributed to the limited supply of oxygen. Under natural conditions (as, for instance, on the ruptured surface of a grape) operations are on a small scale, and the supply of oxygen is continuous.

N. H. J. M.

**Carboxylase.** V. PALLADIN, N. GROMOV, and N. N. MONTEVERDE (*Biochem. Zeitsch.*, 1914, 62, 137—156).—It is shown that yeast will not cause fermentation of the free pyruvic acid, although it rapidly ferments the potassium salt; the free acid inhibits the auto-fermentation of yeast. Neutral phosphate mixture, and to a less extent dipotassium phosphate, promote the fermentation of potassium pyruvate. A series of experiments on the joint fermentation of the pyruvate and sucrose were carried out. In these experiments less carbon dioxide was evolved than was evolved by the fermentation of the products separately. Pyruvate added to sucrose fermentation mixtures which had become inactive caused fresh evolution of carbon dioxide. Hefanol, which had been extracted with methyl alcohol and lost the property of fermenting sucrose, was still capable of fermenting pyruvate with practically undiminished intensity. The carboxylase is not stimulated by heated taka-diastase solution, and only very weakly stimulated by heated hefanol. The carboxylase is gradually destroyed by the autolysis of hefanol, almost to the same extent as the zymen. Strong glycerol solutions inhibit the carboxylase action, whilst weaker solutions extend the action over several hours. Hydrogen peroxide (0.5%) destroys pyruvate with about the same intensity as carboxylase, and the action is not increased by the presence of a peroxydase.

S. B. S.

**Rôle of Glycogen in Fermentation by Living Yeast.** HANS EULER (*Zeitsch. physiol. Chem.*, 1914, 90, 355—366. Compare *ibid.*, 89, 337).—Further evidence is given that the difference between the amount of sugar which disappears during fermentation with living yeast, and the amount of carbon dioxide produced, cannot be due to formation of glycogen.

N. H. J. M.

**Phytochemical Reductions. II. The Change of Aliphatic Nitro-compounds into Amino-compounds.** CARL NEUBERG and ERNST WELDE (*Biochem. Zeitsch.*, 1914, 62, 470—476).—Experiments are described which demonstrate that living yeast, when in a state of active fermentation, can reduce nitroethane and nitromethane to ethylamine and methylamine, which were isolated in the form of their platinichlorides. S. B. S.

**Phytochemical Reductions. III. The Conversion of Aromatic and Fatty Aromatic Aldehydes into Alcohols.** CARL NEUBERG and ERNST WELDE (*Biochem. Zeitsch.*, 1914, 62, 477—481).—Benzaldehyde can be reduced by living yeast to benzyl alcohol, a yield in one case of 32% of the theoretical being obtained. As only traces of benzoic acid were obtained at the same time, the formation of the alcohol cannot be ascribed to the Cannizzaro reaction. In a similar way, phenylethyl alcohol could be produced from phenylacetaldehyde. S. B. S.

**Phytochemical Reductions. IV. (a) The Formation of *n*-Amyl Alcohol by Yeast. (b) The Natural Occurrence of *n*-Amyl Alcohol.** CARL NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1914, 62, 482—488).—*n*-Amyl alcohol was obtained by means of fermenting yeast, in a yield of 70% of the theoretical, from *n*-valeraldehyde. Its formation is not due, therefore, to the Cannizzaro reaction. The authors have further succeeded in showing that the *n*-alcohol is a normal constituent of fusel oil, from which small quantities can be separated by careful, slow fractionation. The alcohol was identified by oxidation to *n*-valeric acid, of which the calcium salt (with one molecule of water of crystallisation) was obtained in a pure state. The *n*-alcohol probably owes its origin to *n*-aminohexanoic acid, which has recently been obtained by the hydrolysis of proteins by Abderhalden and Weil (A., 1913, i, 456). S. B. S.

**Fermentations with Yeast in Absence of Sugar. XVI. The Question of the Formation of Lactic Acid in the Fermentation of Pyruvic Acid by Living Yeast, and some Observations on the Processes of Fermentation.** C. NEUBERG and JOH. KERB (*Biochem. Zeitsch.*, 1914, 62, 489—497).—It is shown that under strictly aseptic conditions lactic acid is not formed during the fermentation of pyruvic acid by living yeast. It is shown that commercial dry yeast preparations are contaminated by bacteria. The authors discuss the theory of alcoholic fermentation, especially in reference to some recent experiments and theoretical deductions of M. Oppenheimer (A., 1914, i, 363). S. B. S.

**Fermentations in the 3-Carbon Series.** C. NEUBERG and JOH. KERB (*Ber.*, 1914, 47, 1308—1315).—The authors confirm Lebedev's discovery that acetaldehyde is formed during the fermentation of glyceric acid by dried yeast, but do not agree with the general conclusions which he drew from this fact (this vol., i, 464,

635). Experiments are described which indicate that glyceric acid is not fermented by pure cultures of living yeast under conditions which are favourable to the destruction of sugar or pyruvic acid. The fermentation of glyceric acid by dead yeast is therefore abnormal, and further experiments are necessary before it can be rightly understood. It may be that the acid stimulates auto-fermentation. This process (compare A., 1912, ii, 973) takes place even in presence of acetic acid. An estimation of the amount of carbon dioxide evolved does not, therefore, give a true idea of the "fermentation" of glyceric acid. A titration of the non-volatile acid before and after fermentation with dried yeast shows that very little acid is destroyed during the process. The existence and action of a dehydrating enzyme, as suggested by Lebedev, are also criticised.

J. C. W.

**The Formation of Saligenin from Salicylaldehyde by Yeast.** PAUL MEYER (*Biochem Zeitsch.*, 1914, 62, 459—461).—Under certain conditions described, small quantities of saligenin can be produced from salicylaldehyde by a certain top-yeast. Owing to the toxic action of the aldehyde on yeast, the reaction was difficult to realise. The author failed to isolate salicylic acid, which, according to the Cannizzaro reaction, should be formed together with the saligenin.

S. B. S.

**The Fermentation of Albumin to Alcohols, Acids and Amines.** F. EHRLICH (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), ii, 320—324).—A review of the author's work on the conversion of albumin or its amino-acids into alcohols and acids by yeast in the presence of sugar, into hydroxy-acids by many moulds, and into amines by certain lactic bacteria. The part played by these changes in alcoholic fermentation (in the production of the aroma and of fusel oil) and in the cheese industry (in the ripening) is believed to represent only a fraction of their importance.

D. F. T.

**Nitrogen Nutrition of Moulds.** WIDAR BRENNER (*Centr. Bakt. Par.*, 1914, ii, 40, 555—647).—Experiments with three races of *Aspergillus niger* showed that the production of dry matter and the economic coefficient, dry matter: sugar consumption, varied greatly with the form in which nitrogen was supplied. Of the compounds tested, the ammonium salts of the aliphatic hydroxy- and dicarboxylic acids, amino-acids, peptides, and peptone were most easily utilised, and ammonium salts of the mineral acids, and those of the monobasic fatty acids, less so. Monoalkylamines with low carbon content, and the lower dialkylamines, as well as acid amides, nitrates, and guanidine salts, were moderately useful, whilst isoamines and all mono-alkylamines with high carbon content, di- and tri-alkylamines, aromatic amines, and hydroxylamine salts proved of little value. Sodium nitrite, ammonium valerate, tribenzylamine sulphate, and potassium cyanide were distinctly toxic. Utilisation of a compound is stated to depend, not only on its

constitution, but also on the character of the by-products and the maintenance of a favourable reaction of the medium. H. B. H.

**Use of Zinc for the Growth of *Aspergillus niger* (*Sterigmatocystis nigra*) Cultivated in Deep Media.** M. JAVILLIER (*Compt. rend.*, 1914, 158, 1216—1219).—Contrary to the results obtained by Lepierre (compare A., 1913, i, 1423), the author finds that zinc is equally as effective in producing an increase in the crop of *Aspergillus niger* in deep as in shallow culture media.

W. G.

**Is Silver, at a Suitable Concentration, able to Increase the Growth of *Aspergillus niger*?** GABRIEL BERTRAND (*Compt. rend.*, 1914, 158, 1213—1216).—The author has examined the influence of silver nitrate at high dilutions on the growth of *Aspergillus niger*. The dilution at which this substance ceases to be injurious is approximately  $N/10^6$ , and the author has been unable to find any dilution greater than this, which gives a growth greater than in the control solutions. He considers Lepierre's views, that the elements such as zinc, manganese, etc., do not play a necessary part in the growth of *Aspergillus niger*, but whilst toxic at moderate concentration exert an accelerating influence on the growth of the mould, when present in minute amounts (compare A., 1913, i, 326, 1423), are incorrect.

W. G.

**Treatment of Seeds with Poisons for the Purpose of Disinfection.** TH. BOKORNY (*Biochem. Zeitsch.*, 1914, 62, 58—88).—The effect of poisons on the germinating power, and the capacity of destroying fungi, was investigated in the case of several varieties of seeds. The following were found to be satisfactory disinfecting methods. Treatment with (a) hot 0.1% copper sulphate solution for half a minute; (b) hot 1% acetic acid for one minute; (c) 96% alcohol for one minute at 15°; (d) 1% hot sodium carbonate solution for half a minute; (e) boiling alcohol (96%) for one minute; (f) a solution containing 50 c.c. of 30% potassium hydroxide and 50 c.c. alcohol for one minute at 15°; (g) alcoholic hydrochloric acid for one minute at 15°. The following methods were found unsuitable. Treatment with (a) 0.5% copper sulphate solution for forty hours at room temperature; (b) 0.5% copper sulphate solution at 60° for a quarter of an hour; (c) 0.1% solution of copper sulphate for two days at room temperature; (d) hot 2—10% copper sulphate for half a minute; (e) 0.1% hot permanganate solution for half a minute; (f) hot water for two minutes; (g) alcoholic solutions of formaldehyde, phenol, or acetic acid at ordinary temperature; (h) glacial acetic acid for half a minute at room temperature; (i) 10% copper sulphate for five minutes at room temperature.

S. B. S.

**The Action of Plant Metabolism Products on Plants. I. The Action of Nitrogenous Metabolism Products on the Germination of Seeds. (Alkaloids.)** WILHELM SIGMUND (*Biochem. Zeitsch.*, 1914, 62, 299—338).—The action of alkaloids on

various seeds was investigated, the percentage germinating after treatment, and the rate of growth of roots and stems being investigated. Coniine has little toxic action;  $M/250$  nicotine behaves similarly. In higher concentrations it is more toxic than coniine. Piperine and piperic acid are only slightly toxic, even in  $M/100$ -solution. The combined action of piperidine and piperic acid increases the toxicity.  $M/100$ -atropine is slightly toxic, but considerably toxic in  $M/50$ - and  $M/25$ -solutions. Of the scission products, tropine is less, and tropic acid more, toxic than atropine itself. Tropine exerts an antagonistic action to the toxicity of both tropic and the still more toxic atropic acid. The action of hyoscyamine is about equal to that of atropine. Pilocarpine is but slightly toxic, but the toxic action of larger quantities is not antagonised by atropine, as is the case in the action of these alkaloids on animals. Cocaine, even in  $M/50$ -solution (as hydrochloride), is only slightly toxic; its scission products, benzoyl-ecgonine and ecgonine, are even less so. Lupine, lupidine, and sparteine are only slightly toxic, and in concentrations as low as  $M/200$  to  $M/250$  they increase the germinating power of yellow and blue lupines. Cytisine is but slightly toxic. Cinchonine, cinchonidine, and quinine are distinctly toxic in concentrations of  $M/50$  to  $M/25$  (as sulphates or hydrochloride). Quinine is the most toxic of the three. Morphine and narcotine hydrochlorides are toxic in concentrations of  $M/50$ . Berberine is strongly toxic to seeds, even in  $M/222$ -solutions. 0.2% Tannin exerts a partial antagonistic action. Strychnine exerts a distinct toxic effect only when the solution reaches  $M/50$ . Brucine is slightly less toxic than strychnine. Aconitine hydrochloride,  $M/50$ , is but slightly toxic. Veratrine is a little more toxic. Solanine and solanidine have but little toxic action.

S. B. S.

**The Action of Plant Metabolism Products on Plants. II. Action of the Nitrogen Metabolism Products on the Germination of Seeds. (Glucosides, Tannins, and their Scission Products.)** WILHELM SIGMUND (*Biochem. Zeitsch.*, 1914, 62, 339—386).—Arbutin is not toxic even in  $M/13$ -solution. Its hydrolysis product, quinol, is much more so, concentrations of  $M/10$  being quite lethal. Phloridzin and hesperidin, and the scission product phloretin, so far as their solubility in water would permit investigation, are non-toxic. Baptisin in saturated solution ( $<M/500$ ) is distinctly poisonous. Salicin has a slight toxic action in  $M/50$ -solution, but helicin is more poisonous. Populin in saturated solution ( $M/1000$ ) is harmless. Coniferin is only slightly poisonous, but its scission products, produced by the action of emulsin, are more toxic. Syringin ( $M/100$ ) is not toxic. Amygdalin itself is but slightly poisonous, but its scission products are much more so; hence, under aseptic conditions of germination, it is less toxic than under septic conditions. Aesculin,  $M/250$ , is fairly toxic. Sinigrin is slightly toxic, and in  $M/100$ -concentrations it promotes the germination and growth of black mustard. Convallarin in concentrated solutions ( $<M/646$ ) is

slightly toxic. Helleborin (0.2—0.4%) is toxic, byronin only slightly so. Strophanthin (Merck),  $M/50$ , is toxic; digitalin (Merck),  $M/700$  or 0.1%, is slightly toxic, and digitalein even less so. Saponin and sapogenin ( $M/350$ ) are somewhat toxic. Of the bitter substances, aloin,  $M/50$ , is toxic, and picrotoxin even more so. Of the scission products of glucosides, phenol, catechol, resorcinol, quinol, and pyrogallol, as well as *p*-benzoquinone, are all very toxic.

Saligenin,  $M/50$ , is but slightly toxic. Salicylaldehyde,  $M/50$ , is strongly toxic; benzaldehyde is less toxic, exerting a marked effect only when the concentration reaches  $M/20$ . Vanillin,  $M/100$ , is fairly toxic, and piperonal even more so. Benzoic acid is distinctly toxic, even in the concentration  $M/200$ , and is surpassed in this respect by salicylic acid. Cinnamic acid in saturated solution (about  $M/250$ ) is toxic, as is *o*-coumaric acid ( $M/50$ ). Coumarin is still more poisonous. Aesculetin and daphnetin in saturated solutions (about  $M/250$ ) are only slightly poisonous. Mandelic and quinic, and protocatechuic acids are strong poisons (in concentrations  $M/50$ ). Gallic acid is a still more powerful poison. Tannin is, however, less toxic.

S. B. S.

**Share of the Intermediate Products of Alcoholic Fermentation in Oxygen Respiration.** LEONID IVANOV (*Ber. deut. bot. Ges.*, 1914, 32, 191—196).—A reply to Kostytshev (*A.*, 1913, i, 944).

N. H. J. M.

**The Mechanism of the Phenomena of Oxidation and Reduction in Plant Tissues.** J. WOLFF (*Compt. rend.*, 1914, 158, 1125—1127).—The phenomena of oxidation and reduction going on side by side in the plant tissue are apparently regulated by the same mechanism. In the case of the apple, there is a reducing agent present, which acts on the pigment produced by the oxydase in a freshly-cut slice of the fruit, thus tending to check its formation. These reactions are apparently controlled by the acidity of the fruit. Apple pulp when brown reacts with potassium iodide in the presence of its own acid, liberating iodine, but if the acid is previously removed by washing the pulp with dilute disodium hydrogen phosphate solution, no iodine is liberated until the acidity is artificially restored.

W. G.

**Carbon Dioxide and Plants.** R. KLEIN and E. REINAU (*Chem. Zeit.*, 1914, 38, 545—547).—Vegetation experiments with various plants grown in a glass-house, divided into two equal parts by means of an air-tight partition, on one side of which the air was supplied with 0.35—0.45% carbon dioxide. As compared with ordinary air, the growth under the influence of an increased supply of carbon dioxide was increased by 50—100% in four weeks.

It is suggested that, under natural conditions, growth may sometimes be limited by the supply of carbon dioxide, and that manuring with carbon dioxide, if not too costly, would be desirable. Where irrigation is in use, water saturated with carbon dioxide might be employed.

N. H. J. M.

**Alleged Relation between Nitrate Assimilation and the Separation of Manganese in Plants.** E. HOUTERMANS (*Bied. Zentr.*, 1914, 43, 282—283; from *Anz. k. Akad. Wiss. Wien*, 1912, 246; *Bot. Centr.*, 1913, 122, 552).—Acqua's statement that the roots of plants, in contact with manganese nitrate, secrete manganese in certain places in which the nitrate is assimilated, is not confirmed. In experiments with beans and wheat, it was found that blackening occurs when the manganese is combined with indifferent or injurious anions; it is, therefore, not connected with nitrate assimilation.

N. H. J. M.

**Action of Zinc, Arsenic, and Boron Compounds on the Growth of Plants.** WINIFRED E. BRENCHELY (*Ann. Bot.*, 1914, 28, 283—301. Compare A., 1910, ii, 889).—Water-culture experiments, in which peas and barley were grown in presence of varying amounts of the following substances: Zinc sulphate, arsenious acid, arsenic acid, sodium arsenite, and arsenate and boric acid.

As regards zinc and arsenic, no stimulating effect was observed with any strength down to 0.005 mg. per litre in the case of zinc, and 0.02 mg. with arsenious acid. The toxic effect varies with different plants, and with the period of growth, plants being usually more resistant in the summer months than in spring and autumn. So that the highest indifferent amount of zinc sulphate varied between 0.2 and 0.04 mg. per litre in the case of barley, and between 0.2 and 0.05 mg. with peas. Arsenious acid and arsenites are more toxic, especially to peas, than arsenic acid and arsenates.

Boric acid is less toxic than zinc and arsenic, being injurious only when the amount exceeds 10 per million. Smaller amounts down to 0.05 per million have a stimulating action.

Whilst the appearance of barley grown in presence of boric acid would seem to indicate stimulation, the weights of the produce show that this is not the case.

N. H. J. M.

**Simultaneous Presence of Carbamide and Urease in the Same Plant.** R. FOSSE (*Compt. rend.*, 1914, 158, 1374—1376).—The author has proved the presence of carbamide in *Aspergillus niger* and in the plantule of the green pea, and of the soja plant. The same plants, either crushed or through their expressed juice, have furnished urease, which has decomposed carbamide in aqueous solution at 46°. The crushed plant or juice previously heated in an autoclave was without action on the carbamide.

W. G.

**Flower Pigments of *Antirrhinum Majus*. III. Red and Magenta Pigments.** MURIEL WHELDALE and HAROLD LLEWELYN BASSETT (*Biochem. J.*, 1914, 8, 204—206).—Two kinds of anthocyanin, red and magenta, occur in *Antirrhinum*, which give rise to tinged, pale and deep varieties; in presence of luteolin, bronze and crimson colours are produced. Both anthocyanins, especially magenta, contain considerably more oxygen than the flavones; and there is evidence that the anthocyanin mols. are larger than the flavone mol. So that if a flavone constitutes the chromogen, con-

densation of two flavone mols., or of flavone and an aromatic acid, or other compound, must take place.

Results of analyses of the two anthocyanins and their lead salts, and estimations of mol. weight, indicate that the red and magenta compounds have, respectively, the formulæ  $C_{24}H_{27}O_{15}$  and  $C_{30}H_{36}O_{20}$ . The number of hydroxyl groups was found to be twelve in red, and fifteen in magenta anthocyanin.

N. H. J. M.

**Vegetable Galls.** KURT R. VON STOCKERT and JULIUS ZELLNER (*Zeits. physiol. Chem.*, 1914, **90**, 495—501).—Analyses of galls of *Cynips conglomerata*, *C. tinctoria*, *C. folii*, and *Rhodites rosae*. The galls contain considerably more water and much less crude fibre than the plants; the amount of substances soluble in water, especially tannins, is higher in the galls than in the plants. The galls of *Cynips conglomerata*, *C. tinctoria*, and *Rhodites* contained less reducing sugar than the plants, whilst in those of *C. folii* the amount of reducing sugar was very high. The amount of total ash is sometimes more and sometimes less than in the normal parts of the plant; the soluble mineral matter is, however, higher in the galls. Estimations of manganese failed to show any regularity.

N. H. J. M.

**The Australian Melaleucas and their Essential Oils.** V. R. T. BAKER and H. G. SMITH (*J. Roy. Soc., New South Wales*, 1914, **47**, 193—214).—The authors have made a botanical study of the members of the genus *Melaleuca*, and have compared the oils obtained from the leaves of the Australian "tea trees" with cajuput oil. The latter oil consists very largely of cineole (68% in one specimen), whereas the Australian samples contain much less of this compound but considerable quantities of an aliphatic, sesquiterpene alcohol. The authors have therefore re-classified the various *Melaleucas*, and consider that *M. minor*, Smith, the East Indian source of cajuput oil, and *M. leucadendron*, Linn., are not represented in Australia.

The oils were examined by the usual processes, and full details of the physical constants and fractionations are given. The oils obtained from various specimens of *M. Maidenii*, common to northern New South Wales, contained about 31—39% of cineole and 16·8% of a sesquiterpene alcohol, which is probably identical with that which is described below. The oils from three specimens of *M. Smithii*, which grows in the Sydney district, contained from 1—5% of cineole and roughly 50% of the characteristic aliphatic sesquiterpene alcohol,  $C_{15}H_{26}O$ . The latter does not agree with nerolidol or farnesol, and is named *melaleucol*. It has a faint, pleasant odour, b. p. 163—165°/33 mm., 275—277°/atm.,  $D^{15}_D$  0·886,  $n^{20}_D$  1·488, which corresponds with three double linkings, and is dextrorotatory. One of the specimens was also found to contain about 6% of pinene and 4% of limonene.

J. C. W.

**The Occurrence of Trimethylamine and its Origin in the Australian Salt Bush (*Rhagodia hastata*).** R. W. CHALLINOR (*J. Roy. Soc., New South Wales*, 1914, **47**, 236—243).—The Australian



"Salt bush," which is largely cultivated as an ornamental hedge, is noted for the strong herring-brine odour which it emits during the spring and summer months. Trimethylamine was detected in the distillate after boiling the fresh shoots with alkali hydroxide or with water alone. Search was therefore made for a complex substance which would yield this base by decomposition in the plant, and a compound which is very closely allied to choline has been isolated. The author hopes to obtain enough of this substance to characterise it. Schulze and Trier (A., 1912, ii, 1203) have shown that choline, betaine, and allied bases are normal constituents of many other members of the order *Chenopodiaceae*. The presence in the plant of acetic acid and a glucoside of quercetin is also indicated.

J. C. W.

**The Nitrogenous Matter of Grape-must.** R. MARCILLE (*Compt. rend.*, 1914, 158, 1199—1201. Compare A., 1913, i, 685).—The author has repeated his previous work on the fermentation of grape-must containing varying amounts of organic and volatile nitrogen, and has obtained results agreeing in some cases with his previous work and in others with the work of Laborde (compare *Ann. Inst. Pasteur*, 1898, 517). The musts contained fixed organic nitrogen and volatile ammoniacal and amino-nitrogen, the absolute and relative proportions of which are very variable. Both diminish in amount as the ripening of the fruit progresses. The musts, which show the greatest resistance to fermentation, are generally characterised by a low content of volatile nitrogen.

W. G.

**Carbohydrates of Savoy Cabbages.** ERNST BUSOLT (*J. Landw.*, 1914, 62, 117—120).—Mannitol and glucose were isolated and identified. The yields of pure substances were respectively about 0.1 and 0.02%, the amounts actually present being, no doubt, considerably greater.

N. H. J. M.

**Solubility and Decomposition of the Nitrogen Compounds in Soil.** VALMARI (*Bied. Zentr.*, 1914, 43, 217—219; from *Abh. Agric.-wiss. Ges. Finnland*, 1912, Heft 3).—The examination of peat and garden soil showed that most of the nitrogen (85—97%) was in the form of proteins, mainly nucleins.

The soluble nitrogen obtained by the action of acids and alkalis on soil is chiefly in the form of amino-acids. Evidence was obtained that the nitrogen compounds of only slightly decomposed peat are more readily broken down than those of the more humified kinds of peat.

N. H. J. M.

## Organic Chemistry.

**Thermal Reactions in Carburetting Water Gas. II. Experimental.** M. C. WHITAKER and W. F. RITTMAN (*J. Ind. Eng. Chem.*, 1914, 6, 472—479. Compare this vol., i, 645).—Experimental proof is given of the correctness of the assumption that, in oil gas manufacture, diminished pressure increases the yield of gaseous hydrocarbons; the gas also contains much less hydrogen than do products obtained at the same temperature under higher pressure. It is shown that the end products resulting from cracking oil in an atmosphere of hydrogen, which reacts chemically with the end products of the cracking, are a function of both the composition and the quantity of gas produced. W. P. S.

**$\Delta^\beta$ -Pentene and Some of its Derivatives.** (Mlle.) H. VAN RISSEGHEM (*Compt. rend.*, 1914, 158, 1694—1698\*).— $\Delta^\beta$ -Pentene has been prepared from diethylcarbinol, using *p*-toluenesulphonic acid as the dehydrating agent in order to avoid too great a rise in temperature (compare Wuyts, A., 1912, i, 598).

The reaction takes place at 135—140°, and gives a yield of 82%. The product has the following physical constants: m. p.  $-147^\circ (\pm 0.01^\circ)$ , b. p.  $36.40^\circ (\pm 0.05^\circ)/760$  mm.,  $D_4^{11}$  0.6595,  $D_4^{17.2}$  0.6535,  $n_{H_a}^{11}$  1.3832,  $n_D^{11}$  1.3857,  $n_{H_\beta}^{11}$  1.3927,  $n_{H_a}^{17.2}$  1.3793,  $n_D^{17.2}$  1.3817, and  $n_{H_\beta}^{17.2}$  1.3878. The fixity of these values points to the product consisting of one only of the two possible stereoisomerides. Attempts to bring about isomerisation by iodine, hydrogen iodide, bromine or hydrogen bromide have all failed. In the use of iodine it was noticed that iodine unites with the pentene according to a reversible reaction:  $C_5H_{10} + I_2 \rightleftharpoons C_5H_{10}I_2$ , in which equilibrium is reached at 13.5°, when the molecular concentration of the di-iodopentane is forty-nine times that of the iodine. In the use of bromine,  $\beta$ -dibromopentane (compare Wagner and Saytzeff, this Journ., 1876, i, 547) was obtained, and found to have the following physical constants: m. p.  $-66^\circ$ , b. p.  $60.5$ — $61^\circ/14$  mm.,  $D_4^{11}$  1.6857,  $D_4^{17.2}$  1.6766,  $n_{H_a}^{11}$  1.5085,  $n_D^{11}$  1.5119,  $n_{H_\beta}^{11}$  1.5204,  $n_{H_a}^{17.2}$  1.5058,  $n_D^{17.2}$  1.5093, and  $n_{H_\beta}^{17.2}$  1.5177. By removal of hydrogen bromide by means of alcoholic potassium hydroxide a mixture of two position-isomeric bromopentenes was obtained, which could not be separated by fractional distillation. Further treatment of the mixture with alcoholic potassium hydroxide yielded  $\Delta^\beta$ -pentinene (compare Faworsky, A., 1888, 798), of which the physical constants were m. p.  $-101^\circ (\pm 1^\circ)$ , b. p.  $55.5^\circ (\pm 0.05^\circ)/760$  mm.,  $D_4^{17.2}$  0.7127,  $n_{H_a}^{17.2}$  1.4020,  $n_D^{17.2}$  1.4045, and  $n_{H_\beta}^{17.2}$  1.4116. From these the increment of refraction of the acetylenoid linking were calculated for  $H_a$  2.448,  $H_\beta$  2.581, D 2.493, and a comparison of these with the values obtained by Moureu for heptylidene and octylidene shows that the position of the triple linking has a notable influence on the value of the increment of refraction.

The controlled addition of bromine to  $\Delta^\beta$ -pentinene yielded  $\beta\gamma$ -di-

\* and *Bull. Soc. chim. Belg.*, 1914, 187—198.

*bromo- $\Delta^{\beta}$ -pentene*, m. p.  $-78.5^{\circ}$  to  $-77^{\circ}$ , b. p.  $64-66^{\circ}/23$  mm.,  $D_4^{18}$  1.7068,  $n_{D_H}^{18}$  1.5175,  $n_D^{18}$  1.5215, and  $n_{H\beta}^{18}$  1.5316, this being the *cis-trans* isomeride, and not a mixture. On further treatment with bromine in sunlight this compound yielded a mixture of  *$\beta\beta\gamma\gamma$ -tetrabromopentane*, m. p.  $127-128^{\circ}$ , b. p.  $140-142^{\circ}/17$  mm., and a *tri-bromopentene*, b. p.  $103-105^{\circ}/16$  mm., which was probably a mixture of two position-isomerides or two stereoisomerides. W. G.

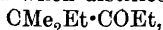
**Some Products Isolated from Soot.** EDMUND KNECHT and (Miss) EVA HIBBERT (*Mem. Manchester Phil. Soc.*, 1914, 58, No. 2, pp. 1-5. Compare A., 1905, ii, 703).—Soot collected from ordinary household chimneys in London and in Prague contains much less extractive matter than soot collected in Manchester. A sample of household soot from the Warrington district has been extracted with benzene, and from the extract a hydrocarbon,  $C_{27}H_{54}$ , m. p.  $65^{\circ}$ , colourless crystals, has been isolated, which seems to be König and Kiesow's cerotene (this Journ., 1873, 26, 1215). The same hydrocarbon can be isolated in other ways, and from soot from other sources.

From the glacial acetic acid solution of the residue left by the evaporation of the benzene extract (above), a yellow oil has been obtained, which has b. p.  $300^{\circ}$  ("in vacuo") and  $d_4$   $8^{\circ}$  in chloroform, and is apparently an alcohol.

The portion of the benzene extract which is soluble in aqueous sodium hydroxide contains an *acid*,  $C_{10}H_{10}O_2$  (?), m. p.  $135^{\circ}$ . C. S.

**$\Delta^{\alpha\gamma\epsilon}$ -Hexatriene.** P. VAN ROMBURGH and P. MULLER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 1090-1093).—Various methods have been tried for the preparation of  $\Delta^{\alpha\gamma\epsilon}$ -hexatriene (van Romburgh and van Dorssen, A., 1906, i, 130) in a state of higher purity than before. The hydrocarbon can be obtained by heating  $\Delta^{\alpha\epsilon}$ -hexadiene- $\gamma$ -diol with 99% formic acid and by dehydrating  $\Delta^{\alpha\epsilon}$ -hexadien- $\delta$ -ol (van Romburgh and Le Heux, A., 1913, i, 695) with potassium pyrosulphate or phthalic anhydride. The most satisfactory method, however, was by the action of zinc dust on the boiling alcoholic solution of  $\gamma\delta$ -dibromo- $\Delta^{\alpha\epsilon}$ -hexadiene (Griner, A., 1893, i, 241), when a product was obtained, b. p.  $80-80.5^{\circ}/755$  mm., m. p.  $-10.5^{\circ}$ ,  $D_4^{13.5}$  0.740,  $n_D^{13.5}$  1.5172. D. F. T.

**A New Hydrocarbon from the Pinacone of Methyl Ethyl Ketone.** P. VAN ROMBURGH and (Miss) D. W. WENSINK (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 1088-1090).—When the pinacone of methyl ethyl ketone is warmed with an equal weight of 97% formic acid, the mixture first becomes red and then separates into a deep red lower layer and an almost colourless upper one. The product was washed with water, and when distilled gave the pinacolin,



and also a *hydrocarbon*,  $C_{16}H_{28}$ ,  $D_4^{13.5}$  0.8741,  $n_D^{13.5}$  1.4864, which could be distilled under reduced pressure. This same hydrocarbon can also be obtained by the action of hot formic acid on the hydrocarbon,  $C_8H_{14}$ , which is formed in the action of dilute sulphuric acid on the pinacone (Herschmann, A., 1893, i, 547). Bromination, oxidation and

reduction have hitherto failed to give definite results which would be of value in elucidating the constitution of the new substance.

D. F. T.

Dichloroacetylene. (A Warning.) J. BÖESEKEN and J. F. CARRIERE (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1093—1095).—In an attempt to prepare ditrichlorovinyl ketone,  $\text{CO}(\text{CCl}_2\text{CCl}_2)_2$ , by dry distillation of barium trichloroacrylate it was found that, contrary to expectation, the barium remained as chloride, whilst carbon dioxide and a gas which fumed in the air were expelled.

By distilling one gram of the salt in a current of hydrogen and condensing less volatile products by passage through a cold tube, a small amount of a colourless solid substance, m. p. below  $-50^\circ$ , could be separated by further passage through a tube at  $-70^\circ$ . Treatment with a current of chlorine, the temperature being still  $-50^\circ$ , converted the substance into hexachloroethane. The decomposition of the barium trichloroacrylate is therefore believed to have followed the course  $(\text{CCl}_2\cdot\text{CCl}\cdot\text{CO}_2)_2\text{Ba} = \text{BaCl}_2 + 2\text{CO}_2 + 2\text{C}_2\text{Cl}_2$ , the new product being *dichloroacetylene*.

The serious results of an unexpected explosion of the product from three grams of barium trichloroacrylate indicates that dichloroacetylene is more dangerous than dibromoacetylene (Lemoult, A., 1903, i, 595, 673). Dichloroacetylene is a colourless gas of disgustingly sweet odour (compare Prins, *Diss.*, Delft, 1912); in a very dilute condition its oxidation in the air is attended by luminescence, whilst in more concentrated admixture with hydrogen it fires in the air.

D. F. T.

The Ethylenic Isomerism of the  $\alpha$ -Bromopropenes. G. CHAVANNE (*Compt. rend.*, 1914, **158**, 1698—1701. Compare Wislicenus and Langbein, A., 1889, 236).—Starting with propyl alcohol, this has been converted into propene by passing it over chromium phosphate at  $380^\circ$  (compare *Bull. Soc. Chim. Belg.*, 1909). The product on bromination gave  $\alpha\beta$ -dibromopropane which under the influence of sodium phenoxide in alcoholic solution gave a mixture of  $\alpha$ - and  $\beta$ -bromopropenes. These were separated by repeated fractional distillation into  $\beta$ -bromopropene, m. p.  $-126^\circ (\pm 1^\circ)$ , b. p.  $48\cdot35^\circ (\pm 0\cdot1^\circ)/760$  mm.,  $D_4^{15\cdot75} 1\cdot3965$ ,  $n_{\text{H}_a}^{15\cdot75} 1\cdot44335$ ,  $n_{\text{D}}^{15\cdot75} 1\cdot44665$ ,  $n_{\text{H}_\beta}^{15\cdot75} 1\cdot45523$ , and a mixture of stereoisomeric  $\alpha$ -bromopropenes. These could not be separated by ordinary fractional distillation, but with ethyl or methyl alcohols gave binary mixtures which could be separated by fractionation. The spacial structure of the two isomerides was determined by the rate at which they lost hydrogen bromide under the influence of alcoholic potassium hydroxide. The *cis*-isomeride has m. p.  $-113^\circ$ , b. p.  $57\cdot8^\circ/760$  mm.,  $D_4^{15\cdot75} 1\cdot4338$ ,  $D_4^{16\cdot2} 1\cdot4333$ ,  $n_{\text{H}_a}^{16\cdot2} 1\cdot4529$ ,  $n_{\text{D}}^{16\cdot2} 1\cdot4564$ ,  $n_{\text{H}_\beta}^{16\cdot2} 1\cdot4649$ , and the *trans*-isomeride, m. p.  $-76\cdot5^\circ$ , b. p.  $63\cdot25^\circ/760$  mm.,  $D_4^{15\cdot75} 1\cdot4169$ ,  $n_{\text{H}_a}^{15\cdot75} 1\cdot4515$ ,  $n_{\text{D}}^{15\cdot75} 1\cdot4549$ ,  $n_{\text{H}_\beta}^{15\cdot75} 1\cdot4634$ . The molecular refractive power of the *cis*-isomeride is inferior to that of the *trans*-isomeride. Neither isomeride is stable at the ordinary temperature, each yielding a well-defined binary mixture of the two isomerides, having  $D_4^{15\cdot75} 1\cdot430$  and containing 82% of the *cis*-

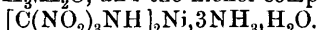
isomeride. Both forms on bromination yield the same tribromopropane, b. p. 202—203°/762.5 mm. and 79°/12 mm., as compared with the tribromopropane, b. p. 191—192°/762 mm., from  $\beta$ -bromopropene.

W. G.

**Ethylenic Isomerism of the Acetylene Di-iodides.** G. CHAVANNE and (Mlle.) J. Vos (*Compt. rend.*, 1914, 158, 1582—1585. Compare A., 1912, i, 330, and van de Walle, A., 1913, i, 950).—A study of the two acetylene di-iodides, as prepared by Keiser's method (compare A., 1899, i, 398) by the action of acetylene on iodine at 150—160°. By this method after removal of the excess of iodine, the products are the solid and liquid isomerides and a eutectic mixture, which cannot be separated by fractional distillation or by fractional precipitation with water of its solution in methyl alcohol. The solid isomeride has m. p. 72°, b. p. 76.5—77°/16 mm. and 190.5°/760 mm., and the liquid isomeride, m. p. -13.8°, b. p. 72.5°/16 mm., 188°/760 mm. (decomp.),  $D_4^{15.2}$  3.023,  $n_{D_a}^{11.2}$  1.697,  $n_{D_b}^{11.2}$  1.706,  $n_{D_s}^{11.2}$  1.730. The elimination of hydrogen iodide in the presence of alcoholic potassium hydroxide is at least two hundred times more rapid in the case of the liquid than the solid isomeride, and consequently the *cis*-configuration is attributed to the liquid form. On heating either isomeride at 170° until equilibrium is reached the mixture is found to contain 52.5% of the solid isomeride, whilst at 146° the mixture contains 55% of the solid form. Temperature has a marked effect on the composition of the equilibrium mixture; the lower the temperature the higher is the percentage of the solid isomeride.

W. G.

**A Reaction of Tetranitromethane.** W. R. HODGKINSON and F. R. J. HOARE (*J. Soc. Chem. Ind.*, 1914, 33, 522—523).—Tetranitromethane (T., 1910, 97, 2099) in alcoholic ammoniacal solution reacts with metals such as copper, zinc, cadmium, and nickel, that is, with metals which form amides or ammine compounds, but it has no action on iron or aluminium. The action is accelerated by the addition of a small quantity of the ammine compound of the metal, and results in the formation of crystalline compounds; these are also produced when an ammonium double salt, such as nickel ammonium nitrate, is added to the tetranitromethane solution. The compounds crystallise well from hot alcohol or acetone, but hydrolyse rapidly when heated with water. The copper compound appears to have the composition:  $[C(NO_2)_3NH]_2Cu, 3NH_3, H_2O$ , and the nickel compound:



W. P. S.

**Preparation of Glycide.** JEAN NIVIÈRE (*Bull. Soc. chim.*, 1914, [iv], 15, 464—465).—The author has increased the yield in Bigot's method (compare *Ann. Chim. Phys.*, 1891, [vi], 22, 481) for the preparation of glycide,  $\begin{array}{c} O \\ | \\ CH_2 \end{array} > CH \cdot CH_2 \cdot OH$ , from 29 to 55% by reducing the size of the pieces of sodium used from 20 grams to 2 grams. The reaction under these conditions is complete in one day instead of three.

W. G.

**Isomorphism of the Ethyl Sulphates of the Metals of the Rare Earths and the Problem of Eventual Morphotropic Relations of these Salts with Analogous Salts of Scandium, Indium, and Glucinum.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 1095—1105).—The author has examined the crystalline form of the ethyl sulphates of yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, thulium, erbium, and neo-ytterbium. These substances, which have the general formula  $\text{Me}_2(\text{EtSO}_4)_6 \cdot 18\text{H}_2\text{O}$ , form a strictly isomorphous series. From angular measurements and Röntgen ray patterns, it has been found that the salts belong to the hexagonal-bipyramidal (hemiedric) group of the hexagonal system. The parameters vary about the most probable mean value  $a:c = 1:0.5062 \pm 0.0012$ , and the deviations can in no way be regarded as typical for each salt of the series.

The corresponding salts of scandium and indium could only be obtained in the form of very small crystals, but it was possible to draw the conclusion that these salts are not of the same crystalline form as that which is exhibited by the ethyl sulphates of the rare earth metals. The crystals are of monoclinic symmetry, and possess characteristic optical properties. Glucinum ethyl sulphate stands quite apart from the other salts examined. Its composition corresponds with the formula  $\text{GlO} \cdot \text{Gl}(\text{EtSO}_4)_2 \cdot 4\text{H}_2\text{O}$ , and crystallises in tetragonal forms.

The acetylacetates of scandium, indium, and iron are isomorphous, and crystallise in large, flat crystals which are quite different from the fine needles in which the corresponding salts of the rare earth metals separate out. Glucinum acetylacetate is monoclinic and widely different from the other salts of this acid. H. M. D.

**Trimethylene Trisulphide and its Oxides.** O. HINSBERG (*J. pr. Chem.*, 1914, [ii], 89, 547—551).—In the preparation of trimethylene trisulphoxide by heating trimethylene trisulphide with hydrogen peroxide on the water-bath, the author (A., 1913, i, 818) obtained a by-product which was considered to be a disulphonesulphoxide of the following constitution:  $\text{CH}_2 \begin{smallmatrix} \text{SO}_2 \cdot \text{CH}_2 \\ \text{SO}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SO}$ .

The formation of this compound is now found to be due to the presence of an amorphous impurity in the commercial trimethylene trisulphide employed in the oxidation. When pure, neither the  $\alpha$ - nor  $\beta$ -trisulphide yields this compound, and it is therefore doubtful whether it has the above constitution.

A *trimethylene disulphonesulphoxide* has, however, been prepared by heating trimethylene trisulphide or trimethylene trisulphoxide for several hours with 30% hydrogen peroxide and glacial acetic acid on the water-bath. It forms a crystalline powder (decomp. above  $280^\circ$ ) insoluble in the usual organic solvents, but dissolves in aqueous alkalis with the formation of salts. When kept for a week in contact with hydriodic acid (D 1.96) it is converted into *trimethylene disulphide-sulphone*,  $\text{CH}_2 \begin{smallmatrix} \text{S} \cdot \text{CH}_2 \\ \text{S} \cdot \text{CH}_2 \end{smallmatrix} \text{SO}_2$ , which is separated from the accompany-

ing trimethylene disulphonesulphide by taking advantage of the solubility of the latter in aqueous sodium hydroxide.

The disulphidesulphone has m. p.  $218^{\circ}$ , and does not form salts with alkalis.

It has been shown previously that oxidation of trimethylene trisulphide with hydrogen peroxide in glacial acetic acid solution results in the formation of trimethylene trisulphoxide, together with a sparingly soluble substance which was considered to be a pentoxide. The latter substance is now found to be isomeric with the trisulphoxide, and is termed *isotrimethylene trisulphoxide*. It crystallises in slender, colourless needles, which become brown at  $260^{\circ}$  (decomp.  $280^{\circ}$ ). It is reduced by hydriodic acid to  $\beta$ -trimethylene trisulphide and yields yellowish-red solutions in aqueous sodium hydroxide. The author considers that the isomerism of the trisulphoxides is of the same type as that of the  $\alpha$ - and  $\beta$ -trisulphides, and is determined by the spatial configuration of the sulphur-atom.

F. B.

**A Simple Method for the Preparation of Lecithin.** HUGH MACLEAN (*J. Path. Bact.*, 1914, 18, 490—494).—The essential part of the method consists in the purification of the crude lecithin obtained by extraction with alcohol. This is carried out by emulsification with water and treatment with acetone. Lecithin, after purification, is readily oxidised, and many of the new lecithin-like substances described are merely oxidation products, or consist of lecithin plus nitrogenous impurities. No definite conclusions can be based on solubility alone; the degree of oxidation and the presence of impurities influence solubility greatly.

W. D. H.

**Electrolysis of Molten Salts of Fatty Acids.** JULIUS PETERSEN (*Zeitsch. Elektrochem.*, 1914, 20, 328—332).—A eutectic mixture of lead acetate and zinc acetate was electrolysed in a porcelain tube at  $174^{\circ}$  by a current of 0.65 ampere. The gases evolved at the anode consisted of 2.1% olefines, 29.0% carbon monoxide, 28.9% hydrogen, 25.6% methane, and 13.4% ethane; the carbon dioxide was removed before the analysis was carried out. A mixture of 3 molecules of lead acetate and 1 molecule of sodium acetate gave, at  $140^{\circ}$ , 2.6% olefines, 6.0% carbon monoxide, 12.1% hydrogen, 55.5% methane, and 22.3% ethane. Similarly, results were obtained with molten acid potassium acetate. Lead propionate was electrolysed at  $130^{\circ}$  with a current of 0.6 ampere, and gave 40.0% olefines, 3.0% carbon monoxide, 0.3% hydrogen and paraffins,  $C_nH_{2n+2}$ , for which the value of  $n$  is 2.02, and hence they consisted of ethane with a little methane. Lead butyrate electrolysed at  $85^{\circ}$  gave 42.6% olefines, 18.3% carbon monoxide, 25.0% hydrogen and paraffins,  $n = 2.05$ . Consequently, it is shown that the products of the electrolysis of molten salts of the fatty acids are of the same type as those of the electrolysis of aqueous solution, although the amount is very much smaller in the present case. The figures given above vary very much in the different experiments, and are very different at different periods in the electrolysis. A further series of experiments was carried out, which consisted in heating lead salts of the fatty acids with sulphur at  $180^{\circ}$  for ten hours and collecting the

gases over sodium hydroxide. One hundred grams of lead acetate gave 15 grams of a mixture of acetic acid and methyl acetate and 30 c.c. of gas, which consisted of 11·8% olefines, 0·8% oxygen, 37·0% carbon monoxide, 36·2% hydrogen, and paraffins,  $n = 1·9$ . One hundred grams of lead propionate gave 20 grams of propionic acid and 12 c.c. of gas, which consisted of 2·4% oxygen, 57·3% carbon monoxide, 3·7% hydrogen, and paraffins,  $n = 2·06$ . One hundred grams of lead butyrate gave 23 grams of pure butyric acid and 40 c.c. of gas which consisted of 1·0% oxygen, 16·2% carbon monoxide, 60·0% hydrogen, and paraffins,  $n = 1·44$ . One hundred grams of lead isovalerate gave 13 c.c. of isovaleric acid and 2 c.c. of gas which was not analysed. It is thus shown that there is practically no production of ethyl esters as is the case when silver salts of the fatty acids are heated with iodine (Simonini, A., 1892, 1301).

J. F. S.

**Some Organic Uranium Salts of the Monocarboxylic Acids of the Fatty Series.** G. COURTOIS (*Compt. rend.*, 1914, 158, 1511—1514).—In addition to uranyl acetate, already known, the author has prepared a number of its homologues by solution of uranium hydroxide,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ , in an excess of a boiling aqueous solution of the acid. On cooling, the hydrated salt crystallises out. The following have been prepared:

*Uranyl formate*,  $(\text{H} \cdot \text{CO}_2)_2\text{UO}_2 \cdot \text{H}_2\text{O}$ , yellow, octahedral crystals, which lose their water at  $150^\circ$ , and in aqueous solution in the dark gradually form the *basic* salt,  $(\text{H} \cdot \text{CO}_2)_2\text{UO}_2 \cdot \text{H}_2\text{O} \cdot \text{UO}_3 \cdot 2\text{H}_2\text{O}$ , which is almost insoluble in formic acid.

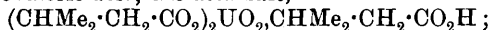
*Uranyl propionate*,  $(\text{C}_3\text{H}_5 \cdot \text{CO}_2)_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , yellow crystals, giving the anhydrous salt at  $100^\circ$ , and crystallising from propionic acid in the anhydrous form.

*Uranyl butyrate*,  $(\text{C}_3\text{H}_7 \cdot \text{CO}_2)_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , yellow crystals, giving the anhydrous salt at  $100^\circ$ , and from solution in butyric acid, the *acid* salt,  $(\text{C}_3\text{H}_7 \cdot \text{CO}_2)_2\text{UO}_2 \cdot \text{C}_3\text{H}_7 \cdot \text{CO}_2\text{H}$ .

*Uranyl isobutyrate*,  $(\text{CHMe}_2 \cdot \text{CO}_2)_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , small, yellow crystals, giving the anhydrous salt at  $100^\circ$ , and from solution in isobutyric acid, the *acid* salt,  $(\text{CHMe}_2 \cdot \text{CO}_2)_2\text{UO}_2 \cdot \text{CHMe}_2 \cdot \text{CO}_2\text{H}$ .

*Uranyl valerate*,  $(\text{C}_4\text{H}_9 \cdot \text{CO}_2)_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , yellowish-white, pearly plates, becoming anhydrous in dry air or at  $100^\circ$ . This salt is the least soluble in water of the whole series.

*Uranyl isovalerate*,  $(\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , yellowish-white plates, becoming anhydrous in dry air or at  $100^\circ$ , and giving from solution in isovaleric acid, the *acid* salt,



100 c.c. of the saturated aqueous solutions of these salts contain the following weights at the temperatures given:

	Temperature.	Grams.
Uranyl formate.....	$15^\circ$	7·20
Uranyl acetate .....	17	7·73
Uranyl propionate .....	19	8·48
Uranyl butyrate .....	17	10·53
Uranyl isobutyrate .....	20	4·25
Uranyl isovalerate .....	14	3·72



The formate and acetate are insoluble in anhydrous ether, whilst all the others are soluble, a compound, containing  $\frac{1}{2}$  mol. ether to 1 mol. of the dihydrate, being obtained in the case of the butyrate and isovalerate.

A concentrated solution of the formate decomposes in the dark, and of the acetate in diffused light, giving basic salts. All the others are stable in diffused light. Their saturated aqueous solutions are all decomposed by sunlight, a mixture of carbon dioxide and saturated hydrocarbons being evolved.

W. G.

**The Acyclic  $\gamma$ -Halogenated Acids.** HENRI WOHLGEMUTH (*Compt. rend.*, 1914, 158, 1577—1579).—The three  $\gamma$ -halogenated valeric acids are readily obtained by the action of hydrochloric, hydrobromic, and hydriodic acids respectively on  $\gamma$ -valerolactone.

$\gamma$ -Chloro-*n*-valeric acid, b. p. 115—116°/10 mm., is obtained by the action of hydrochloric acid on the  $\gamma$ -lactone in a sealed tube at 150°. With sulphuric acid and alcohol it gives the *ethyl* ester, a colourless liquid, b. p. 70·5°/9 mm., and with thionyl chloride at 80—100°, the *acid chloride*, a colourless, mobile liquid with a strong, disagreeable odour, b. p. 61°/9 mm. This chloride reacts with ammonia, aniline, and phenylhydrazine to give respectively the *amide*, m. p. 79—79·5°, the *anilide*, white needles, m. p. 104°, the *phenylhydrazide*, m. p. 100°. Attempts at cyclisation by the action of heat on these amides were not successful, the only products being resins.

$\gamma$ -Bromovaleric acid, m. p. 21°, gives an *ester*, b. p. 89·5—91·5°/12 mm., and an *acid chloride*, a yellow liquid, b. p. 79—80°/11 mm. In the preparation of the latter the temperature must be kept at 50°, or if the temperature rises to 100° the product is  $\gamma$ -bromovaleric anhydride, b. p. 189—190°/13 mm.

$\gamma$ -Iodovaleric acid, m. p. 18°, rapidly decomposing to a dark brown tar, yields an *ethyl* ester, b. p. 102°/10·5 mm., decomposed by light;  $\gamma$ -chlorobutyric acid has also been prepared (compare Henry, A., 1886, 215) and found to distil unchanged at 114°/15 mm.

None of these  $\gamma$ -halogenated acids reacts with magnesium in anhydrous ether, even in the presence of the usual starting agents.

A further example of the relative passivity of the halogen atom in the  $\gamma$ -halogenated esters is furnished by their behaviour towards diethylamine. This substance readily reacts with chloroacetic and  $\beta$ -chloropropionic acids in ether, but it only reacts at 100° in a sealed tube, without solvent, with ethyl  $\gamma$ -chlorobutyrate, giving *ethyl  $\gamma$ -diethylaminobutyrate*, an alkaline liquid, b. p. 98°/13 mm., which yields a *picrate*, m. p. 78°, and a *hydrochloride* of the free acid, m. p. 106°. Diethylamine reacts with ethyl  $\gamma$ -chlorovalerate at 180°, or with ethyl  $\gamma$ -bromovalerate at 100° to give *ethyl  $\gamma$ -diethylaminovalerate*, b. f. 96°/8 mm., yielding a *picrate*, m. p. 90—90·5°, and a *platinichloride* of the amino-acid, m. p. 153—155°, crystallising with  $2\frac{1}{2}$  H<sub>2</sub>O. Ethyl  $\gamma$ -diethylaminovalerate on reduction with sodium in absolute alcohol yields  $\gamma$ -diethylaminoamyl alcohol, b. p. 104·5°/11·5 mm., giving a *picrate*, m. p. 70—71°, and a *hydrochloride* of the benzoyl derivative, m. p. 70—71°

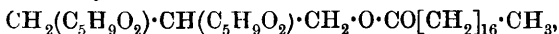
W. G.

**Preparation of Optically Active Fats. I. Synthesis of Optically Active Halogen-hydrins.** EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1914, 47, 1856—1866).—The preparation and characterisation of fats which are asymmetrically constructed in the glycerol component is of great physiological interest, especially in regard to the action of lipolytic ferments and the isolation of separate ferments, specific to different stages in fat degradation.

In the first place, the obvious method was pursued, namely, the preparation of triglycerides with different acid residues in the  $\alpha$ - $\alpha'$ -positions. It was expected that lipase would hydrolyse one of the isomerides and not the other, but, although hydrolysis did take place, no development of optical activity was observed. Optically active fatty acids were therefore condensed with halogen-hydrins, but the resulting compounds were so similar that differentiation of the active components was impossible. A certain measure of success has been attained, however, in the preparation of optically active halogen-hydrins.  $\beta$ -Dibromopropylamine was resolved by *d*-tartaric acid, and the components were converted by nitrous acid into the active dibromohydrins. Unfortunately, these compounds are so quickly racemised that the replacement of both bromine atoms means a loss of optical activity. However, the active *epibromohydrins* could be prepared, and these may lead to the desired end.

Monochlorohydrin was treated with acetic anhydride, and the resulting  *$\alpha$ -chlorodiacetin*, b. p. 123—128°/vacuum, was heated with silver propionate in a current of hydrogen at 150°. The first distillate was warmed with propionyl chloride, since some chlorine had been removed without the introduction of the propionyl group, and refractionated. *Diacetylpropionin*,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{O}\cdot\text{COEt}$ , has b. p. 150°/12 mm. An emulsion of the glyceride with physiological salt solution and a minute trace of manganese sulphate was digested with castor oil lipase in an incubator, then extracted with ether, and the residue left on evaporation was examined in the polarimeter. A control with tributyrin showed that no development of optical activity, due to selective fermentation, had taken place.

Monochlorohydrin was also condensed with hexoyl chloride.  *$\alpha$ -Chlorodihexoin*,  $\text{C}_{15}\text{H}_{27}\text{O}_4\text{Cl}$ , had b. p. 200—210°/12 mm., but no definite product could be obtained by treating it with sodium or silver oleates. Similarly,  $\alpha$ -monovalin did not give a desired valylolein under the influence of the acid chloride. Glycerides of the stearic acid series were therefore prepared.  $\alpha$ - $\beta$ -Dibromohydrin was heated with silver *isovalerate* when a 10% yield of *di-isovalin*, b. p. 170—175°/15 mm., was obtained. The latter was warmed with stearyl chloride and the resulting *di-isovalylstearin*,



was recrystallised from light petroleum. Propylene glycol was also acylated by the chlorides of stearic and oleic acids. The *distearin* has m. p. 40°, and the *diolein* is neutral.

The reaction between  $\alpha$ -chlorohydrin and  $\alpha$ -bromopropionyl chloride is rather complicated, but  $\alpha\beta$ -dibromohydrin gives inactive  $\alpha\beta$ -*dibromo- $\gamma$ -a-bromopropionin*,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CHBrMe}$ , b. p. 165—170°/

15 mm. *l*- $\alpha$ -Bromopropionyl chloride yields *dibromo-l*- $\alpha$ -bromopropionin, but attempts to separate the two isomerides, by fractional distillation, freezing in liquid air, or partial hydrolysis, were unsuccessful.

The aqueous solution of allylamine, as obtained by hydrolysing allyl-carbimide, was neutralised by hydrobromic acid and treated with bromine. The hydrobromide of  $\beta$ - $\gamma$ -dibromopropylamine so obtained was dissolved in water, mixed with *d*-tartaric acid, and then poured into a suspension of silver *d*-tartrate. The filtrate was evaporated and fractionally crystallised, when the *d*-tartrate of the *d*-base was obtained, m. p.  $131^{\circ}$ ,  $[\alpha]_D + 31.17^{\circ}$ , leaving the salt of the *l*-base in solution. These salts were treated with sodium nitrite, when *d*-dibromohydrin,  $[\alpha]_D + 6.25^{\circ}$ , and *l*-dibromohydrin,  $[\alpha]_D - 2.65^{\circ}$ , were isolated. Finally, by the action of alcoholic potassium hydroxide, these compounds were respectively converted into *d*-epibromohydrin,  $[\alpha]_D + 6.45^{\circ}$ , and its isomeride.

J. C. W.

Uranyl Glycollate and Lactate and Some Uranyl Salts of the Polyacids of the Aliphatic Series. G. COURTOIS (*Compt. rend.*, 1914, 158, 1688—1691. Compare this vol., i, 799).—A number of salts prepared by the method already given (*loc. cit.*) are described, and their properties given.

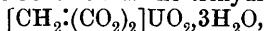
Uranyl glycollate,  $(\text{OH} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{UO}_2$ , is obtained in the form of yellow crystals, stable at  $100^{\circ}$ . Its solubility in water at  $19^{\circ}$  is 15.60 grams in 100 c.c. of solution. A saturated solution in the dark slowly deposits a basic salt,  $(\text{OH} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{UO}_2 \cdot \text{UO}_3 \cdot \text{H}_2\text{O}$ , whilst in sunlight this is followed by the deposition of a green uranous compound.

Uranyl lactate,  $(\text{OH} \cdot \text{CHMe} \cdot \text{CO}_2)_2\text{UO}_2$ , yields pale yellow crystals of which 100 c.c. of a saturated aqueous solution at  $18^{\circ}$  contain 2.92 grams. Its aqueous solutions are stable in the dark, but in sunlight a deposit of a green, uranous compound is formed. The uranyl salt is stable at  $200^{\circ}$ .

Uranyl oxalate was obtained as the trihydrate,  $\text{C}_2\text{O}_4\text{UO}_2 \cdot 3\text{H}_2\text{O}$ , which lost  $2\text{H}_2\text{O}$  at  $100^{\circ}$ , and was completely dehydrated at  $160^{\circ}$ .

Both the anhydrous salt and the monohydrate are hygroscopic in air reverting to the trihydrate. These results are in accord with those of Ebelen (*Ann. Chim. Phys.*, 1842, [iii], 5, 189), but disagree with those of Oechsner de Coninck and Raynaud (compare A., 1912, i, 535).

Uranyl malonate was obtained as the trihydrate,



a greenish-yellow, crystalline compound, scarcely soluble in water (compare Fay, A., 1896, i, 464). It loses  $2\text{H}_2\text{O}$  at  $100^{\circ}$  or in a vacuum over sulphuric acid, and becomes anhydrous at  $180^{\circ}$ .

Uranyl succinate was obtained as the monohydrate,

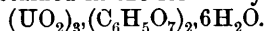


by the ordinary method (compare Rammelsberg, *Jahresb. Chem.*, 1855, 467), and as the *dihydrate* by decomposition of uranyl acetate in the cold with succinic acid. Both hydrates yield a yellowish-white, anhydrous salt at  $190$ — $195^{\circ}$ .

Uranyl tartrate has been prepared as the monohydrate and the

tetrahydrate identical with those of Péligo<sup>t</sup> (compare *Ann. Chim. Phys.*, 1844, [iii], 12, 463) and Itzig (compare *A.*, 1902, i, 76).

*Uranyl citrate* was obtained in the form of yellow crystals,



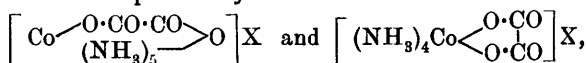
It is very soluble in water. At 100° or in a vacuum over sulphuric acid it loses 4H<sub>2</sub>O, and at 160° it is converted into the monohydrate. At 180° this begins to decompose, and it is impossible to dehydrate it completely. Exposure to air regenerates the hexahydrate.

Concentrated solutions, either cold or warm, yield a deposit of a *basic salt*,  $(\text{UO}_2)_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 2\text{H}_2\text{O} \cdot 2(\text{UO}_3 \cdot \text{H}_2\text{O}) \cdot 20\text{H}_2\text{O}$ . The basic salt loses 20H<sub>2</sub>O at 150°, but decomposes before becoming completely dehydrated. W. G.

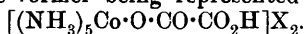
**Preparation of Ethyl Acetoacetate.** A. COBENZL (*Chem. Zeit.* 1914, 38, 665—666).—Details are given of a method of procedure for the preparation of ethyl acetoacetate on a large scale. D. F. T.

**Metallic Compounds Containing Oxalo-complexes. I. Mono-oxalo-compounds.** A. WERNER [with E. BINDSCHIEDLER, F. BLATTER, CH. SACKUR, H. SCHWARZ, and H. SURBER] (*Annalen*, 1914, 405, 212—241).—The author has long been engaged on researches with the object of furnishing indisputable evidence of the applicability of the co-ordination theory to the many substances containing oxalo-complexes. Mono-, di- and tri-oxalo-compounds of tervalent metals have been chiefly investigated; the present paper deals with the simplest class, the mono-oxalo-compounds.

Jørgensen's oxalopentamminecobalt and oxalotetramminecobalt salts are similar in appearance, but differ fundamentally in that the former yield acid salts with mineral acids, whilst the latter are unchanged. This difference is expressed by the formulæ:



the acid salts of the former being represented by

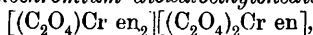


In the oxalopentammine salts the oxalo-group occupies only one co-ordination position, and therefore is directly bound to the central atom by only one oxygen atom. This arrangement gives rise to abnormal phenomena in certain circumstances. For example, when equal molecular quantities of aquopentamminechromium nitrate and 30% aqueous oxalic acid are heated on the water-bath, the product is not the expected oxalopentamminechromium salt, but oxalotetramminechromium nitrate, (Pfeiffer, *A.*, 1905, i, 855) red crystals, the oxalo-group displacing one mol. of ammonia in order that it may unite with the chromium by two valencies. The oxalotetramminechromium nitrate does not react with calcium chloride, and yields with aqueous potassium iodide the corresponding iodide (Pfeiffer, *loc. cit.*).

The oxalo-group is present, not in any two co-ordination positions, but only in two having the *cis*-configuration. This follows from the facts that only one series of the type  $[(\text{C}_2\text{O}_4)\text{MA}_4]\text{X}$  is known, and

that in this series oxalodiethylenediaminecobalt salts have been obtained in optically active forms. The oxalo-group is much more firmly bound to cobalt than to chromium; the oxalo-group is expelled from chromium salts, but not from cobalt salts by short boiling with hydrochloric or hydrobromic acid.

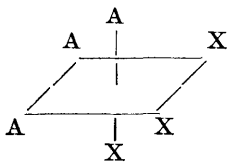
*Oxalodiethylenediaminechromium* salts,  $[(C_2O_4)Cr en_2]X$ , have been prepared. The first member of the series is obtained by boiling potassium trioxalochromate with 10% ethylenediamine solution, whereby *oxalodiethylenediaminechromium dioxaloethylenediaminechromate*,



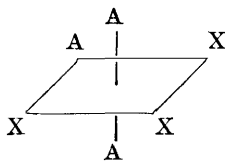
crimson crystals, is obtained. By treatment with concentrated hydrochloric acid and solid potassium iodide, this salt is converted into *oxalodiethylenediaminechromium iodide*,  $[(C_2O_4)Cr en_2]I$ , yellowish-red needles; the following salts have also been prepared: *nitrate*, yellowish-red needles; *bromide*,  $[(C_2O_4)Cr en_2]Br \cdot H_2O$ , yellowish-red leaflets; *chloride*, yellowish-red needles containing  $H_2O$ , and *thiocyanate*, yellowish-red leaflets.

*Oxaloaquotriamminecobalt* salts,  $[(C_2O_4)Co(OH_2)(NH_3)_3]X$ , have been very thoroughly examined. Chloro-oxalotriamminecobalt reacts with aqueous silver nitrate or with boiling dilute nitric acid to form *oxaloaquotriamminecobalt nitrate*,  $[(C_2O_4)Co(OH_2)(NH_3)_3]NO_3 \cdot H_2O$ , crimson needles, from which have been prepared the *chloride*, violet-red, microcrystalline powder; *bromide*, bluish-red prisms containing  $H_2O$ ; *dithionate*, red needles, and *sulphate*, violet leaflets containing  $H_2O$ . These salts react smoothly with aqueous ammonia, and are converted into *oxalohydroxotriamminecobalt*,  $[(C_2O_4)Co(OH)(NH_3)_3] \cdot \frac{1}{2}H_2O$ , bluish-red powder; this substance in the hydrated or the anhydrous form reacts with acids to regenerate oxaloaquotriamminecobalt salts.

By the action of concentrated acids or of certain salts, oxaloaquotriamminecobalt salts lose the aquo-group and are converted into *acido-oxalotriamminecobalts*,  $[(C_2O_4)CoX(NH_3)_3]$ , where X is Cl,  $NO_3$ , or  $-NCS$ . These substances furnish the long-sought illustration of the geometrical isomerism of compounds of the type  $[MA_3X_3]$  which is demanded by Werner's theory. Such compounds can exist in *cis*- and *trans*-modifications. Jörgensen has prepared from



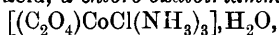
cis.



trans.

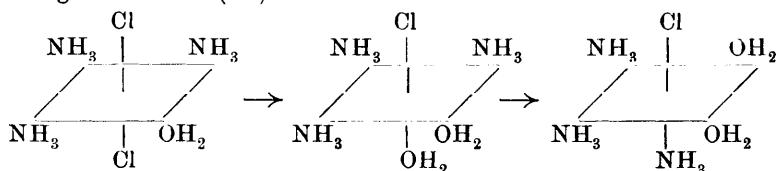
1:6-dichloroaquotriamminecobalt chloride and oxalic acid a chloro-oxalotriamminecobalt, which is indigo-blue and contains  $\frac{1}{2}H_2O$ . The authors now find that the water can be expelled at  $70-80^\circ$  without affecting the colour of the substance. It is therefore of the type  $[MA_3X_3]$  and from its method of formation has the *trans*-configuration. When it is converted by silver nitrate or dilute nitric acid into

oxaloaquotriamminecobalt nitrate and the latter is treated with concentrated hydrochloric acid, a *chloro-oxalotriamminecobalt*,

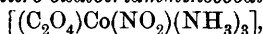


violet crystals, is obtained which loses its water of crystallisation at  $110^\circ$  without change of colour, and is the *cis*-isomeride. Evidently during the conversion of *trans*-chloro-oxalotriamminecobalt into oxaloaquotriamminecobalt nitrate, one  $NH_3$  changes its position. The *cis*-isomeride does not undergo a similar change when it is converted into oxaloaquotriamminecobalt nitrate by silver nitrate because the aquo-salt regenerates *cis*-chloro-oxalotriamminecobalt by heating with hydrochloric acid. The relation between the colours and the constitutions of *cis*- and *trans*-chloro-oxalotriamminecobalt is the same as in the case of bromothiocabimidodiethylenediaminecobalt salts, of which the *cis*-isomeride is red or reddish-lilac, whilst the *trans*-isomeride is blue.

The interchange of positions of an ammonia molecule and an aquo-group exemplified above is also illustrated by the following example. When dichloroaquotriamminecobalt hydrogen sulphate is treated with water, the initially formed chlorodiaquotriamminecobalt sulphate is greyish-blue (*trans*-isomeride), but by keeping in aqueous solution it changes to a violet (*cis*-)isomeride.



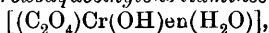
An example of geometrical isomerism quite analogous to that of *cis*- and *trans*-chloro-oxalotriamminecobalt has been found in the nitro-oxalotriamminecobalts. Trinitrotri-*trans*-amminecobalt and boiling aqueous oxalic acid yield *trans*-nitro-oxalotriamminecobalt,



brownish-red, prismatic crystals. The *cis*-isomeride, brick-red crystals, obtained from oxaloaquotriamminecobalt salts and nitrous acid, has a solubility in water at  $96^\circ$  only one-twentieth of that of the *trans*-isomeride.

*Thiocyanato-oxalotriamminecobalt*,  $[(NH_3)_3Co(C_2O_4)(SCN)]$ , dark red rhombohedra, obtained from oxaloaquotriamminecobalt nitrate and aqueous potassium thiocyanate on the water-bath, is oxidised by chlorine water to oxaloaquotriamminecobalt sulphate.

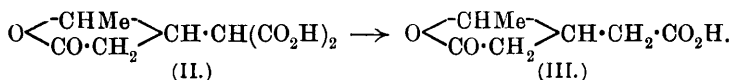
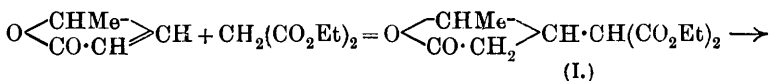
Oxalodiethylenediaminechromium dioxaloethylenediaminechromate (or an additive compound of potassium iodide and dioxaloethylenediaminechromium potassium) to be described in a subsequent paper) reacts with hydrobromic acid (saturated at  $0^\circ$ ) to form *oxalodiaquoethylenediaminechromium bromide*,  $[(C_2O_4)Cr en(H_2O)_2]Br \cdot H_2O$ , red, crystalline powder; the *oxalate*, the *chloride*, and the *nitrate*, all three red, crystalline powders containing  $H_2O$ , are also described. These salts have an acid reaction, and are converted by concentrated aqueous ammonia into *oxalohydroxoquoethylenediaminechromium*,



a violet, crystalline powder, which is reconverted into the diaquo-salts by acids. C. S.

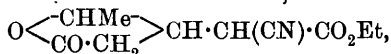
**Equilibrium at the Ordinary Temperature of the Enolic and Aldehydic Forms of Ethyl Formylsuccinate and Ethyl Formylethylsuccinate.** E. CARRIÈRE (*Compt. rend.*, 1914, 158, 1429—1432. Compare Wislicenus, A., 1900, i, 9; and Wislicenus, Böklen, and Reuthe, A., 1909, i, 9).—The author has used Meyer's method (compare A., 1912, i, 940; this vol., ii, 351) to study the equilibrium between the enolic and aldehydic forms of these substances. Several hours after fractional distillation all the fractions of ethyl formylsuccinate contain 50% of the enolic form, as does the undistilled product. Ethyl formylethylsuccinate behaves similarly, but in this case the content of the enolic form is 37%. The equilibrium points of solutions of these two esters in absolute alcohol is different, and the establishment of equilibrium, which begins very slowly, then takes place more rapidly, becoming very slow again after a few hours. In each case the amount of enolic form present, is greatly diminished by solution in alcohol. The addition of alcoholic potassium hydroxide, on the other hand, causes a rapid rise in the percentage of the enolic form to 97% in the case of ethyl formylsuccinate, and to 72% in the case of the other ester. Ethyl formylsuccinate distils over a range of temperature from 129—145°/15 mm., and the more volatile fractions, examined at once, are found to contain less of the enolic form and more of the aldehydic, whilst the reverse is true of the less volatile fractions. In both cases, after a few hours the content has altered to the equilibrium point, namely, 50% of the enolic form. W. G.

**The Susceptibility of Ethylenic Lactones to Fix Sodium Methylenic Compounds.** MILIVOYE LOSANITCH (*Compt. rend.*, 1914, 158, 1683—1686).—The ethylenic lactones behave like esters in that they combine with the sodium derivative of methylenic compounds (compare this vol., i, 693).  $\Delta^1$ -Angelolactone reacts with the sodium derivative of ethyl malonate on warming in ether for eight hours under a reflux condenser. The product of the reaction after decomposing the sodium derivative with sulphuric acid is a *lactone* ester, a colourless liquid, b. p. 204—205°/10 mm. (corr.). Its constitution is represented by formula I. The lactone ester is hydrolysed in half-an-



hour on heating with aqueous sodium hydroxide giving an uncrystallisable sodium salt, which is decomposed by hydrochloric acid, giving the acid (formula II) in the form of a syrup. This acid on warming at 100° loses one molecule of carbon dioxide, giving valerolactoneacetic acid (formula III), m. p. 83—84° (compare Fittig, A., 1901, 121).

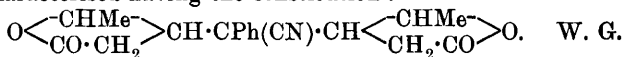
If the sodium derivative of ethyl malonate is replaced by that of ethyl cyanoacetate a similar reaction occurs, and the *compound*,



is obtained as a yellow liquid, m. p.  $62^\circ$ , b. p.  $220\text{--}221^\circ/11$  mm. (corr.), soluble in the usual organic solvents, and dissolving in warm water, giving an odour of hydrogen cyanide. Ethyl acetoacetate reacts in the same way in the form of its sodium derivative, but the product decomposes on distilling at  $210^\circ/10$  mm.

The sodium derivative of benzoylacetone, on the other hand, simply causes polymerisation of the lactone, giving a crystalline *dimeride*. Sodium ethoxide brings about a condensation of two molecules of the lactone with the elimination of one molecule of water to give a *compound*,  $\text{C}_{10}\text{H}_{10}\text{O}_3$ , m. p.  $103\text{--}104^\circ$ .

The sodium derivative of phenylacetone nitrile reacts with  $\Delta^1$ -angelolactone, yielding a number of derivatives of which only one *compound* has been characterised having the constitution :



**Formation of Thioformaldehyde.** L. VANINO and A. SCHINNER (*Ber.*, 1914, 47, 1776—1779).—The reaction by which trithioformaldehyde is obtained when hydrochloric acid is added to a mixture of formaldehyde and sodium thiosulphate (A., 1908, i, 318) has been investigated in the case of polythionic acids. Dithionic acid, since it does not contain bivalent sulphur, gives no thioformaldehyde, but all the other polythionic acids do react in the above manner. These acids

have the general formula :  $\text{HO} \begin{array}{c} \diagdown \\ \text{O} = \text{S} \cdot \text{S} \cdot \text{R} \\ \diagup \\ \text{O} \end{array}$ , where R may be H,  $\cdot\text{SO}_3\text{H}$ ,

$\cdot\text{S}_2\text{O}_3\text{H}$ ,  $\cdot\text{S}_3\text{O}_3\text{H}$ , etc., and therefore it is probable that the reaction follows the same course in each case. One suggestion is that the first step is analogous to the bisulphite reaction, thus: (I)  $\text{S} \cdot (\text{SO}_3\text{H})_2 + \text{CH}_2\text{O} = \text{SO}_3\text{H} \cdot \text{S} \cdot \text{SO}_3 \cdot \text{CH}_2 \cdot \text{OH}$ ; (II)  $3(\text{SO}_3\text{H} \cdot \text{S} \cdot \text{SO}_3 \cdot \text{CH}_2 \cdot \text{OH}) + 3\text{H}_2\text{O} = (\text{CH}_2\text{S})_3 + 6\text{H}_2\text{SO}_4$ .

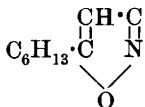
Sodium trithionate (Willstätter, A., 1903, ii, 543) and the tetrathionate are very stable towards concentrated hydrochloric acid. The former gives a quantitative yield of thioformaldehyde, but, in the case of the latter, some bivalent sulphur is lost to the reaction and is deposited in the free state. Details are given of a convenient process for preparing sodium tetrathionate. J. C. W.

**The Action of Dilute Solutions of Barium and other Hydroxides on Maltose.** LORENZ KOLB (*Biochem. Zeitsch.*, 1914, 63, 1—57).—The stronger the base used the more rapid and complete is the decomposition of the maltose. The solubility of the hydroxides in water is of subordinate significance, as those of the smallest solubility readily dissolve in the sugar solution. A maltose solution can be rendered completely inactive optically in the presence of sufficient hydroxide. The free hydroxyl ions disappear; as soon as



no more are present, the reaction comes to a standstill. The course of the reaction is determined therefore, not by the absolute quantities of base and sugar present, but by their relative proportions. The rate of reaction is increased by raising the temperature. The decomposition is accompanied by a brown coloration of the solution, from which the pigments can be removed by charcoal. Maltose under the action of barium hydroxide yields in the first instance dextrose. This process, accompanied by a fall in the rotatory power, takes place rapidly. The dextrose is then converted into an active mixture of lævulose, mannose, dextrose, and possibly glucose. This latter reaction takes place at a slow rate. Arabinose is not formed. In addition to these products, lactic and other more complex organic acids, which have not yet been isolated, and carbon dioxide are formed. S. B. S.

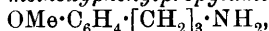
**The Diagnosis of Primary, Secondary, and Tertiary Bases.**  
 CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1914, 158, 1624—1631. Compare Sudborough and Hibbert, T., 1909, 95, 477; Hibbert, P., 1912, 28, 15).—The authors have applied the reaction indicated by Meunier in the case of aniline, methylaniline, and dimethylaniline, namely, their behaviour towards magnesium ethyl iodide (compare A., 1903, i, 544) to some thirty-nine bases of different types, and find that it is a ready and general method of distinguishing primary and secondary from tertiary amines. They have used magnesium ethyl bromide instead of the iodide and operated as follows. An amount of bromide corresponding with one gram of the metal is dissolved in 30 c.c. of ether in a 100 c.c. flask, fitted with a two-holed cork, through one hole of which passes a tap funnel, and through the other a tube connected to a vertical condenser. The top end of the condenser is fitted with a delivery tube bent to dip under an inverted measuring cylinder in water. The flask is heated in a constant temperature water-bath, and when equilibrium is established, the measuring cylinder is placed over the mouth of the delivery tube and the base under examination dissolved in three times its weight of ether gradually introduced into the flask in small portions through the tap funnel. An amount of base varying from 1/200th to 1/40th of a gram-molecule is used. When the reaction is finished, the volume of gas collected in the measuring cylinder is read, after standing over and shaking with water, and corrected to 0° and 760 mm. From a molecule of the base for each primary or secondary nitrogen atom present there is liberated one molecule of ethane, whilst for a tertiary base there is theoretically no ethane evolved, but in practice there is generally a negligible volume (0—20 c.c.) evolved. This reaction has been applied to simple and complex bases containing one or two primary, secondary or tertiary amino-groups, one primary and one secondary or tertiary amino-group, one secondary and one tertiary, one secondary and two tertiary, and four tertiary groups, and was successful in every case save one, namely 5-hexylisooxazole (annexed formula), in which case there was a slow, steady evolution of gas for one and a-half hours, due probably to the hydrogen of the  $\cdot\text{CH}\cdot$  group adjacent to the nitrogen atom being



slowly attacked. In all cases each amino-group exerts its own independent action. Where the base is not soluble in ether a fine suspension may be used, and in one case benzene was used as the solvent.

W. G.

**$\gamma$ -p-Hydroxyphenylpropylamine.** GUIDO GOLDSCHMIEDT and OSKAR VON FRAENKEL (*Monatsh.*, 1914, 35, 383—390).—The synthesis of  $\gamma$ -p-hydroxyphenylpropylamine described below was undertaken with the object of comparing the base with that obtained by the removal of carbon dioxide from ratanhia. The latter base, however, has since been identified as  $\beta$ -p-hydroxyphenylethylmethylamine (A., 1913, i, 643). *p*-Methoxycinnamonitrile,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CN}$ , prepared by heating *p*-methoxycinnamic acid with lead thiocyanate at  $190$ — $240^\circ$ , has m. p.  $64^\circ$ , b. p.  $165$ — $172^\circ/18$  mm. or  $200^\circ/57$  mm., and is reduced by sodium amalgam to  $\beta$ -p-methoxyphenylpropionitrile, which forms a strongly refractive, colourless liquid, b. p.  $158^\circ/11$  mm. or  $290$ — $300^\circ$  at atmospheric pressure. The latter compound is best prepared by heating  $\beta$ -p-methoxyphenylpropionic acid with lead thiocyanate, a crystalline substance, m. p.  $123.5^\circ$ , b. p.  $220^\circ/15$  mm., of unknown constitution being simultaneously produced. On reduction with sodium and alcohol it is converted into  $\gamma$ -p-methoxyphenylpropylamine,



the hydrochloride of which crystallises in scales, m. p.  $220$ — $225^\circ$ , and is hydrolysed by hydriodic acid to  $\gamma$ -p-hydroxyphenylpropylamine. This crystallises in white prisms, m. p.  $103^\circ$ , and forms a hydriodide, long needles, m. p.  $136^\circ$  (decomp.), hydrochloride, m. p.  $158$ — $159^\circ$ , and a pale yellow platinichloride.

F. B.

**Migration of a Methoxy-group During the Decomposition of a Quaternary Ammonium Hydroxide by Hofmann's Method.** M. TIFFENEAU (*Compt. rend.*, 1914, 158, 1580—1582).—A study of the decomposition of the quaternary ammonium hydroxide,  $\text{Ph} \cdot \text{CMe}(\text{OMe}) \cdot \text{CH}_2 \cdot \text{NMe}_3 \cdot \text{OH}$ , by Hofmann's reaction. The product of the reaction is  $\alpha$ -methoxy- $\beta$ -phenyl- $\Delta^a$ -propene,  $\text{CPhMe} : \text{CH} \cdot \text{OMe}$ , the methoxy-group and not the methyl or phenyl groups migrating during the reaction. The liberation of two valencies of one carbon atom, as occurs in such reactions, although it explains the necessity for certain migrations, does not allow the nature of the migrating group to be foreseen. In all probability the molecular reorganisation commences at the moment the reaction commences, and its nature depends on the conditions of the reaction.

W. G.

**The Behaviour of Some Metallic Oxides and Hydroxides towards Solutions of Ethylenediamine.** WILHELM TRAUBE and BERNHARD LOEWE (*Ber.*, 1914, 47, 1908—1919).—Traube has shown previously (A., 1912, i, 9; ii, 257) that the ethylenediamine hydroxides of copper, nickel, zinc, and silver can exist in aqueous solution. The authors now show that if solutions of the nickel compound are evaporated under diminished pressure (12 mm.) at temperatures not higher than  $40^\circ$ , long, dark violet needles are obtained, having the

composition  $[\text{Ni en}_3](\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . These crystals are strongly alkaline and deliquescent, absorb carbon dioxide from the air, and lose  $6\text{H}_2\text{O}$  in a vacuum over concentrated sulphuric acid. With sulphuric acid they give triethylenediaminenickel sulphate (compare Werner and Spruck, A., 1899, i, 856), and from this sulphate the hydroxide can be obtained by the use of barium hydroxide.

The corresponding hydroxides of copper and silver could not be isolated; on evaporation, their solutions lose the greater part of the ethylenediamine, leaving a black, powdery residue containing nitrogen, which is not completely soluble in water. The nitrogen is, however, still present as ethylenediamine, which has combined with the metal forming an imide salt, for example,  $\text{C}_2\text{H}_4(\text{NCu})_2$ ; some of the metal is also present as oxide.

Mercuric oxide requires seven to ten times its molecular equivalent of an ethylenediamine solution in order to dissolve it. Evaporation of the solution at a low temperature gives a citron-yellow residue of *dihydroxymercuri-ethylenediamine*,  $\text{C}_2\text{H}_4(\text{NH} \cdot \text{Hg} \cdot \text{OH})_2$ , or possibly  $\text{C}_2\text{H}_4(\text{NH} \cdot \text{Hg})_2\text{O}$ . It decomposes readily on trituration, or on touching with a hot glass rod; also on contact with water. With hydrochloric acid it gives glistening needles of *ethylenediaminemercuric chloride*,  $(\text{C}_2\text{H}_8\text{N}_2, 2\text{HCl})_2, \text{HgCl}_2$ , which compound is also readily obtained by the interaction of ethylenediamine hydrochloride and mercuric chloride in concentrated aqueous solution. The corresponding *bromide* has the formula  $(\text{C}_2\text{H}_8\text{N}_2, 2\text{HBr})_2, \text{HgBr}_2$ . The compound  $\text{Hg}(\text{C}_2\text{H}_8\text{N}_2)\text{Cl}_2$  is obtained as a voluminous precipitate by the precipitation of an alcoholic solution of mercuric chloride with ethylenediamine.

Cadmium hydroxide does not dissolve in ethylenediamine solutions in definite molecular proportions.

When cobalt is shaken with a 10% solution of ethylenediamine in the presence of air, it dissolves, giving dark wine-red solutions in which the cobalt and ethylenediamine are present in the ratio of 1 atom to 2 molecules, the cobalt being in the tervalent condition. Ethylenediamine solutions of cobalt in which the metal is present in the bivalent condition are obtained by treating a solution of copper hydroxide in ethylenediamine with powdered cobalt in an atmosphere of hydrogen. The solution is pale rose-red in colour; it readily absorbs oxygen, the amount absorbed corresponding with that necessary to convert the cobalt into the tervalent condition. The solution readily dissolves silk. T. S. P.

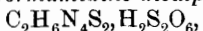
**Limits of the Attachment of Amino-groups to a Single Carbon Atom; Attempts to Prepare Tetra-aminomethane.** JITENDRA NATH RAKSHIT (*J. Amer. Chem. Soc.*, 1914, **36**, 1221—1222).—All attempts to prepare substances containing more than two amino-groups attached to a single carbon atom have hitherto resulted in the formation of compounds in which the additional nitrogen is present as a cyano- or imino-group. Experiments have now been made on the reduction of tetranitromethane by nickel-coated zinc and hydrochloric acid, and by tin and hydrochloric acid, but in each case ammonia and guanidine were produced, and tetra-aminomethane could not be obtained. E. G.

### Electrolytic Oxidation of Organic Sulphur Compounds.

III. FR. FICHTER and FRITZ BRAUN (*Ber.*, 1914, **47**, 1526—1534).—In continuation of former experiments (compare A., 1912, i, 423) the authors have made a more complete study of the formation of formamidine disulphide salts from thiocarbamide and substituted thiocarbamides.

In a sufficiently concentrated solution of thiocarbamide (3.04 grams) in concentrated hydrochloric acid (35 c.c.), formamidine disulphide hydrochloride is readily obtained (67.3% yield) by electrolytic oxidation at a platinum anode in a divided cell, using a temperature near 0°. At the same time some of the thiocarbamide is completely oxidised to carbon dioxide and ammonium sulphate. Using a lead cathode, formamidine disulphide hydrochloride is readily reduced to thiocarbamide.

Attempts to prepare other formamidine disulphide salts were unsuccessful when the following acids were used: phosphoric, perchloric, benzenesulphonic, *m*-nitrobenzenesulphonic, benzene-*m*-disulphonic, and methylenedisulphonic acids. Oxidation occurs, but the salts formed are very soluble and do not crystallise out. By the use of dithionic and trichloroacetic acids, *formamidine disulphide dithionate*,



and *formamidine disulphide trichloroacetate*,  $\text{C}_2\text{H}_6\text{N}_4\text{S}_2, 2\text{CCl}_3 \cdot \text{CO}_2\text{H}$ , were readily obtained.

Ethyl thiocarbamide, *s*- and *as*-diethylthiocarbamide, phenyl- and allyl-thiocarbamide are all oxidised in acid solution to the corresponding formamidine disulphide salts, but only in the case of *s*-diethylformamidine disulphide perchlorate,  $\text{S}_2[\text{C}(\text{NEt}) \cdot \text{NHEt}]_2, 2\text{HClO}_4$ , could the pure substance be obtained in well-defined crystals. Phenylformamidine disulphide hydrochloride,  $[\text{NHPh} \cdot \text{C}(\text{NH})]_2\text{S}_2, 2\text{HCl}$ , is deposited in the form of a voluminous, crystalline mass, but it is so readily hydrolysed by water that it was not obtained pure. When allylthiocarbamide is oxidised electrolytically in hydrochloric or sulphuric acid solution, it is necessary, in the former case, to pass three times the theoretical quantity of current in order to obtain crystals in quantity; these, however, consist of  $\beta\gamma$ -dichloropropylformamidine disulphide hydrochloride,  $[\text{CH}_2\text{Cl} \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}(\text{NH})]_2\text{S}_2, 2\text{HCl}$ . Doubt is thrown on the isolation of the free base, formamidine disulphide, by Hector (A., 1892, 292).

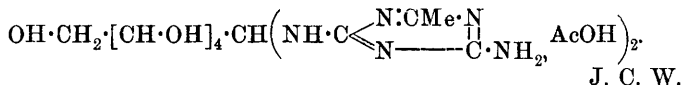
According to Fichter and Wenk (A., 1912, i, 423),  $\beta\beta$ -diethylthionylpropane is formed by the electrolytic oxidation of acetone diethylmercaptol at graphite anodes. The authors show that this statement is incorrect; the product formed is ethyl disulphoxide, the mercaptol being first oxidised to acetone and ethyl disulphide, and the latter compound then giving the disulphoxide. When the oxidation is carried out with hydrogen peroxide, the reaction comes to a stand at ethyl disulphide.

In a solution in glacial acetic acid saturated with hydrogen chloride,  $\beta$ -trithioacetaldehyde is not oxidised, but chlorinated, at a graphite anode. The product trichlorotrithioacetaldehyde,  $\text{CMeCl} \begin{smallmatrix} \text{S} \cdot \text{CMeCl} \\ \text{S} \cdot \text{CMeCl} \end{smallmatrix} \text{S}$ , is an unpleasant smelling oil, b. p. 85—87°/10 mm.

Details are given of the electrolytic oxidation of diphenyl sulphide to diphenyl sulfoxide, and of the latter to diphenylsulphone (compare Fichter and Sjöstedt, A., 1910, i, 41). Diphenyl sulfoxide, in glacial acetic and hydrochloric acid solution, is readily reduced to phenyl sulphide at a rotating lead cathode. T. S. P.

**Thiocarbimides.** M. ROSCHDESTVENSKI (*Ber.*, 1914, 47, 1947).—Methyl allylthiocarbamate, prepared by Schneider, Clibbens, Hüllweck, and Steibelt (this vol., i, 668), has already been described by the author (A., 1910, i, 107). T. H. P.

**A Condensation of Acetoguanamine Acetate with Dextrose.** L. RADLBERGER (*Chem. Zentr.*, 1914, i, 872—873; from *Österr.-ung. Zeitsch. Zucker.-Ind. Landw.*, 1913, 42, 915—917).—Aqueous solutions of acetoguanamine acetate (3 grams in 200 c.c.) and dextrose (3 grams in 50 c.c.) were mixed when, after a few hours, the compound,  $C_{18}H_{32}O_9N_{10}$ , crystallised in microscopic needles. It does not reduce Fehling's solution, and probably has the formula:



**Transformation of Calcium Cyanamide into Ammonia.** C. MANUELLI (*Ann. Chim. Applicata*, 1914, 1, 388—396).—When heated with excess of water in an autoclave at 160—170° or thereabouts, calcium cyanamide gives up the whole of its nitrogen as ammonia. With smaller proportions of water, contact of the latter with the cyanamide is hindered by the formation of hard crusts, but yields of 97—98% of ammonia are obtainable by a number of successive treatments with water at the ordinary pressure. T. H. P.

**Solubility in Water of the Nitrogenous Compounds of Calcium Cyanamide.** C. MANUELLI (*Ann. Chim. Applicata*, 1914, 1, 412—413).—The nitrogenous compounds of calcium cyanamide, as estimated by Kjeldahl's method, mostly dissolve readily in water. Thus, when 4 grams of fresh, finely divided cyanamide are shaken with 100 c.c. of water at 13.2—13.4°, about 80% of the total nitrogen is extracted in an hour. Subsequent dissolution is slow, only 88% of the nitrogen being dissolved in six hours. With a granular sample of low nitrogen-content, the nitrogen extracted under the above conditions amounted to 90% of the whole in eight hours. Protracted agitation with a large excess of water does not result in complete extraction of the nitrogenous constituents of calcium cyanamide. T. H. P.

**Cyclic Hydrazides of Dibasic Acids.** E. SERNAGIOTTO and MARIA DESSI PARAVAGNO (*Gazzetta*, 1914, 44, i, 538—542).—When the monohydrazides of dibasic acids are heated at about 150° in a current of dry air, 2 mols. of water are eliminated and the cyclic hydrazide,  $R \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{array}$ , is formed. In this way cyclic phthalhydrazide

and oxalhydrazide can be prepared. *Succinmonohydrazide*,  $C_4H_{10}O_4N_2$ , is a white, crystalline substance. Cyclic *succinhydrazide*,  $(CHON)_n$ , dissolves in alkalis, reduces Fehling's solution, and gives with ammoniacal silver nitrate an unstable, white precipitate, metallic silver being subsequently deposited. It is slowly hydrolysed by prolonged boiling with very dilute hydrochloric acid, and the solution contains hydrazine and oxalic acid. R. V. S

**Uranyl Thiocyanate.** PAUL PASCAL (*Compt. rend.*, 1914, 158, 1672—1674).—Uranyl thiocyanate can be prepared by mixing in the cold equimolecular solutions of uranyl sulphate and barium thiocyanate, filtering off the barium sulphate, and leaving the red filtrate in a vacuum over sulphuric acid. The residue after evaporation crystallises in bright orange-yellow needles having the composition  $UO_2(CNS)_2 \cdot 8H_2O$ . It is highly deliquescent, dissolving in a trace of water, and is very soluble in alcohol, acetone, ether or amyl alcohol, the two latter extracting it from its aqueous solutions. In solution in water it is strongly ionised, and presents all the characteristics of a uranyl salt and a thiocyanate. The addition of dilute pyridine in just sufficient amount to an aqueous solution gives a crystalline precipitate of a *basic* salt having the composition  $5UO_2(CNS)_2 \cdot UO_3 \cdot nH_2O$ . The addition of a metallic thiocyanate to a solution of the uranyl salt gives, on evaporation, in almost all cases one or more crystalline double salts, very deliquescent and generally orange-coloured. The alkali metals give double salts of the types  $UO_2(CNS)_2 \cdot 3MCNS \cdot 6H_2O$  and  $UO_2(CNS)_2 \cdot 5MCNS \cdot 2H_2O$ , whilst the alkaline earth metals only give one series of the type  $UO_2(CNS)_2 \cdot M(CNS)_2 \cdot 6H_2O$ .

None of these salts in aqueous solution presents the properties of a complex salt. W. G.

**Formation of Hydrogen Cyanide in Plants.** A. JORISSEN (*Bull. Acad. roy. Belg.*, 1914, 130—137).—It has been shown by von Pechmann (A., 1885, 138) and by Denigès that citric acid is readily converted into acetonedicarboxylic acid, and further that hydrogen cyanide is formed by the action of sodium nitrite on the latter (von Pechmann and Wehsarg, A., 1887, 28). The latter action is now shown to take place in very dilute aqueous solution even in the dark, whilst, also, the presence of hydrocyanic acid can be readily detected in a solution of citric acid which has been oxidised with cold potassium permanganate and subsequently treated with potassium nitrite. It is further shown that ferric sulphate or chloride (or ferrous sulphate in the presence of air) brings about the oxidation of citric acid to acetonedicarboxylic acid in the presence of light, although the action does not appear to take place in the absence of the latter. Under similar conditions, hydrogen cyanide does not appear to be formed by the successive action of iron salts and potassium nitrite on solutions of tartaric, succinic, malic, malonic or oxalic acids, or of acetone in the presence of acetic acid. Further, hydrogen cyanide is produced when a dilute solution containing citric acid, potassium nitrite, and ferrous bicarbonate is exposed to diffused light.

The possible bearing of these results on cyanogenesis in plants is discussed.  
H. W.

**Electrolytic Preparation of Potassium Ferricyanide.** G. GRUBE (*Zeitsch. Elektrochem.*, 1914, 20, 334—344).—The anodic oxidation of potassium ferrocyanide to potassium ferricyanide has been investigated, using electrodes of nickel, platinum, copper, iron and lead peroxide in glass cells provided with a porous porcelain diaphragm. A 0.5 mol. solution of potassium ferrocyanide was placed in the anode compartment and a 0.1*N*-potassium hydroxide solution was placed in the cathode compartment. The influence of the current density on the anode was investigated at 18° with nickel anodes, and it is shown that with 0.005 ampere per sq. cm. a current efficiency of 94.51% is obtained, and with 0.02 ampere per sq. cm. an efficiency of 80.57%, the anode liquid being vigorously stirred the while. The current efficiency is independent of the anode material. The influence of temperature is such that a maximum current efficiency is obtained at 50°, which decreases rapidly if the temperature is further raised. The cause of the decreased efficiency is twofold: (1) an hydrolysis of the ferricyanide with precipitation of ferric oxide; (2) a reduction of some of the ferricyanide to ferrocyanide. The precipitated ferric oxide coats the anode, and gives rise to a potential loss. Potassium ferricyanide can be directly oxidised and obtained crystalline at the ordinary temperature by keeping the anode liquid saturated with potassium ferrocyanide, when the ferricyanide separates as a fine, crystalline powder of a high degree of purity. In the course of the work the solubility of potassium ferricyanide and potassium ferrocyanide in water and in aqueous potassium hydroxide has been determined, as well as the solubility of potassium ferrocyanide in neutral and alkaline ferricyanide solutions. The following figures have been obtained at 25°. Potassium ferrocyanide at 25°, in water 319.4 grams of crystallised salt per litre; in 0.09984*N*-KOH, 308.5 grams; in 0.2496*N*-KOH, 283.5 grams; in 0.4963*N*-KOH, 247.1 grams; in 0.7036*N*-KOH, 217.4 grams; in 0.9415*N*-KOH, 184.8 grams; in 1.395*N*-KOH, 132.1 grams, and in 1.883*N*-KOH, 86.12 grams. Potassium ferricyanide at 25°, in water 385.5 grams per litre; in 0.4687*N*-KOH, 343.7 grams; in 0.9628*N*-KOH, 302.3 grams, and in 1.949*N*-KOH, 215.1 grams. J. F. S.

**Preparation of Dimethylglyoxime without the Use of Hydroxylamine.** J. M. JOHLIN, jun. (*J. Amer. Chem. Soc.*, 1914, 36, 1218—1221).—During the preparation of dimethyl diketone by Diels and Stephan's method (A., 1907, i, 1000) it was observed that if the product of the reaction of methyl ethyl ketone, *iso*amyl nitrite, and hydrochloric acid, after being shaken with sodium hydroxide, is acidified with sulphuric acid and left for twenty-four to thirty-six hours, dimethylglyoxime crystallises from the mixture. From 850 c.c. of methyl ethyl ketone, 50—60 grams of dimethylglyoxime can thus be obtained as a by-product.

A study of the reactions of dimethylglyoxime and oximinoacetone has shown that treatment with sulphuric acid, if not too concentrated,

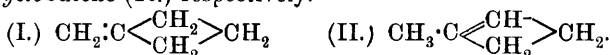
affords the best conditions under which the monoxime will dissociate and the less soluble dioxime be precipitated. E. G.

**Basic Dialkyl Tin Salts.** P. PFEIFFER and O. BRACK (*Zeitsch. anorg. Chem.*, 1914, **87**, 229—234).—Basic dialkyl tin salts crystallise very readily. Their melting points are higher than those of the corresponding normal haloids. They dissolve readily in organic solvents and cryoscopic measurements in benzene show them to be polymerised.

*Diethyl stannic oxychloride*,  $\text{Sn}_2\text{Et}_4\text{OCl}_2$ , prepared by dissolving diethyl stannic oxide in an alcoholic solution of diethyl stannic chloride, forms colourless crystals, m. p.  $175.5^\circ$ . The *oxybromide*,  $\text{Sn}_2\text{Et}_4\text{OBr}_2$ , has m. p.  $170\text{--}171^\circ$ .

*Dipropyl stannic oxychloride*,  $\text{Sn}_2\text{Pr}_4\text{OCl}_2$ , has m. p.  $122^\circ$ , and the *oxybromide*,  $108^\circ$ . C. H. D.

**Gustavson's Vinyltrimethylene and Ethylidenetrimethylene.** AL. FAVORSKI and W. BATALIN (*Ber.*, 1914, **47**, 1648—1651).—The researches of Demjanov (compare A., 1908, i, 329) have rendered it highly probable that "vinyltrimethylene" and "ethylidenetrimethylene" (A., 1896, i, 669) are methylenecyclobutane (I.) and methylcyclobutene (II.) respectively.



That this is, indeed, the case is now confirmed by oxidising the latter compound by 3% permanganate, lævulic acid being isolated from the products and identified by physical constants, silver salt and phenylhydrazone. J. C. W

**Bromination of Toluene.** A. F. HOLLEMAN (*Rec. trav. chim.*, 1914, **33**, 183—191).—The investigations of van der Laan (A., 1906, i, 490) have left the question undecided whether *m*-bromotoluene is formed by the bromination of toluene in addition to *o*- and *p*-bromotoluenes and benzyl bromide. The author has therefore examined this point, and is led to the conclusion that *m*-bromotoluene is not produced when bromine reacts with a large excess of toluene at the ordinary temperature in the absence of catalyst. Cohen and Dutt (T., 1914, **105**, 504) have arrived at a precisely opposite conclusion; in their case, however, aluminium is used as catalyst, whilst, according to the author, the experimental proof of the presence of *m*-bromotoluene is not sufficiently definite.

Preliminary experiments show that *m*-bromotoluene cannot be detected with sufficient accuracy in the presence of preponderating amounts of its isomerides by oxidation of the aryl haloids with potassium permanganate and subsequent isolation of the respective bromobenzoic acids.

[With Mlle. J. HOEFLAKE.]—The following method has given satisfactory results. Bromine is allowed to act on an excess of toluene in the dark until decolorisation is practically complete. The product is shaken with water, dried over sodium sulphate, and excess of toluene removed by distillation (compare van der Laan, *loc. cit.*). Benzyl



bromide is removed by means of dimethylaniline, the crystallisation of the product being greatly accelerated by bringing the mixture into contact with the walls of fresh vessels. The filtrate is well washed with dilute nitric acid to remove excess of base, heated under diminished pressure at 70—80° during several hours, and subsequently distilled. Observations of the index of refraction and of the first and second points of solidification of the distillate lead the authors to the conclusion that *m*-bromotoluene is not present. H. W.

*o*-Fluoronitrobenzene and the Nitration of Fluorobenzene. FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1914, 178—195).—*o*-Fluoronitrobenzene has been prepared in small quantity and by an indirect method by Holleman (A., 1904, i, 486; 1905, i, 515), who has also shown that it is present to the extent of 12.6% in the product obtained by nitrating fluorobenzene at 0° with a mixture of nitric acids (D 1.478 and 1.51 respectively). This process, however, can only be applied on the small scale, as prolonged contact with the acid causes the formation of fluorodinitrobenzene. The author has therefore performed a series of experiments on the nitration of fluorobenzene under different conditions, and has been able to increase the yield of the ortho-compound and to establish a process suited to experiments on a larger scale.

Fluorobenzene has been nitrated (1) by adding a mixture of nitric (D 1.52) and sulphuric acid to it at about 0°; (2) by adding the haloid to the mixture of acids; (3) in the presence of acetic anhydride and glacial acetic acid; (4) in carbon tetrachloride solution in the presence of phosphoric oxide at -5°; (5) by a solution of nitrogen pentoxide in pure nitric acid; (6) by addition of a mixture of nitric (D 1.52) and sulphuric acids to the boiling haloid; (7) by the same reagents as in 6, but commencing nitration in the cold and allowing the mixture to heat spontaneously; (8) by nitric acid (D 1.4) at the boiling point; (9) by nitric acid (D 1.52) in the presence of phosphoric oxide at the boiling point. It is found that the proportion of para-derivative is greater at lower temperatures than at the boiling point of fluorobenzene, and that the difference in temperature is of greater importance than the dehydrating agent or the medium. The latter influence is not, however, negligible; sulphuric acid, particularly when used in excess with regard to the fluorobenzene, favours the production of the para-derivative, whilst acetic anhydride has a slight opposite effect. An inert solvent, such as carbon tetrachloride, increases the proportion of para-compound. The method most favourable for the production of ortho-compound consists in the addition of nitric acid to a hot mixture of fluorobenzene and phosphoric oxide. In these circumstances, practically all the fluorobenzene is nitrated, whilst the production of dinitro-derivative is insignificant (less than 1%).

*o*-Fluoronitrobenzene can be separated from the para-isomeride by fractional crystallisation or distillation, the latter process being the more satisfactory if a pure product is required. Contrary to Holleman's statement, distillation can be effected at the ordinary pressure without decomposition or action on glass vessels. The pure substance has m. p. -5.9° (stable form), b. p. 214.55°/761 mm., D<sup>17</sup><sub>20</sub>

1.3375,  $n_D^{17.2}$  1.53231. Like the para-isomeride, it exists in two crystalline modifications; when crystallisation is induced in the considerably supercooled liquid, semi-transparent needles are formed in which little particles of the stable modification slowly make their appearance. When the acicular crystals are slowly heated, fusion starts at  $-7.5^\circ$ , but at  $-7^\circ$  the liquid portion becomes partly solid and then re-melts at  $-6.2^\circ$  to  $-5.9^\circ$ .

Holleman's observation that *m*-fluoronitrobenzene is only formed in minute quantity during the nitration of fluorobenzene is confirmed.

H. W.

**1 : 2 : 4-Trinitrobenzene.** W. KÖRNER and A. CONTARDI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 633—635).—1 : 2 : 4-Trinitrobenzene,  $C_6H_3(NO_2)_3$ , can be prepared from ordinary dinitroaniline by way of the nitrate of the diazo-compound (compare *ibid.*, 1904, [v], 13, i, 281); it crystallises in almost colourless plates, m. p.  $61^\circ$ .

R. V. S.

**Aromatic Nitro-compounds. I. Solubility of Some Nitro-derivatives of Toluene in the Solid State.** MICHELE GIUA (*Ber.*, 1914, 47, 1718—1723).—Lepsius (*Chem. Zeit.*, 1896, 20, 839) has already remarked on the considerable lowering observed in the melting point in mixtures of 2 : 6- and 2 : 4-dinitrotoluenes, and 2 : 4 : 6-trinitrotoluene.

The author has submitted the binary mixtures *p*-nitrotoluene and 2 : 4-dinitrotoluene, 2 : 6-dinitrotoluene and 2 : 4-dinitrotoluene, 2 : 6-dinitrotoluene and 2 : 4 : 6-trinitrotoluene, and 2 : 4-dinitrotoluene and 2 : 4 : 6-trinitrotoluene to thermal analysis. The formation of compounds which are completely dissociated in the liquid state was observed (compare Kremann, A., 1909, ii, 28).

The system *p*-nitrotoluene—2 : 4-dinitrotoluene gave indications of the formation of a compound containing 3 molecules of the former to 2 of the latter, the eutectic with *p*-nitrotoluene having m. p.  $26.35^\circ$ , whilst that with the dinitrotoluene has m. p.  $26.5^\circ$ .

With the system 2 : 6-dinitrotoluene and 2 : 4-dinitrotoluene there was again indication of the formation of a molecular compound, the eutectic with the former component having m. p.  $33.5^\circ$ , whilst with the latter it has m. p.  $33.65^\circ$ .

With the system 2 : 6-dinitrotoluene and 2 : 4 : 6-trinitrotoluene, formation of a compound containing 3 molecules of the former to 2 of the latter was observed, the eutectics with the two constituents being at  $36.6^\circ$  and  $37.45^\circ$  respectively.

The system 2 : 4-dinitrotoluene and 2 : 4 : 6-trinitrotoluene gave indications of a compound of 3 molecules of the former with 2 of the latter, the eutectics with the two constituents being at  $44.55^\circ$  and  $45.1^\circ$  respectively.

Any maximum on each curve between the two eutectics was too small to be determined, but on account of the tardiness with which the compounds were produced, it was found possible to investigate the freezing-point curve in the metastable region below the eutectic temperatures.

D. F. T.

**Dynamic Researches on Friedel and Crafts' Reaction.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1914, 33, 91—182).—A dynamic study has been made of the action of *p*-bromobenzenesulphonyl chloride on benzene and certain of its derivatives in the presence of aluminium chloride in the hope of explaining, as far as possible, the rôle of the latter in Friedel and Crafts' reaction, and of comparing the diverse views of this process.

*p*-Bromobenzenesulphonyl chloride, m. p. 75—76° (corr.), was chosen, since it reacts with measurable velocity, and is not decomposed by water at the ordinary temperature.

In the first series of experiments, known quantities of aluminium chloride were shaken with a solution of the acid chloride in carbon disulphide until a homogeneous mixture was obtained, with the exception of a slight precipitate which never disappears. (Aluminium chloride only dissolves in carbon disulphide to the extent of 0.2 gram per litre at 30°; in this case, solution occurs in consequence of the formation of a compound,  $C_6H_4Br \cdot SO_2Cl \cdot AlCl_3$ .) A solution of benzene in the same solvent was then added. The course of the reaction was followed by the withdrawal of aliquot portions, which were shaken with water to remove aluminium chloride; the unchanged acid chloride was decomposed by boiling with water and dilute sulphuric acid, and the chlorine estimated by Volhard's method after removal of carbon disulphide. (Attempts to use aqueous potassium hydroxide in place of sulphuric acid were unsuccessful, since on adding the ferric indicator a pale brown precipitate of ferric *p*-bromobenzenesulphinate was formed. The corresponding free acid has m. p. 110—115°, after which it solidifies, re-melting at 128—130°; this is shown to be due to a decomposition, one of the products of which is probably the *p*-bromophenyl ester of *p*-bromobenzenethiosulphonic acid,  $C_6H_4Br \cdot S \begin{smallmatrix} \nearrow O \\ \searrow \end{smallmatrix} \cdot C_6H_4Br$ , m. p. 160.5° (corr.), whereas Knoevenagel and Polack [*A.*, 1908, i, 971] give 155.5°.) The most striking result observed is that a solution of the acid chloride and aluminium chloride in carbon disulphide which has been preserved for some time reacts more readily after addition of benzene than does a freshly-prepared solution. A small quantity of the acid chloride is found to be used previous to the addition of the benzene, and, further, the rate of reaction is smaller at the commencement and increases considerably later. The liberated hydrogen chloride does not seem to be the only cause of this auto-catalysis, although it undoubtedly contributes towards a greater rate of action.

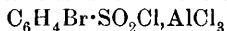
The action of equimolecular quantities of *p*-bromobenzenesulphonyl chloride and aluminium chloride on benzene in carbon disulphide solution does not yield the corresponding sulphone (as in benzene solution), but *p*-bromobenzenesulphinic acid. For each molecule of acid chloride used, a molecule of hydrogen chloride is evolved.

In the hope of obtaining further insight into the above reactions, a series of experiments was made with aluminium bromide which is freely soluble in carbon disulphide and *p*-bromobenzenesulphonyl bromide. The latter is prepared by the addition of bromine to a mixture of sodium *p*-bromobenzenesulphonate and phosphorus tri-

bromide. It has m. p.  $75.5-76.5^{\circ}$  (corr.), and is not attacked by cold water. When mixed with aluminium bromide in carbon disulphide solution, it immediately liberates bromine, and a pale yellow, hygroscopic, crystalline substance,  $C_6H_4O_2BrS \cdot AlBr_3$ , is precipitated, which changes in colour below  $100^{\circ}$  and has m. p.  $125-132^{\circ}$  (decomp.). It is decomposed by water with formation of large quantities of *p*-bromobenzenesulphonic acid. Decomposition of the acid bromide and aluminium bromide into free bromine and the complex compound appears to occur immediately and quantitatively, but the reaction is completely reversed on the addition of water. As a consequence of the first reaction, the sulphone is not obtained when benzene is added.

Further examination of the action of *p*-bromobenzenesulphonyl chloride and aluminium chloride on benzene in carbon disulphide solution has shown the formation of chlorobenzene. Reaction, therefore, occurs, partly at any rate, in accordance with the scheme:  $C_6H_4Br \cdot SO_2Cl, AlCl_3 + C_6H_6 = C_6H_4Br \cdot SO_2AlCl_2 + C_6H_5Cl + HCl$ . A compound of this nature has not been isolated in the pure condition, but a precipitate is obtained from concentrated solutions which greatly resembles the substance  $C_6H_4O_2BrS \cdot AlBr_3$ .

A series of experiments on the function of the carbon disulphide failed to disclose the presence of chlorine which might be formed according to the scheme:  $C_6H_4Br \cdot SO_2Cl, AlCl_3 = C_6H_4Br \cdot SO_2AlCl_2 + Cl_2$ , and did not give any evidence of the formation of a molecular compound from the acid chloride, aluminium chloride and carbon disulphide. However, on adding benzene to the residue obtained after removal of carbon disulphide from a solution of the compound

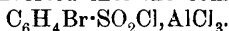


in that solvent, it was found that considerable quantities of *p*-bromobenzenesulphonic acid are formed in addition to the sulphone. It appears, therefore, that traces of some substance must be present in, or formed from, the carbon disulphide which have a catalytic action in the direction of the formation of the sulphonic acid, and it is highly probable that the actual agent is sulphur or sulphur chloride. The autocatalytic nature of the reaction in a solution of aluminium chloride and the acid chloride in carbon disulphide which has been preserved (see above) is explicable on the assumption that the amount of sulphur chloride in the solution gradually increases, and is further augmented during the course of the action with benzene.

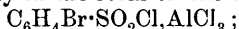
The action between acid chloride, aluminium chloride, and benzene in carbon disulphide solution is accelerated by an excess of aluminium chloride, or by an increase in concentration of benzene, whilst, on the other hand, it is retarded by an excess of acid chloride. The precipitate which is invariably formed before addition of the benzene can be greatly increased in quantity by use of a larger amount of aluminium chloride, but its precise nature has not been ascertained; it does not contain *p*-bromobenzenesulphonic acid. When the benzene in the above reaction is replaced by its derivatives, the rate of reaction is found to diminish in the order: toluene, benzene, chlorobenzene, bromobenzene, nitrobenzene.

A further series of investigations on the formation of the sulphone

has also been carried out. Preliminary investigations show that light petroleum (b. p. 70—80°) is not a suitable solvent; benzene and its derivatives which have been subjected to purification by means of aluminium chloride have, therefore, been exclusively used. The compounds thus formed are readily decomposed at the boiling point with the formation of strongly-coloured condensation products. The same change also occurs slowly at the ordinary temperature, except in the case of nitrobenzene. In the actual experiments, a weighed quantity of aluminium chloride is cautiously melted with the acid chloride, whereby the greater part of it is converted into the compound



The requisite quantity of benzene is now added, and the mixture well shaken until solution is complete, after which it is placed in the thermostat and shielded from light. Aliquot portions are removed at fixed intervals, agitated with ether and water, and boiled with potassium hydroxide solution, after which chlorine is determined by Volhard's method. The main results may be thus stated: (1) The acid chloride reacts solely in the form of the compound



(2) a molecule of aluminium chloride cannot transform more than one molecule of acid chloride; (3) the reaction is unimolecular with respect to the compound,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}, \text{AlCl}_3$ ; (4) the reaction constant (when an excess of aluminium chloride is not used, and if  $K$  is calculated for the compound  $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}, \text{AlCl}_3$ ) is proportional to the concentration of aluminium chloride; (5) the constant is greatly increased by an excess of aluminium chloride. These facts are most readily explained on the assumptions that the acid chloride is activated in the compound  $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}, \text{AlCl}_3$ , whilst the benzene is activated proportionally to the concentration of the combined aluminium chloride, whether the latter is united to the acid chloride or to the sulphone. Free aluminium chloride should, therefore, be a very energetic catalyst. Diffused daylight is found to be without effect on the action, but the influence of direct sunlight has not been investigated. When benzene is replaced by its derivatives, reaction occurs with diminishing rapidity in the order: toluene, benzene, bromobenzene, chlorobenzene; reaction could not be observed with nitrobenzene after twenty-four hours.

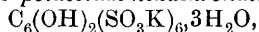
The paper is concluded by an exhaustive critical survey of the experimental work and theories on the Friedel and Crafts' reaction.

H. W.

**Constitution of Thiochronic Acid.** C. LORING JACKSON and S. A. BEGGS (*J. Amer. Chem. Soc.*, 1914, **36**, 1210—1218).—The formula  $\text{OH}\cdot\text{C}_6(\text{SO}_3\text{H})_4\cdot\text{O}\cdot\text{SO}_3\text{H}$ , assigned by Graebe (*Annalen*, 1868, **146**, 40) to thiochronic acid, does not explain several of its properties, and the present investigation was therefore undertaken.

A method is described by means of which thiochronic acid can be obtained in a yield amounting to 32% of the theoretical. When potassium thiochronate is boiled with potassium hydroxide in an atmosphere of hydrogen, potassium euthiochronate,  $\text{C}_6(\text{OK})_2(\text{SO}_3\text{K})_2\text{O}_2$ , is produced. By the action of potassium hydrogen sulphite on di-

bromodiphenoxyquinone, potassium thiochronate is produced together with a small quantity of *potassium hexachronate*,



which forms white crystals, and is converted by potassium hydroxide into potassium euthiochronate. When bromoanilic acid is treated with potassium hydrogen sulphite or with tin and hydrochloric acid, 1:2:4:5-tetrahydroxybenzene is obtained; the tetra-acetyl derivative has m. p. 226—227° (uncorr.). If a solution of the potassium derivative of 1:2:4:5-tetrahydroxybenzene is acidified with concentrated hydrochloric acid and left in the air for two days, a *compound* is produced which forms small, black, slender plates, and is probably a tetrahydroxyquinhydrone.

In view of these results, thiochronic acid must be represented by the quinonoid formula  $\text{O}:\text{C}_6(\text{SO}_3\text{H})_5:\text{OH}$ , which explains its yellow colour, its stability, especially towards alkali hydroxides, and the formation of euthiochronic acid and of hexachronic acid, none of which is explained by Graebe's formula.

E. G.

**Nitrosulphonic Acids of *p*-Xylene.** WILLIAM J. KARSLAKE and RALPH C. HUSTON (*J. Amer. Chem. Soc.*, 1914, 36, 1244—1258).—By the action of nitric acid on *p*-xylene-2-sulphonic acid, fairly good yields of the 6-nitro- and 3-nitro-derivatives are produced together with small quantities of the 5-nitro-derivative; they are best separated by converting them into the sulphonyl chlorides and crystallising the latter from a mixture of ether and light petroleum. Attempts to nitrate *p*-xylenesulphonyl chloride were not very successful; in all cases but one, only small quantities of 3-nitro-*p*-xylene-2-sulphonyl chloride were produced, and in one case a very small yield of the 6-nitro-derivative was obtained. 2-Nitro-*p*-xylene could not be sulphonated with sulphuric acid, but chlorosulphonic acid reacts with it to form 6-nitro- and 5-nitro-*p*-xylene-2-sulphonyl chlorides.

6-Nitro-*p*-xylene-2-sulphonic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ , crystallises in plates; it loses its water of crystallisation at 100°, darkens at 128°, and is not melted at 200°. The *chloride* has m. p. 60—61°; the *amide*, m. p. 172—173°; the *anilide*, m. p. 143—144°; and the *phenyl ester*, m. p. 117—118°; the *sodium*, *potassium*, *calcium*, *barium*, and *silver* salts are described. *Barium* 6-amino-*p*-xylene-2-sulphonate crystallises with 7H<sub>2</sub>O.

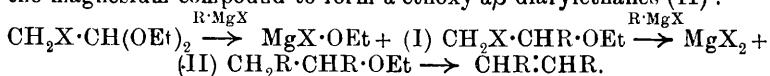
3-Nitro-*p*-xylene-2-sulphonic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{SO}_3\text{H}$ , m. p. 143—145° (decomp.), forms long plates, and is deliquescent. The *chloride* has m. p. 109.5—110.5°; the *amide*, m. p. 191—192°; the *anilide*, m. p. 181.5—182.5°, and the *phenyl ester*, 83—83.5°; the *sodium*, *potassium*, *calcium*, *barium*, and *silver* salts are described.

5-Nitro-*p*-xylene-2-sulphonic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ , forms needle-like plates; it loses its water of crystallisation at 108°, and then has m. p. 138—140° (decomp.). This acid resembles the 6-nitro- and 3-nitro-compounds in being bitter to the taste and very hygroscopic. The *chloride* has m. p. 74.5—75.5°; the *amide*, m. p. 197—198°; the *anilide*, 130.5—131°; and the *phenyl ester*, 120—120.5°; the *sodium*, *potassium*, *calcium*, *barium*, and *silver* salts are described.

5-Amino-*p*-xylene-2-sulphonic acid crystallises in prismatic plates or needles; it begins to char at 230° and is not melted at 300°.

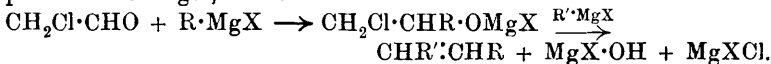
E. G.

**New Syntheses of Stilbenes.** ERNST SPÄTH (*Monatsh.*, 1914, 35, 463—474).—Symmetrical stilbenes may be readily prepared by the interaction of magnesium aryl haloids and chloro- or bromo-acetal at 110—130°, and subsequent hydrolysis of the resulting  $\alpha$ -ethoxy- $\alpha\beta$ -diarylethanes with dilute sulphuric acid. The action of the organo-magnesium compound takes place in two stages, one of the ethoxy-groups being first replaced by the aryl group with the formation of halogenated ethers (I), which then react with a second molecule of the magnesium compound to form  $\alpha$ -ethoxy- $\alpha\beta$ -diarylethanes (II):



During the action of the magnesium compound varying amounts of stilbene are formed as follows:  $\text{CH}_2\text{R}\cdot\text{CHR}\cdot\text{OEt} + \text{R}\cdot\text{MgX} = \text{R}\cdot\text{CH}:\text{CHR} + \text{MgX}\cdot\text{OH} + \text{C}_2\text{H}_5\cdot\text{R}$ .

If different magnesium aryl haloids are employed in carrying out the two reactions, ethers of the type  $\text{CH}_2\text{R}\cdot\text{CHR}'\cdot\text{OEt}$  are produced, which are hydrolysed by dilute sulphuric acid to unsymmetrical stilbenes,  $\text{CHR}:\text{CHR}'$ . The preparation of stilbenes, both symmetrical and unsymmetrical, may also be readily accomplished by the action of magnesium aryl haloids on chloroacetaldehyde, the reaction taking place in two stages, thus:



The magnesium compounds were prepared in the usual manner in ethereal solution, and the excess of ether was removed by heating at 110—130°, the reaction with the chloro- or bromo-acetal being carried out at about the same temperature.

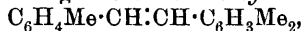
When heated at 120° with magnesium phenyl bromide, chloroacetal yields a small quantity of stilbene together with  $\alpha$ -ethoxy- $\alpha\beta$ -diphenylethane ( $\alpha\beta$ -diphenylethyl ether),  $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{OEt}$ , which has b. p. 149—151°/10 mm., yields dibenzyl on reduction with hydriodic acid, and is converted into stilbene when boiled with dilute sulphuric acid.

$\beta$ -Ethoxy- $\beta$ -phenylethyl bromide,  $\text{CH}_2\text{Br}\cdot\text{CHPh}\cdot\text{OEt}$ , obtained together with  $\alpha\beta$ -diphenylethyl ether by the interaction of magnesium phenyl bromide and excess of bromoacetal at 110°, is a liquid, b. p. 113—116°/10 mm. It is converted by the action of magnesium *p*-tolyl bromide and subsequent hydrolysis with dilute sulphuric acid into *p*-methylstilbene.

*o*:*o*'-Dimethylstilbene, prepared by hydrolysing the product from magnesium *o*-tolyl bromide and chloroacetal, combines with bromine in chloroform solution to form a dibromide, which crystallises in needles, m. p. 126—128°, and on further heating resolidifies and then has m. p. 158° (decomp.).

The preparation of *p*:*p*'-dimethylstilbene from magnesium *p*-tolyl bromide and bromoacetal, and of 2:4:2':4'-tetramethylstilbene from magnesium *m*-4-xylyl bromide and chloroacetal, is also described.

*β-Chloro-α-p-tolyethyl alcohol*,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared from chloroacetal and magnesium *p*-tolyl bromide, is a colourless, oily liquid, b. p. 133—135°/11 mm., having a sweet taste, and becomes greenish-brown on exposure to air. It reacts with magnesium *m*-4-xylyl bromide, yielding 4:3':4'-*trimethylstilbene*,



which crystallises in white leaflets, m. p. 120—121°, b. p. 200—210°, and forms a *dibromide*, crystallising in needles, m. p. 158° (decomp.).

Magnesium *p*-chlorophenyl bromide and chloroacetaldehyde give rise to *β-p-dichloro-α-phenylethyl alcohol*,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Cl}$ , an oily liquid, b. p. 145—147°/10 mm., which reacts with magnesium *p*-tolyl bromide to form 4-*chloro-4'-methylstilbene*, lustrous leaflets, m. p. 203—204°; *dibromide*, m. p. 204° (decomp.).

*Di-p-chlorostilbene*, prepared from magnesium *p*-chlorophenyl bromide and chloroacetal, crystallises in lustrous leaflets, m. p. 177°, and forms a *dibromide*, m. p. 226—227° (decomp.). F. B.

**Existence of Free Radicles.** M. GOMBERG (*J. Amer. Chem. Soc.*, 1914, 36, 1144—1170).—An address on the triarylmethyls, including an account of their most important chemical and physical properties, a discussion of the arguments which have been advanced in favour of or against the conception of free radicles, and a historical review of the work which has been carried out with a view to establish their constitution. E. G.

**Triarylmethyls. XII. The Addition of Metals to Free Organic Radicles.** W. SCHLENK and E. MARCUS (*Ber.*, 1914, 47, 1664—1678).—As might be expected from analogy to the behaviour of compounds containing multiple linkings (Schlenk, Appenrodt, Michael, and Thal, this vol., i, 396), the free organic radicles possess the power of uniting with sodium or potassium. The action of the metal was allowed to proceed in an atmosphere of nitrogen, the organic compound being in solution in ether.

Of the triarylmethyls, only triphenylmethyl offered difficulties, owing to the catalytic effect of the sodium in aiding a change into benzhydryltetraphenylmethane according to the equation:



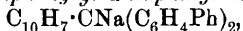
The difficulty was obviated by allowing triphenylmethyl chloride to react with sodium amalgam, when, after shaking for twelve hours, a deep orange-red solution of sodium triphenylmethyl was obtained. When isolated, *sodium triphenylmethyl*,  $\text{CPh}_3\text{Na}$ , forms a brick-red mass which is very sensitive to the air, and in solution is oxidised successively to triphenylmethyl and triphenylmethyl peroxide. It is exceedingly reactive, and its ethereal solution is immediately decomposed by water or hydrochloric acid with formation of triphenylmethane, whilst carbon dioxide converts it into triphenylacetic acid. Methyl iodide and benzyl chloride instantaneously decolorise the solution of the sodium compound, giving triphenylethane and *as*-tetraphenylethane respectively whilst benzoyl chloride and triphenylmethyl chloride yield respectively *β*-benzopinacolin and triphenylmethyl. The result of Harriot and St. Pierre (*A.*, 1889, 882) as to the production of two isomeric hydro-



carbons in the action of benzyl chloride on potassium triphenylmethyl (which they obtained by heating triphenylmethane with potassium at 200°) is discredited (compare Gomberg and Cone, A., 1906, i, 821).

The preparation of *sodium phenyldiphenyl- $\alpha$ -naphthylmethyl*,  $C_{10}H_7 \cdot CPhNa \cdot C_6H_4Ph$ , was combined with that of the corresponding phenyldiphenyl- $\alpha$ -naphthylmethyl by allowing phenyldiphenyl- $\alpha$ -naphthylmethyl chloride to react in ethereal solution with copper bronze and sodium powder. The resulting solution was an intense bluish-violet, and the solid obtained an evaporation resembled indigotin in appearance. Water, acid, and air again all immediately decompose the substance.

Bidiphenyl- $\alpha$ -naphthylmethyl chloride in an analogous manner to the last gave *sodium bidiphenyl- $\alpha$ -naphthylmethyl*,

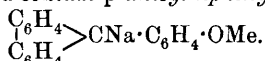


a black solid with metallic lustre, the solution of which is of a deep violet-black colour. Air immediately turns it yellowish-brown.

Although, judging by the colourless nature of its solutions diphenyl-bidiphenylene-ethane can be but little dissociated into free radicals in comparison with hexaphenylethane, yet the occurrence of dissociation to a slight extent has been demonstrated by the formation of a peroxide in its atmospheric oxidation (Gomberg and Cone, *loc. cit.*), and this is now confirmed by its slowly yielding *sodium phenyldi-*

*phenylenemethyl*,  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > CPhNa$ , orange-red needles (with  $1Et_2O$ ), when

treated in ethereal solution with sodium. The sodium derivative is immediately decolorised on exposure to the air and also when dissolved in alcohol, the solution in the latter case containing phenyldiphenylene-methane. Sodium affects di-*p*-anisylbidiphenylene-ethane in a similar manner, giving deep red *sodium p-anisyl-diphenylenemethyl*,



The behaviour of pentaphenylethane towards sodium promised to be of especial interest, as this substance is intermediate between the stable tetraphenylethane and the labile hexaphenylethane (compare Schlenk and Herzenstein, A., 1911, i, 122). The alkali metals did detect the existence of dissociation with this substance, but on account of its influence in converting triphenylmethyl into benzhydryl-tetraphenylmethane (see above), sodium was less satisfactory than potassium. On treating the product with carbon dioxide, diphenylacetic and triphenylacetic acids were obtained, this result indicating the following course for the action of the potassium:  $CPh_3 \cdot CHPh_2 \rightarrow \cdot CPh_3 + \cdot CHPh_2 \rightarrow CPh_3K + CHPh_2K$ .

From the existence of such a substance as the potassium derivative of diphenylamine, it was anticipated that compounds like the tetra-arylhydrazines would react with sodium in the same way as the triarylmethyls. It was actually found that tetraphenylhydrazine gave potass-diphenylamide,  $NPh_2K$ , the presence of which in the ethereal solution was indicated by treatment with carbon dioxide producing *potassium diphenylcarbamate*, pearly leaflets; this salt on the addition of acid gave carbon dioxide and diphenylamine.

In a similar manner, but more readily, tetra-*p*-tolylhydrazine gave *sodium ditolylamine* as a yellowish-white, crystalline powder, which on treatment with carbon dioxide gave *sodium ditolylcarbamate*, pearly scales (with  $2\text{H}_2\text{O}$ ); acids decomposed this salt into carbon dioxide and ditolylamine.

The authors consider the above metallic compounds of the triaryl-methyls to be of analogous constitution to the corresponding coloured derivatives of the triarylcarbinols, and they incline to Baeyer's "carbonium" representation of the structure, which they believe not to be disproved by the photochemical evidence of Hantzsch. The electrical conductivity of triphenylmethyl perchlorate (Hofmann, A., 1910, i, 168) is shared by sodium triphenylmethyl; this in ethereal solutions possesses a conductivity which diminishes rapidly on diluting, the behaviour being referred to the existence of the labile complex,  $[(\text{CPh}_3)_m\text{Na}_{m-n}]\text{Na}_n$ , which is more stable in concentrated solution.

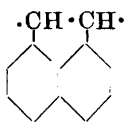
D. F. T.

**Hydrogenation by Sodammonium of Cyclic Hydrocarbons.** Preparation of Tetrahydronaphthalene. P. LEBEAU and M. PICON (*Compt. rend.*, 1914, 158, 1514–1517).—On adding liquid ammonia to a mixture of powdered naphthalene and excess of sodium, enclosing the mixture in an autoclave and allowing the temperature to rise gradually to that of the room, hydrogenation takes place, giving 1:2:3:4-tetrahydronaphthalene, in a 90% yield (compare Leroux, A., 1904, i, 986), together with a small quantity of a crystalline compound, m. p.  $99^\circ$ , of which the composition seems to correspond with  $\text{C}_{20}\text{H}_{18}$ .

W. G.

**The Thermochemical Transformation of Acenaphthylene and Synthesis of some Hydrocarbons of High Molecular Weight.** K. DZIEWOŃSKI and Z. LEYKO (*Ber.*, 1914, 47, 1679–1690).—It has already been shown that acenaphthylene undergoes polymerisation into two stereoisomeric heptacyclenes under the influence of light (Dziewoński, A., 1912, i, 844; 1913, i, 847), and the parent hydrocarbon has now been examined as to its behaviour when heated.

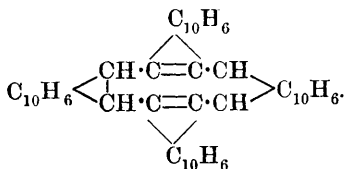
Already at  $90$ – $100^\circ$  acenaphthylene undergoes polymerisation; the reaction product is an orange-coloured, vitreous, resin-like mass from which the polymeride can be separated by first removing unaltered acenaphthylene with alcohol and repeatedly dissolving the residue in benzene, reprecipitating each time by the addition of alcohol. The new substance, termed *polyacenaphthylene*, for which cryoscopic measurements in bromoform as also ebullioscopic experiments in nitrobenzene indicate a molecular weight  $(\text{C}_{12}\text{H}_8)_{22}$ , is an amorphous, almost colourless mass, m. p.  $345$ – $350^\circ$ , with decomposition into acenaphthene, acenaphthylene, fluorocyclene (see below), decacyclene and other substances. On oxidation in acetic acid suspension with sodium chromate, the polyacenaphthylene yielded naphthalic anhydride in good yield, and it is consequently regarded as consisting



of an aggregation of residues of the annexed structure.

When heated for half an hour at  $280\text{--}290^\circ$  the formation of the above polymeride occurs to the extent of about 70%, and is accompanied by the formation of acenaphthene (3—4%) and of two hydrocarbons of high molecular weight, decacyclene (2%) and *fluorocyclene* (4—5%), the two last substances being sparingly soluble in benzene. Decacyclene,  $\text{C}_{36}\text{H}_{18}$ , was obtained in golden-yellow needles, m. p.  $387^\circ$ , identical with the substance obtained by the action of sulphur on acenaphthene, whilst fluorocyclene,  $\text{C}_{48}\text{H}_{28}$  (by ebullioscopic measurement in nitrobenzene), which is also formed by heating the photo-polymerides ( $\alpha$ - and  $\beta$ -heptacyclenes) of acenaphthylene for a short time at  $280^\circ$ , is a yellow, granular powder consisting of minute prisms, m. p.  $395\text{--}396^\circ$  (corr.). Fluorocyclene is sparingly soluble in most organic solvents, and its solutions have strong bluish-violet fluorescence. Sulphuric acid dissolves it to a green solution with blue fluorescence, nitric acid converts it into an orange-coloured, sparingly soluble *nitro*-derivative, bromine in chloroform solution gives a non-fluorescent additive *bromo*-compound, whilst oxidation in acetic acid by sodium dichromate gives rise to naphthalic anhydride. From the latter results the conclusion is drawn that the naphthylene residues are linked together by the carbon

atoms in the side-chains possibly as represented in the annexed formula.



In addition to the changes described in the foregoing, acenaphthylene undergoes yet other transformations under the catalytic influence of mineral acids.

D. F. T.

**Linear Dinaphthanthracene.** III. ERNST PHILIPPI (*Monatsh.*, 1914, 35, 375—382. Compare A., 1911, i, 793; 1913, i, 627).—By reducing 5:7:12:14-dinaphthanthradiquinone with phosphorus and hydriodic acid below  $135^\circ$ , Mills and Mills (T., 1912, 101, 2194) have obtained two hydrocarbons, m. p.  $240^\circ$  and  $270^\circ$  (with slight previous decomposition at  $240^\circ$ ), which they consider to be isomeric  $\alpha$ - and  $\beta$ -tetrahydronaphthanthracenes respectively.

In repeating their observations the author finds that the less fusible  $\beta$ -compound contains too little hydrogen to be a tetrahydro-derivative, and may be obtained by distilling the  $\alpha$ -compound (for which the m. p.  $244\text{--}245^\circ$  is given) with zinc dust.

When passed over hot metallic copper in an atmosphere of carbon dioxide, the  $\alpha$ -derivative is converted into a hydrocarbon which resembles Mills and Mill's  $\beta$ -tetrahydronaphthanthracene in that it gives with concentrated sulphuric acid an amethyst coloration, slowly turning to olive-green, but has m. p.  $270\text{--}271^\circ$  without previous decomposition. The results of analyses and molecular weight determinations show that this hydrocarbon is  $\beta\beta'\beta'$ -dinaphthanthracene, which has already been obtained in an impure condition by Harten-

stein (*Diss.*, Jena, 1892). From these results the conclusion is drawn that Mills and Mills'  $\beta$ -tetrahydronaphthanthracene is a mixture, consisting mainly of dinaphthanthracene.

In discussing the constitution of dinaphthanthracene the author points out that the hydrocarbon is neither unstable nor coloured, and therefore cannot have the *o*-quinonoid structure assigned to it by Hinsberg (*A.*, 1913, i, 849). F. B.

**Perchlorates of Aromatic Amines.** R. SPALLINO (*Ann. Chim. Applicata*, 1914, 1, 435—440).—Perchlorates of aromatic amines may be obtained readily by neutralising the acid with the base or by heating a mixture of the sulphate of the base with the calculated proportion of barium perchlorate dissolved in a little water. They are moderately stable to the action of air and light and remain unchanged at 100°, but at 200—220° they begin to decompose without exploding. The crystals may be readily powdered, but when ground in a porous mortar they emit the characteristic crackling of explosives sensitive to shock. When struck with a hammer they explode, but on platinum foil they burn rapidly without exploding and leave a carbonaceous residue. The perchlorates of aniline, *p*-nitroaniline, *p*- and *m*-phenylenediamines are described. T. H. P.

**2:5-Difluoroaniline.** FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1914, 176—177).—2:5-Difluoroaniline is obtained by the reduction of 2:5-difluoronitrobenzene by iron and hydrochloric acid at a temperature below 60°. It has b. p. 84.5—85.8°/30 mm., m. p. 13.45°,  $D_{17.2}^{17.2}$  1.28795,  $n_{D_a}$  1.5107. It is colourless, and does not become yellow when preserved. The *acetyl* derivative has m. p. 122.5°. When dissolved in hydrofluoric acid it is readily diazotised, but the diazo-compound is not decomposed when the solution is boiled: the introduction of copper powder causes an abundant evolution of nitrogen, but the product is completely resinified. H. W.

**The Nature of Subsidiary Valencies. VII. The Stability Limits of Complex Anions.** FRITZ EPHRAIM (*Ber.*, 1914, 47, 1828—1843).—In order to compare the stability of complex anions with that of complex cations (compare *A.*, 1912, ii, 546; 1913, ii, 129, 130; this vol., i, 17) the author has prepared a number of acid chlorides of organic bases, possessing the general formula  $M[Cl(HCl)]$ , and determined the dissociation pressure of the hydrogen chloride at various temperatures. The acid chlorides were prepared by treating the anhydrous base with hydrogen chloride, and the dissociation pressure was measured as described previously.

The results show that the dissociation temperature for a given pressure varies very little for the majority of the acid salts of tertiary amines. Negative groups do not make more difficult the addition of a second molecule of hydrogen chloride to the amine, as was supposed to be the case by Kaufer and Kunz (compare *A.*, 1909, i, 136, 556); for example, dinitrodimethylaniline hydrochloride has a greater affinity for hydrogen chloride than mononitrodimethylaniline hydrochloride.

Also, the position of the substituent in the benzene nucleus has very little effect.

Details are given of the preparation and investigation of the acid chlorides of the following bases: dimethylaniline, diethylaniline, *m*- and *p*-nitrodimehtylaniline, 1:3-dinitrodimehtylaniline, 4-nitrodimehtyl-*o*-toluidine, *p*-nitrosodimehtyl- and *p*-nitrosodiethyl-aniline, *o*-, *m*-, and *p*-chlorodimehtylaniline, *m*- and *p*-bromodimehtylaniline, *p*-bromodiethylaniline, *p*-dimethylaminobenzaldehyde, dimethyl- $\alpha$ -naphthylamine, pyridine, quinoline, cinchonine, trimethylamine, dimethylamine, and diethylamine.

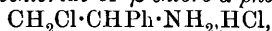
The only three which give dissociation temperatures appreciably different from the others are *p*-bromodiethylaniline, *p*-dimethylaminobenzaldehyde, and trimethylamine.

*m*-Dimethylaminophenol gives only a monochloride, and not a dichloride. Trinitrodimehtylaniline gives no compound with hydrogen chloride.

T. S. P.

**$\beta$ -Chloro- $\alpha$ -phenylethylamine.** S. GABRIEL and J. COLMAN (*Ber.*, 1914, 47, 1866—1873).—In extension of the investigation of  $\beta$ -chloro- $\beta$ -phenylethylamine recently described by Wolfheim (this vol., i, 677) the authors have studied the isomeric base.

For the preparation of the amine, crude  $\omega$ -bromoacetophenone was converted by potassium acetate into phenacyl acetate, which was hydrolysed by barium carbonate to benzoylcarbinol, and this was condensed with hydroxylamine to  $\beta$ -oximino- $\beta$ -phenylethyl alcohol (Meyer and Nægeli, A., 1883, 1076). On attempting the reduction of the latter by stannous chloride, simple hydrolysis took place, and, as was feared, sodium amalgam gave a large amount of  $\alpha$ -phenylethylamine. However, a larger part of the oxime was reduced to the hydroxy-amine, which was not volatile in steam, and could therefore be freed from the oxygen-free base. The contents of the flask were allowed to concentrate during the distillation, and, after liberating the base, extracting the oil with ether and neutralising, a 44% yield of  $\beta$ -hydroxy- $\alpha$ -phenylethylamine hydrochloride,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NH}_2\cdot\text{HCl}$ , was obtained. The salt has m. p. 137—138°, and the *picrate* forms short, rhombic prisms, m. p. 207°. Unlike the isomeride, this base is very stable towards hydrochloric acid, and displacement of the hydroxyl group could only be effected by a mixture of phosphorus chlorides. The hydrochloride of  $\beta$ -chloro- $\alpha$ -phenylethylamine,



forms rhombic leaflets, m. p. 190° (decomp.). The free base is sparingly soluble in water, is strongly alkaline, and forms a *picrate*, elongated, hexagonal tablets, m. p. 160°, and a *platinichloride*, m. p. about 225°.

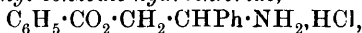
In aqueous solution, the free base undergoes the same transformation as the isomeride, namely, into phenylethyleneimine [styreneimine] although with a poorer yield. With carbon disulphide it forms 2-*thiol*-4-

*phenylthiazoline*,  $\begin{array}{c} \text{CHPh}\cdot\text{N} \\ | \\ \text{CH}_2-\text{S} \end{array} \gg \text{C}\cdot\text{SH}$ , in short prisms, m. p. 191°. On

benzoylation, it forms *benzo- $\beta$ -chloro- $\alpha$ -phenylethylamide*,  

$$\text{CH}_2\text{Cl}\cdot\text{CHPh}\cdot\text{NHBz},$$

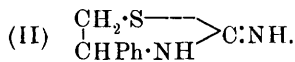
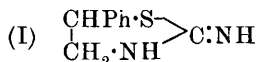
delicate needles, m. p. 137°, which undergoes rearrangement to *β*-amino-*β*-phenylethyl benzoate hydrochloride,



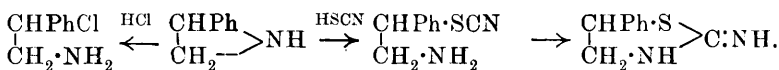
when boiled with water. This salt forms radiating, slender needles, m. p. 205—205·5°, and the *picrate*,  $1\text{H}_2\text{O}$ , has m. p. 188—189°, whilst the free base is an oil which spontaneously changes on warming with water into *benzo-β-hydroxy-α-phenylethylamide*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NHBz}$ , m. p. 154—154·5°. The intermediate product in this migration of the

benzoyl group, namely, 2 : 4-diphenyloxazoline,  $\begin{array}{c} \text{CHPh}\cdot\text{N} \\ | \\ \text{CH}_2-\text{O} \end{array} > \text{CPh}$ , may be isolated by warming the benzo-*β*-chloro-*α*-phenylethylamide with alcoholic potassium hydroxide. The base is a viscous oil, b. p. 210°/19 mm., which forms a *picrate*, m. p. 161°.

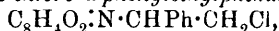
When *β*-chloro-*α*-phenylethylamine hydrochloride is evaporated with a solution of potassium thiocyanate, the product is 5-phenylethylene *ψ*-thiocarbamide [2-amino-5-phenylthiazoline] (I) (Wolfheim, *loc. cit.*), whereas the isomeride (II) was expected.



That formula (I) is correct for the product from both *β*-chloroamines is shown by the formation of the substance by the action of thiocyanic acid on a solution of styreneimine, since it may be assumed that the opening of the ring and addition of the acid follows the same course as in the case of hydrochloric acid, thus :



Finally, phthalic anhydride and the hydrochloride were heated to about 210°, whereby *β*-chloro-*α*-phenylethylphthalimide,



was produced, in flat needles, m. p. 106—107°.

J. C. W.

**Action of Acids on Diphenylnitrosoamine in Aqueous Alcoholic Solution.** MARQUEYROL and HENRI MURAOUR (*Bull. Soc. chim.*, 1914, [iv], 15, 510—514).—The action of hydrochloric acid on a solution of diphenylnitrosoamine in absolute alcohol leads to the formation of *p*-nitrosodiphenylamine; in the presence of water, on the other hand, the action takes a different course, and even minute quantities of hydrochloric, sulphuric or nitric acids cause the hydrolysis of the nitrosoamine, nitrous acid or ethyl nitrite being formed together with dinitrosodiphenylbenzidine mixed with a small quantity of the mononitroso-derivative. The reaction appears to take place in three stages: (1) liberation of nitrous acid; (2) oxidation of diphenylamine to diphenylbenzidine by nitrous acid, and (3) conversion of diphenylbenzidine into its nitroso-derivative by the excess of nitrous acid. In addition, a violet dye and a black condensation product are formed. When the quantity of nitric acid is increased the reaction becomes more complex, intensely yellow substances, readily soluble in alcohol, being formed together with a red precipitate containing dinitro-

derivatives of diphenylamine, and a red product almost insoluble in alcohol, which has not been completely identified.

The ready hydrolysis of diphenylnitrosoamine is comparable with that of other compounds containing the group  $\text{Ph}_2\text{N}\cdot\text{N}\cdot$ . When *as*-diphenylhydrazine hydrochloride is added to concentrated sulphuric acid and the product subsequently reduced by sodium hydrogen sulphite, diphenylamine and carbazole are obtained in addition to diphenylbenzidine, *p*-hydroxydiphenylamine, and *o*-aminodiphenylamine (compare Wieland and Müller, A., 1913, i, 1386). The formation of carbazole confirms the accuracy of Wieland's hypothesis that *as*-diphenylhydrazine is decomposed by concentrated sulphuric acid with intermediate formation of diphenylhydroxylamine. H. W.

**A New Class of Nitrogenous Compounds: the Ketisoketimines.** CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1914, 158, 1395—1400).—A description of a new class of compounds obtained from ketimines of the types  $\text{CH}_2\text{R}\cdot\text{CR}'\cdot\text{NH}$  (compare A., 1913, i, 873) by heating them in a current of hydrogen at  $115^\circ$ , condensation taking place with the elimination of ammonia. To these compounds the name ketisoketimines is assigned. Under these conditions phenylethylketimine,  $\text{CPhEt}\cdot\text{NH}$ , yields a compound,  $\text{C}_{18}\text{H}_{19}\text{N}$ , according to the reaction:  $2\text{CPhEt}\cdot\text{NH} = \text{C}_{18}\text{H}_{19}\text{N} + \text{NH}_3$ .

This compound is a very viscous, odourless, greenish-yellow oil, b. p.  $158\text{—}158.5^\circ/2.5\text{ mm.}$ ,  $171\text{—}172^\circ/6\text{ mm.}$ ,  $D_4^{30} 1.0272$ ,  $n_D^{30.5} 1.5986$ . It rapidly absorbs bromine, and under the influence of warm dilute hydrochloric acid is decomposed, giving ammonia and phenyl ethyl ketone. Its constitution may be represented by either of the formulæ: (I)  $\text{NH}(\text{CPh}\cdot\text{CHMe})$  or (II)  $\text{CPhEt}\cdot\text{N}\cdot\text{CPh}\cdot\text{CHMe}$ , according as it is considered to be formed by condensation of two molecules of an isoketimine,  $\text{NH}_2\cdot\text{CPh}\cdot\text{CHMe}$ , or of one molecule of the ketimine with one molecule of the isoketimine.

In the presence of magnesium ethyl bromide there is no evolution of ethane, such as takes place with the original ketimine, thus indicating that there is no longer a hydrogen atom attached to the nitrogen atom (compare Meunier, A., 1903, i, 544), and the authors therefore assign the constitution represented by formula (II) to this new class of compounds. It is of interest to note that the linking with respect to the nitrogen and adjacent carbon atoms is similar to that in the case of pyridine, the stability of pyridine as compared with the ketisoketimines being probably accounted for by the fact that the functional grouping forms part of the cyclic nucleus. W. G.

**Optically Active and Inactive Diphenylethylthiocarbamides.** J. M. LOVÉN and ERIK OHLSSON (*Ber.*, 1914, 47, 1534—1536).—The *s*-di- $\alpha$ -phenylethylthiocarbamide, obtained by warming carbon disulphide and inactive  $\alpha$ -phenylethylamine in alcoholic solution (Michaelis, Schroeter, and Linow, A., 1893, i, 703), is a mixture of the dextro-, lævo-, and meso-forms of the substance.

*l*-Di- $\alpha$ -phenylethylthiocarbamide,  $\text{CS}(\text{NH}\cdot\text{CHPhMe})_2$ , obtained by condensing carbon disulphide with *l*-phenylethylamine (Lovén, A., 1905, i, 875), forms long needles, m. p.  $195.5^\circ$ ,  $[\alpha]_D +22.5^\circ$  (in alcohol,

D 0·81), whilst *d-di- $\alpha$ -phenylethylthiocarbamide* was obtained in similar crystals of the same m. p., but of  $[\alpha]_D - 22\cdot1^\circ$ .

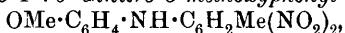
The mixture of meso- and racemic compounds obtained with the use of racemic  $\alpha$ -phenylethylamine is easily separable by recrystallisation, the meso-*di- $\alpha$ -phenylethylthiocarbamide* forming tablets, m. p. 125·5—126°, whilst the *racemic* substance, whether obtained in this way or synthesised from its enantiomorphous constituents, forms needles, m. p. 165·5—166°.

The inactive substance, m. p. 163°, described by Michaelis, Schroeter, and Linow (*loc. cit.*), must therefore have consisted almost entirely of the racemic form. D. F. T.

*m*-Anisidine and Dimethyl-*m*-anisidine. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Ber.*, 1914, **47**, 1537—1545; *Arch. Sci. phys. nat.*, 1914, [iv], **37**, 423—434).—An investigation of some of the derivatives of *m*-anisidine.

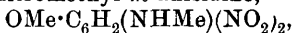
The parent base, b. p. 243°/755 mm., was obtained by acetylating *m*-aminophenol, methylating the resulting acetyl derivative, and hydrolysing the aceto-*m*-anisidine with diluted hydrochloric acid; each stage of the process gave a yield exceeding 90% of the theoretical. 3-*p*-Toluenesulphonylamino-phenol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ , colourless octahedra, m. p. 158°, did not prove satisfactory as a means of passing from *m*-aminophenol to *m*-anisidine.

The following derivatives of *m*-anisidine were isolated: *hydrochloride*; *sulphate*; *picrate*, lemon-yellow needles, m. p. 169° (decomp.); *formyl* derivative, colourless prisms, m. p. 57°; *p*-toluenesulphonyl derivative, colourless needles, m. p. 68°. By treatment with 4-chloro-1:3-dinitrobenzene in alcoholic solution, *m*-anisidine is converted into 2:4-dinitro-3'-methoxydiphenylamine  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , yellow needles, m. p. 137—138°, whilst in an analogous manner 5-chloro-2:4-dinitrotoluene gave rise to 4':6'-dinitro-3-methoxyphenyl-*m*-tolylamine,

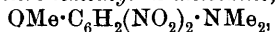


lemon-yellow prisms, m. p. 129°. When warmed with an equimolecular proportion of 2:3:5-trinitro-*p*-anisidine (Meldola and Reverdin, T., 1913, **103**, 1490), *m*-anisidine is converted into 2:4-dinitro-5-amino-6:3'-dimehoxydiphenylamine  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}(\text{OMe})\cdot(\text{NO}_2)_2\cdot\text{NH}_2$ , black crystals with a green metallic lustre, m. p. 144°. When diazotised and coupled with  $\beta$ -naphthol, *m*-anisidine gives *m*-anisoleazo- $\beta$ -naphthol,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ , red needles, m. p. 140°.

Dimethyl-*m*-anisidine (compare Grimaux, A., 1891, 694; 1901, i, 269), obtained by treatment of *m*-anisidine with methyl sulphate, is a colourless oil, b. p. 237°; it has a characteristic odour and turns brown when exposed to light. On nitration, dimethyl-*m*-anisidine can be made to yield 4:6-dinitromethyl-*m*-anisidine,



and 2:4:6-trinitro-5-methylnitroaminoanisole, which are already known (compare Blanksma, A., 1904, i, 577; van Romburgh, A., 1889, 1154), and also 4:6-dinitrodimethyl-*m*-anisidine,



lemon-yellow needles, m. p. 198°, and 4:6-dinitro-3-methylnitroamino-



*anisole*,  $\text{OMe} \cdot \text{C}_6\text{H}_2 \cdot (\text{NO}_2)_2 \cdot \text{NMe} \cdot \text{NO}_2$ , pale yellow crystals, m. p.  $138^\circ$ . The last substance on warming with phenol is converted by loss of the *N*-nitro-group into 4:6-dinitromethyl-*m*-anisidine (Blanksma, *loc. cit.*), and on heating with potassium hydroxide solution gives methylamine and a substance, yellow crystals, m. p.  $182^\circ$ ; *barium* salt, sparingly soluble. D. F. T.

**Preparation and Properties of Some Higher Phenols and Their Ethers.** TREAT B. JOHNSON and EDWARD F. KOHMANN (*J. Amer. Chem. Soc.*, 1914, **36**, 1259—1268).—Johnson and Hodge (A., 1913, i, 1055) have described a method for the preparation of alkyl derivatives of phenols and phenol ethers by reducing the corresponding acyl derivatives with zinc amalgam and hydrochloric acid. This method has now been applied to certain higher phenols.

Tetradecylveratrole (Majima and Nakamura, this vol., i, 167) exists in two modifications, one of which, m. p.  $37-38.5^\circ$ , slowly changes into the other, m. p.  $49^\circ$ , at the ordinary temperature. *Nitrotetradecylveratrole*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{C}_{14}\text{H}_{29}$ , has m. p.  $91-93^\circ$ . The following new compounds are described.

4-*Myristylphenetole*,  $\text{C}_{13}\text{H}_{27} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ , m. p.  $66-67^\circ$ , obtained by the action of myristyl chloride on phenetole in presence of aluminium chloride, forms colourless crystals. On reduction it yields 1:4-tetradecylphenetole,  $\text{C}_{14}\text{H}_{29} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ , m. p.  $36-36.5^\circ$ , which is converted by hydrolysis into 1:4-tetradecylphenol,  $\text{C}_{14}\text{H}_{29} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p.  $73-74^\circ$ .

1:4-*Myristylphenol*,  $\text{C}_{13}\text{H}_{27} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p.  $74-74.5^\circ$ , obtained by the action of myristyl chloride and aluminium chloride on a solution of phenetole in carbon disulphide, could not be reduced, except to a very slight extent, by zinc amalgam.

*Myristylquinol dimethyl ether*,  $\text{C}_{13}\text{H}_{27} \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$ , m. p.  $51-52^\circ$ , prepared by the action of myristyl chloride on quinol dimethyl ether in presence of aluminium chloride, crystallises in plates, and on reduction is converted into *tetradecylquinol dimethyl ether*,

$\text{C}_{14}\text{H}_{29} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$ ,  
b. p.  $260-275^\circ/25-35$  mm., m. p.  $65^\circ$ , which forms short needles.

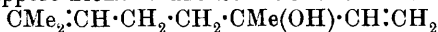
E. G.

**Incompatibility between Salol, Sulphonal and  $\beta$ -Naphthol.** GINO BIANCHINI (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 608—615).—Sulphonal and  $\beta$ -naphthol form an eutectic corresponding with  $67^\circ$  and 38 mol. % of sulphonal. For the system salol- $\beta$ -naphthol, the author's results agree with those of previous investigators. Salol and sulphonal form an eutectic corresponding with  $34^\circ$  and 8 mol. % of sulphonal. The thermal diagram of the ternary system, salol-sulphonal- $\beta$ -naphthol, shows an eutectic lying at  $27^\circ$  and corresponding with 78 mol. % of salol, 7 mol. % of sulphonal and 15 mol. % of  $\beta$ -naphthol.

R. V. S.

**The Constitution of Linalool.** PH. BARBIER and R. LOCQUIN (*Compt. rend.*, 1914, **158**, 1554—1558. Compare Enklaar, A., 1908, i,

934).—From a study of the behaviour of linalool on reduction, the authors now support Tiemann and Semmler's formula for this alcohol,



(compare A., 1894, i, 833), rather than the one originally put forward by Barbier (compare A., 1901, i, 731). Linalool on hydrogenation in the presence of platinum black yields  $\beta\zeta$ -dimethyloctan- $\zeta$ -ol, identical in every respect chemically with that prepared synthetically by the action of magnesium ethyl bromide on methyl isohexyl ketone. The alcohol obtained from *l*-linalool is, however, slightly active, whilst the synthetic dimethyloctanol is inactive, and the *allophanate* of the former has m. p.  $88^\circ$ , whilst that of the latter has m. p.  $110-111^\circ$ .

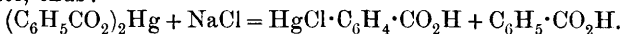
W. G.

**The Phytosterols.** "Hydrocarotin." ERICH BESCHKE (*Ber.*, 1914, 47, 1853—1856).—The substance which Husemann discovered in 1861 in the carrot, and called "hydrocarotin," has been shown by many workers to belong to the class of the phytosterols. An examination of a large quantity of material has enabled the author to demonstrate that "hydrocarotin" is really a mixture of about 90% sitosterol and 10% stigmasterol, that is, it consists of the same phytosterols as are found in many other plants, notably the calabar bean (Windaus and Hauth, A., 1907, i, 129).

For the isolation of the crude phytosterol, it is better to use Reintzer's process (A., 1887, 265) and to neglect the carotene, but should it be desired to save this hydrocarbon, the method of Euler and Nordenson (A., 1908, ii, 724) may be adopted. A yield of 0.01% was obtained from 1500 kilos. of carrots. The separation of the two alcohols was carried out by taking advantage of the different solubilities of the bromides of their acetyl derivatives (Windaus and Hauth, *loc. cit.*).

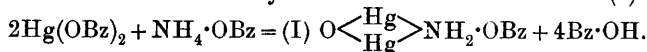
J. C. W.

**Mercuric Benzoate.** E. RUPP and A. HERRMANN (*Arch. Pharm.*, 1914, 252, 3—9).—The similarity in the therapeutic action of mercurisalicyclic anhydride,  $\text{OH}\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CO} \\ \text{Hg} \end{smallmatrix}\rangle\text{O}$ , and a solution of mercuric benzoate in aqueous sodium chloride suggested the possibility of the two latter substances reacting to form sodium chloromercuribenzoate, thus:



According to this view, one molecular proportion of sodium chloride should be sufficient completely to dissolve the mercuric benzoate. It is found, however, that two molecules of sodium chloride are necessary, and that only traces of benzoic acid can be extracted from the solution. The conclusion is therefore drawn that the solubility of mercuric benzoate in sodium chloride is due to the formation of mercuric chloride and sodium benzoate. Contrary to previous statements, the solution of mercuric benzoate in sodium chloride precipitates albumin from solution; the extent of the precipitation is exactly the same as that produced by a solution containing the equivalent amounts of mercuric chloride and sodium benzoate, thus confirming the above view. Mercuric benzoate is sparingly soluble in sodium benzoate, but

dissolves readily in ammonium benzoate. In this case the solubility is due to the formation of an oxydimercuriammonium benzoate (I):



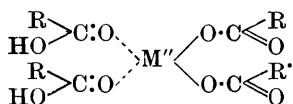
The benzoic acid combines with the ammonium benzoate to form the acid salt, so that five molecules of ammonium benzoate are necessary for complete solution.

Mercuric benzoate is best prepared by dissolving mercuric oxide in a slight excess of dilute acetic acid, and adding aqueous sodium benzoate in quantity insufficient for complete precipitation. F. B.

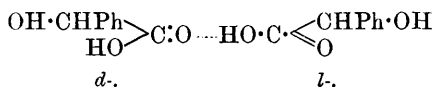
**Tribenzoin.** L. BALBIANO (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 654—658. Compare Lipp and Miller, A., 1913, i, 1038).—Further experiments confirm the author's view (A., 1913, i, 547) that practically the esterification of glycerol with benzoyl chloride does not occur in stages, but that tribenzoin is formed by the first drop of benzoyl chloride added, but it is none the less possible that it may be accompanied by small quantities of dibenzoin which escaped detection by the methods employed. R. V. S.

**Acid Salts of Carboxylic Acids.** P. PFEIFFER. [With G. BIRENCEWIG, A. HOFMANN, and C. WINDHEUSER] (*Ber.*, 1914, 47, 1580—1596).—About sixty or seventy examples of acid salts of carboxylic acids are known, most of them being sodium, potassium, or ammonium compounds. A large number of similar pyridine salts are now described. The majority of these compounds contain two carboxyl groups to one univalent metal or radicle, thus:  $\text{R} \cdot \text{CO}_2\text{H}$ ,  $\text{R} \cdot \text{CO}_2\text{M}$  or  $2\text{R} \cdot \text{CO}_2\text{H}, \text{B}$  (B = Base). Others are known of the types  $2\text{R} \cdot \text{CO}_2\text{H}$ ,  $\text{R} \cdot \text{CO}_2\text{M}$  and  $3\text{R} \cdot \text{CO}_2\text{H}, \text{B}$ . In order to explain the constitution of these salts, the author assumes that they are derived from associated acids, that is, of polymerides in which the partial valency of the carbonyl group of one simple molecule is satisfied by the partial valency of the replaceable hydrogen of another molecule. Not only is it well known that carboxylic acids tend very strongly to form double molecules, but there are many examples, to which more are now added, of two different acids condensing. These double molecules are now written thus:  $\begin{smallmatrix} \text{R} \\ \text{HO} \end{smallmatrix} \text{C} \text{O} \cdots \cdots \text{HO} \cdot \text{C} \begin{smallmatrix} \text{R} \\ \text{O} \end{smallmatrix}$ , and the salts of ammonia or pyridine,  $\begin{smallmatrix} \text{R} \\ \text{B, HO} \end{smallmatrix} \text{C} \text{O} \cdots \cdots \text{HO} \cdot \text{C} \begin{smallmatrix} \text{R} \\ \text{O} \end{smallmatrix}$  or  $\begin{smallmatrix} \text{R} \\ \text{B, HO} \end{smallmatrix} \text{C} \text{O} \cdots \cdots \text{HO} \cdot \text{C} \begin{smallmatrix} \text{R} \\ \text{O} \end{smallmatrix} \cdots \cdots \text{HO} \cdot \text{C} \begin{smallmatrix} \text{R} \\ \text{O} \end{smallmatrix}$ .

The metallic salts could be written in two ways. The components may be linked by the partial valency of the metallic atom of the simple salt or by the hydrogen atom of the second acid molecule. The former arrangement is preferred, as in it the metal is more centrally situated, for example,

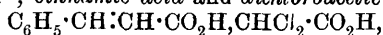


Such a theory of the constitution of associated acids may also be extended to a consideration of racemates. The active mandelic acids, like phenylacetic acid, are considerably polymerised in indifferent solvents, and the solid acids may well be bimolecular compounds of the above type. Since different acids may associate together, the existence of a *dl*-mandelic acid receives a simple explanation on the basis of the formula :



The normal pyridine salts were usually prepared by evaporating a solution of the acid in the base, and the acid salts were obtained by crystallising the normal salts from absolute alcohol. The following pyridine salts are described: *salicylate*, large, colourless tablets and prisms, m. p. about 60°; *hydrogen salicylate*, A<sub>2</sub>Py, thick tablets, m. p. 89°; *o-nitrobenzoate*, yellow, transparent tablets, m. p. 46°; *hydrogen o-nitrobenzoate*, A<sub>2</sub>Py, pale yellow tablets, m. p. 75°; *m-nitrobenzoate*, pale yellow, glistening needles, m. p. 106°; *hydrogen m-nitrobenzoate*, A<sub>2</sub>Py, pale yellow tablets, m. p. 122°; *p-nitrobenzoate*, pale yellow leaflets, m. p. 225°; *hydrogen p-nitrobenzoate*, A<sub>2</sub>Py, pale yellow leaflets, m. p. 225°; *o-p-dinitrobenzoate*, yellow needles, m. p. 115°; *hydrogen o-p-dinitrobenzoate*, A<sub>2</sub>Py, glistening, yellow tablets, m. p. 141—142°; *m-m-dinitrobenzoate*, A<sub>2</sub>Py, colourless, radiating needles, m. p. 172°; *2-chloro-5-nitrobenzoate*, broad, colourless prisms or long, slender needles, m. p. about 114°; *hydrogen 2-chloro-5-nitrobenzoate*, A<sub>2</sub>Py, sheaves of needles, m. p. 129°; *αβ-dichloro-β-phenylpropionate*, m. p. 85°, decomposes on heating with pyridine into α-chlorocinnamic acid; *hydrogen αβ-dichloro-β-phenylpropionate*, A<sub>2</sub>Py, colourless, prismatic needles, m. p. 121—122°, which are dissociated on rubbing with hydrochloric acid; *αβ-dibromo-β-phenylpropionate*, m. p. 110°; *hydrogen αβ-dibromo-β-phenylpropionate*, A<sub>2</sub>Py, large, colourless, rhombic prisms, m. p. 138°, dissociated by hydrochloric acid; *hydrogen oxalate*, A''Py, colourless needles, m. p. 153°, obtained directly from the pyridine solution of the anhydrous or crystallised acid; *trihydrogen malonate*, A<sub>2</sub>''Py, colourless tablets, m. p. about 68°, dissociated by hydrochloric acid; *hydrogen succinate*, A''Py, large, colourless prisms or tablets, m. p. 65°, very quickly crumble in the air and decompose in a desiccator; *dibromosuccinate*, A''Py<sub>2</sub>, stable in pyridine atmosphere, changes into the *hydrogen dibromosuccinate*, A''Py, in a desiccator over phosphoric oxide; *fumarate*, A''Py<sub>2</sub>, from a warm solution of fumaric or maleic acid, colourless, prismatic needles; *hydrogen fumarate*, A''Py, sinters at 125—130°, molten at about 188°; *hydrogen phthalate*, A''Py, colourless needles, m. p. 86°; *hydrogen isophthalate*, A''Py, colourless needles; *terephthalate*, A''Py<sub>2</sub>, large, monoclinic prisms, stable in a pyridine atmosphere.

The following double compounds of acids were prepared by crystallising a solution of one component in the other; *benzoic acid* and *dichloroacetic acid*, C<sub>6</sub>H<sub>5</sub>·CO<sub>2</sub>H·CHCl<sub>2</sub>·CO<sub>2</sub>H, colourless, glistening leaflets, m. p. 104°; *cinnamic acid* and *dichloroacetic acid*,

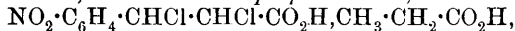


colourless, glistening leaflets, m. p. 84—89°; *cinnamic acid* and *trichloroacetic acid*,  $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ ,  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ , colourless crystals;

$\alpha\beta$ -*dichloro- $\beta$ -p-nitrophenylpropionic acid* and *acetic acid*,



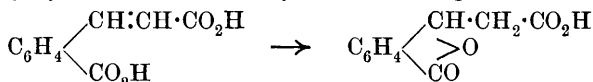
glistening leaflets; the same with *propionic acid*,



pale yellow leaflets;  $\alpha\beta$ -*dibromo- $\beta$ -p-nitrophenylpropionic acid* and *acetic acid*, pale yellow leaflets, m. p. 214—215°; the same with *propionic acid*, glistening, yellow leaflets.

Phenylacetic acid is associated in cold or hot benzene; *dl*-mandelic acid has the normal molecular weight in boiling acetone, but is associated in hot benzene, so is *l*-mandelic acid, and *d*-mandelic acid and *l*-acetylmandelic acid are associated in hot benzene. J. C. W.

***o*-Carboxycinnamic Acid and *o*-Carboxybenzhydrylacetic Acid.** RUDOLF ROTH (*Ber.*, 1914, **47**, 1597—1599).—It was expected that *o*-carboxycinnamic acid would condense with phenols under the influence of acetic and sulphuric acids, from analogy to the formation of phenylhydrocoumarins from cinnamic acid. Such is not the case, however, the only result being the rearrangement of the acid into *o*-benzhydrylacetocarboxylic anhydride, according to the scheme:



This transformation takes place on melting the acid, or even by heating it with dilute acids, and, for this reason, attempts to prepare esters of the cinnamic acid result in the formation of the esters of the anhydride acid. Ehrlich and Benedikt (*A.*, 1888, 1306) effected the same change by the action of acetic anhydride and sodium acetate, but incorrectly designated the product as phthalylacetic acid. The reverse transformation is brought about by the action of alkali hydroxide.

The reduction of phthalylacetic acid to *o*-carboxycinnamic acid is best performed in alkaline solution by an electric current, using a mercury cathode.

The *methyl* and *ethyl* esters of the above anhydride, obtained directly or from *o*-carboxycinnamic acid, have m. p. 62° and 76° respectively.

J. C. W.

**The Bromination of Phenylacetoneitrile.** ST. OPOLSKI and A. WEINBAUM (*Ber.*, 1914, **47**, 1560—1562).—It has already been shown by Reimer (*A.*, 1881, 47; 1882, 169) that on brominating phenylacetoneitrile at higher temperatures, substitution occurs in the side-chain. The authors have now submitted phenylacetoneitrile to bromination at the ordinary temperature in carbon disulphide and in chloroform solution, a little iodine or iron being present as catalyst. The change is more rapid in ether, and after two days the solution was found to contain  $\alpha$ -bromophenylacetoneitrile (Reimer, *loc. cit.*) and  $\alpha$ -bromophenylacetamide, colourless needles, m. p. 144°, the identity of which was proved by direct comparison with a specimen prepared by

the method of Steinkopf and Benedek (A., 1908, i, 981) and by conversion with nitrous acid into  $\alpha$ -bromophenylacetic acid.

The authors incline to the view that the formation of the  $\alpha$ -bromophenylacetamide is due to an intermediate formation of an acetimide bromide,  $\text{CHPhBr}\cdot\text{CBr}\cdot\text{NH}$ , by addition of bromine to phenylacetoneitrile accompanied by slight rearrangement. This explanation receives confirmation from the absence of formation of the bromophenylacetamide if moisture is rigorously excluded, thus precluding the subsequent hydrolysis of the above intermediate compound. However, a substance described as  $\alpha$ -bromophenylacetimide bromide is stated by Reimer not to form the amide on treatment with water. Experiments are being made to solve this difficulty. D. F. T.

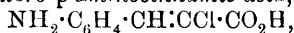
### The Nitration of Stereoisomeric Halogen Cinnamic Acids.

PAUL PFELFFER [with R. FRITSCH, A. PANSKY, and C. WINDHEUSER] (*Ber.*, 1914, 47, 1755—1773).—It is possible to nitrate the stereoisomeric halogen substituted cinnamic acids with persistence of the isomerism.

When normal  $\alpha$ -chlorocinnamic acid, m. p.  $139^\circ$ , is treated with fuming nitric acid at a temperature below  $-5^\circ$ , there is obtained an  $\alpha$ -chloro-*p*-nitrocinnamic acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{H} > \text{C}:\text{C} < \begin{smallmatrix} \text{Cl} \\ \text{CO}_2\text{H} \end{smallmatrix}$ , m. p.  $220\text{--}221^\circ$ , identical with an acid described earlier, for example, by Naar (A., 1891, 562), who prepared it by the oxidation of  $\alpha$ -chloro-*p*-nitrocinnamaldehyde. This acid was also produced by other processes, as, for example, the hydrolysis of ethyl  $\alpha\beta$ -dichloro-*p*-nitrophenylpropionate when it accompanied  $\alpha\beta$ -dichloro-*p*-nitrophenylpropionic acid in the resulting mixture. The latter acid gave an *ethyl* ester, colourless needles, m. p.  $89^\circ$ , whilst the above  $\alpha$ -chloro-*p*-nitrocinnamic acid gave a *methyl* ester, pale yellow needles, m. p.  $139\text{--}140^\circ$ , and an *ethyl* ester, almost colourless needles, m. p.  $113^\circ$ .

Cautious treatment of *allo*- $\alpha$ -chlorocinnamic acid, m. p.  $114^\circ$ , with fuming nitric acid gave rise to *allo*- $\alpha$ -chloro-*p*-nitrocinnamic acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{H} > \text{C}:\text{C} < \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{Cl} \end{smallmatrix}$ , asbestos-like needles, m. p.  $153\text{--}154^\circ$ ; *potassium* salt, needles; *methyl* ester, pale yellow needles, m. p.  $81\text{--}82^\circ$ ; *ethyl* ester, pale yellow leaflets or tablets, m. p.  $67\text{--}68^\circ$ . These *allo*-isomerides pass fairly readily into the compounds of the normal series; thus, the *ethyl* ester of the *allo*-acid changes into the normal ester when exposed either in the solid state or in alcoholic solution to sunlight, whilst the free *allo*-acid also undergoes transformation when warmed with a pyridine solution of pyridine hydrochloride.

The above stereoisomeric chloronitrocinnamic acids are both reducible by ferrous sulphate in ammoniacal solution, giving respectively the corresponding  $\alpha$ -chloro-*p*-aminocinnamic acid,



very pale yellow leaflets, decomp. near  $219^\circ$  (*hydrochloride*, pale yellow needles; *acetyl* derivative, yellow leaflets, m. p.  $230^\circ$ ), and *allo*- $\alpha$ -chloro-*p*-aminocinnamic acid, a brownish-yellow powder (*acetyl* derivative, yellow leaflets, m. p.  $197\text{--}198^\circ$ ).

On diazotisation and boiling the resulting solution, the normal

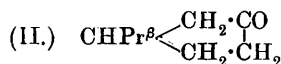
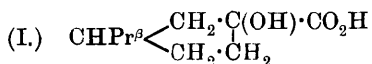
$\alpha$ -chloro-*p*-aminocinnamic acid was converted into  $\alpha$ -chloro-*p*-hydroxycinnamic acid, a yellow, crystalline powder, m. p. 242° (decomp.), the acetyl derivative of which (needles, m. p. 164—167°), was also obtainable by submitting acetyl-*p*-coumaric acid in carbon disulphide to the action of chlorine and eliminating hydrogen chloride from the resulting  $\alpha\beta$ -dichloro-*p*-acetoxypheylpropionic acid, colourless leaflets or tablets, m. p. 158—162°, by heating with pyridine.

When *allo*-chlorocinnamic acid is nitrated, the corresponding nitro-derivative described above is accompanied by  $\alpha$ -chloro-*p*-*o*-dinitrostyrene,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CCl}\cdot\text{NO}_2$ , yellow needles, m. p. 150—153°. In nitrating normal chlorocinnamic acid this substance is obtained only if the temperature is not kept low, and its constitution is indicated by its formation from *p*-*o*-dinitrostyrene by the addition of chlorine to give  $\alpha\beta$ -dichloro- $\beta$ -nitro- $\alpha$ -*p*-nitrophenylethane,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}\cdot\text{CHCl}\cdot\text{NO}_2$ , a pale yellow, crystalline powder, m. p. 72—74°, with subsequent removal of the elements of hydrogen chloride by sodium hydroxide solution.

Normal  $\alpha$ -bromocinnamic acid, m. p. 130—131°, and its *allo*-isomeride, m. p. 120—121°, on treatment with cooled fuming nitric acid gave  $\alpha$ -bromo-*p*-nitrocinnamic acid, asbestos-like needles, m. p. 210° (*methyl* ester, needles, m. p. 131—132°; *ethyl* ester, m. p. 94—94·5°), and *allo*- $\alpha$ -bromo-*p*-nitrocinnamic acid, needles, m. p. 146—148° (compare Müller, A., 1882, 840); *methyl* ester, m. p. 79—81°. On exposure to sunlight, a methyl-alcoholic solution of this methyl ester deposited needles of the stereoisomeric methyl ester in an almost pure condition, whilst a similar conversion of the acid could be effected by warming with a solution of hydrogen bromide in pyridine.

Normal dibromocinnamic acid, m. p. 139°, on nitration yielded dibromo-*p*-nitrocinnamic acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}_2\text{H}$ , pale yellow leaflets, m. p. 180°, identical with the acid obtained by Drewsen from bromine and *p*-nitrophenylpropionic acid (A., 1882, 846); *methyl* ester, colourless needles, m. p. 92—92·5°. *allo*-Dibromocinnamic acid, m. p. 100°, gave *allo*-dibromo-*p*-nitrocinnamic acid, yellow leaflets, m. p. 166—168°; *methyl* ester, very pale yellow needles, m. p. 107—108°. D. F. T.

**A Further Proof of the Constitution of Dihydrocamphoceanic Acid.** [Camphenilolic Acid.] S. V. HINTIKKA (*Chem. Zentr.*, 1914, i, 788—789; from *Ann. Acad. Sci. Fennicae*, 1914, [A], 5, ii, 1—7).—The relationship between dihydrocamphoceanic acid and *isopropylcyclopentan-3-one*, established by Bouveault and Blanc (A., 1908, i, 134; 1909, i, 108), has been confirmed by more direct transformations. The acid was treated with phosphorus pentachloride, followed by bromine, and the bromo-acid, obtained after decomposition with ice, was warmed with sodium carbonate solution. In this way,  *$\alpha$ -hydroxydihydrocamphoceanic acid* (I.) was isolated in glistening

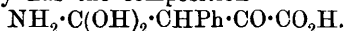


leaflets, m. p. 95—96°. It was transformed into *isopropylcyclopentan-3-one* (II.) by heating a solution in 50% acetic acid with

lead dioxide. The ketone has b. p. 185—190°, and forms a semi-carbazone, m. p. 198°. J. C. W.

**The Process of Saponification of Esters and Amides by Concentrated Sulphuric Acid.** J. BOUGAULT (*Compt. rend.*, 1914, 158, 1424—1426).—In the saponification of substances such as ethyl  $\alpha$ -cyanophenylpyruvate, after the first hydration of the nitrile group to the amide group, the sulphuric acid apparently only intervenes to form an additive product, which on dilution with water then undergoes saponification with the liberation of ammonia and alcohol. If ethyl  $\alpha$ -cyanophenylpyruvate is dissolved in concentrated sulphuric acid and after twenty-four hours is poured into cold ethyl alcohol, on the addition of water a crystalline compound is obtained, m. p. 98—100°, having the constitution  $\text{NH}_2\cdot\text{CO}\cdot\text{CPh}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$ . If the alcohol employed is methyl alcohol, then a mixture of methyl and ethyl esters is obtained.

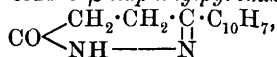
If a solution of the above nitrile in concentrated sulphuric acid is poured on ice, a yellow precipitate is obtained, which on freeing from sulphuric acid by washing with ice-cold water is found to have retained its nitrogen, not as an ammonium salt or as an ordinary amide, since, if the temperature is allowed to rise to 15—20°, the product is spontaneously converted into ammonium phenylpyruvate with the elimination of carbon dioxide. The unstable yellow precipitate probably has the composition



W. G.

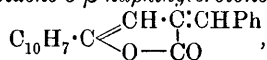
**$\beta$ -2-Naphthoylpropionic Acid.** W. BORSCHÉ and H. SAUERHEIMER (*Ber.*, 1914, 47, 1645—1648).—When succinic anhydride and naphthalene are condensed, one of the products is a  $\beta$ -naphthoylpropionic acid. Graebe (A., 1905, i, 704) showed that the product when phthalic anhydride was used was an  $\alpha$ -derivative of naphthalene, namely,  $o$ - $\alpha$ -naphthoylbenzoic acid, whereas, in the present case, only a  $\beta$ -substituted compound could be isolated. The constitution of the acid was proved by the formation of  $\beta$ -naphthoic acid on fusion with alkali hydroxide at 250°.

Naphthalene, succinic anhydride, aluminium chloride, and carbon disulphide were kept for a day at 50—60°. The solvent and the excess of naphthalene were then removed from the acidified product in a current of steam, and the crude residue was esterified by alcoholic hydrogen chloride solution. The chief fraction of the ester had b. p. 235—240°/11 mm., and deposited crystals which were pressed on a porous plate. The recrystallised *ethyl*  $\beta$ -2-naphthoylpropionate has m. p. 47—48°, and the acid,  $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , forms colourless needles, m. p. 172°, and is only slightly attacked by chromic acid, permanganate, or by potassium hydroxide below 250°. The acid condenses with hydroxylamine, yielding  $\gamma$ -oximino- $\gamma$ -2-naphthylbutyric acid,  $\text{C}_{10}\text{H}_7\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , as a white powder, m. p. 135—136°, and with hydrazine to form 3- $\beta$ -naphthylpyridazinone,





in colourless crystals, m. p. 148°. When the sodium salt is heated with benzaldehyde and acetic anhydride (compare this vol., i, 686) the product is 1-benzylidene-3-β-naphthylcrotonolactone,

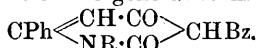


which forms iridescent, golden-yellow leaflets, m. p. 185—186°.

J. C. W.

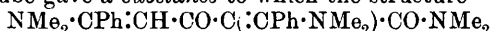
**The Action of Phosphoric Oxide on Dibenzylmalonic Acid.** HUBERT CYRIL CUTTS (*Ber.*, 1914, 47, 1656—1658).—See P., 1914, 30, 39.

**The Action of Amines on Benzoyldehydracetic Acid.** JOH. SCHÖTTLE (*Ber.*, 1914, 47, 1545—1550).—An extension of the earlier work (Schöttle, this vol., i, 408; A., 1912, i, 915; Petrenko-Kritschenko and Schöttle, A., 1911, i, 1020; 1912, i, 128) on the reaction of benzoyldehydracetic acid with organic bases at the ordinary temperature. In the case of the bases mentioned below the reaction follows the same course as with ammonia, methylamine, and aniline, giving lactam derivatives of the general formula



The method of procedure was to treat the acid with an excess of an alcoholic solution of the base and to allow the reaction to proceed at the ordinary temperature for several days. In the case of the aromatic bases the chemical change was accelerated by warming.

The *ethylamine* derivative was a crystalline solid, m. p. 172—173°; *propylamine* derivative, crystals, m. p. 147—147.5°; *isopropylamine* derivative, crystalline, m. p. 180°; *butylamine* derivative, crystalline, m. p. 114°; *sec.-butylamine* derivative, crystals, m. p. 167°; *isobutylamine* derivative, crystals, m. p. 146°; *n-amylamine* derivative, crystalline, m. p. 118°; *isoamylamine* derivative, crystalline, m. p. 125—126°; *benzylamine* derivative, crystalline, m. p. 172—173°; *ω-phenylethylamine* derivative, crystalline, m. p. 150—150.5°; *o-toluidine* derivative, golden crystals, m. p. 200—201°; *m-toluidine* derivative, asbestos-like needles, m. p. 212—214°; *p-toluidine* derivative, crystalline, m. p. 202—203°; *as-diphenylhydrazine* derivative, golden crystals, m. p. 160—161°, to a red liquid. *tert.*-Butylamine failed to react, whilst dimethylamine when heated with benzoyldehydracetic acid in a sealed tube gave a *substance* to which the structure



is ascribed.

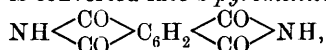
The *ethylamine* derivative when heated with hydrochloric acid gives 2:6-diphenylpyrone, thus behaving differently from both the lactam and its *N*-methyl derivative (A., 1911, i, 1020; A., 1912, i, 128). All the above derivatives resemble the lactam in being resolved by very dilute alcoholic potassium hydroxide or dilute aqueous alcoholic hydrochloric acid into the corresponding base and benzoyldehydracetic acid. The mutual displacement of the various bases from the ring as observed already (A., 1912, i, 128) is also possible with the bases detailed above.

D. F. T.

**Derivatives of Pyromellitic Acid and Isomeric Benzene-polycarboxylimides.** HANS MEYER and KARL STEINER (*Monatsh.*, 1914, **35**, 391—405).—By distilling ammonium mellitate, Wöhler (*Annalen*, 1841, **37**, 283) obtained (*a*) a white, flocculent and (*b*) a bluish-green sublimate, whilst the charred residue contained yellow needles (*c*), and on solution in ammonia gave a white substance (*d*); acidification of the ammoniacal solution yielded (*e*) a bluish-green, amorphous substance and colourless crystals (*f*). The author has repeated Wöhler's work, and finds that the substance (*c*) consists of *as*-pyromellitimide (I or II below), and forms the main product when the distillation is carried out under diminished pressure. The bluish-green sublimate (*b*) consists of a mixture of the imide and a blue substance, which is identical with (*e*), and is always produced when any nitrogen derivative of mellitic acid is heated to a high temperature. The sublimate (*a*) has m. p. 245°, and is possibly a semi-imide of pyromellitic acid. The substance (*d*) is not fusible, and is probably an amide, whilst the product (*f*) consists of pyromellitic acid.

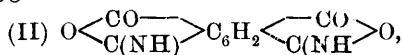
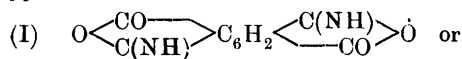
The remainder of the paper deals with the preparation and properties of isomeric pyromellitimides.

*Ammonium pyromellitate* crystallises with 3H<sub>2</sub>O in needles, and when heated at 200° is converted into *s*-pyromellitimide,



which forms colourless crystals, m. p. 440°, and is also produced by passing ammonia over pyromellitic anhydride at 200°. The imide forms with silver nitrate and potassium hydroxide in alcoholic solution amorphous *silver* and *potassium* salts. On treatment with concentrated aqueous ammonia it yields *pyromellitamide*, C<sub>6</sub>H<sub>2</sub>(CO·NH<sub>2</sub>)<sub>4</sub>, a white, crystalline powder, insoluble in organic solvents. When submitted to the Hofmann reaction, the imide is converted into a diaminobenzenedicarboxylic acid, which is probably diaminoterephthalic acid. On sublimation under diminished pressure at a temperature a little below 300°, it is transformed into a yellow modification, crystallising in needles or rhombs, and is possibly an *as*-pyromellitimide of the following constitution: O  $\begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{C(NH)} \diagup \end{array}$  C<sub>6</sub>H<sub>2</sub>  $\begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array}$  NH.

The yellow imide is reconverted into the original colourless modification by crystallisation from dilute acids. A second more stable *as*-pyromellitimide,



is obtained by heating ammonium mellitate or euchronate at about 300° under diminished pressure. It sublimes in small, yellow needles, and yields solutions in organic solvents having a green fluorescence. It differs from the colourless imide in its greater stability towards alkalis, and in not being converted into pyromellitamide by the action of ammonia.

*s*-Dimethylpyromellitimide,  $C_6H_2(\langle \text{CO} \rangle \text{NMe})_2$ , prepared by evaporating pyromellitic acid with aqueous methylamine and heating the resulting crystalline *methylammonium* salt at  $250^\circ$  under diminished pressure, sublimes in colourless needles, m. p.  $370^\circ$ .

A stable, yellow *as*-dimethylpyromellitimide is obtained by heating trimethylparamide and crystallising the sublimate from chlorobenzene, from which it separates in needles, and has about the same m. p. as the preceding *s*-imide.

The products formed by methylating both *s*- and *as*-pyromellitimide by means of diazomethane in ethereal solution appear to be identical with the yellow *as*-dimethylpyromellitimide.

Diphenylpyromellitimide (*pyromellitanil*),  $C_6H_2(\langle \text{CO} \rangle \text{NPh})_2$ , prepared by boiling a solution of pyromellitic anhydride in aniline, crystallises in colourless needles, and is hydrolysed by aqueous barium hydroxide to *pyromellitanilic acid*. The latter compound forms a colourless, crystalline powder, and is also produced by heating pyromellitic anhydride with aniline in toluene solution. When heated with acetyl chloride it is converted into a yellow *isopyromellitanil*.

F. B.

**Syntheses by means of Sodamide. Derivatives of 1-Methyl-3-cyclopentanone.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1914, 158, 1616—1623).—Unlike 1-methyl-2-cyclopentanone (compare this vol., i, 291), 1-methyl-3-cyclopentanone does not readily undergo direct alkylation under the influence of sodamide. It does undergo methylation, but the yield is poor, and drops rapidly on successively introducing methyl groups. Allylation is still more difficult and the yields are worse. 1:3-Dimethyl-4-cyclopentanone, on the other hand, readily undergoes both methylation and allylation. It is readily prepared from ethyl  $\beta$ -methyladipate which under the influence of sodium or sodamide yields ethyl 1-methyl-4-cyclopentanone-3-carboxylate (compare Dieckmann, A., 1894, i, 173, 324). This product is readily methylated by Bouveault's method (compare A., 1900, i, 171) and the resulting ester on boiling with concentrated hydrochloric acid yields 1:3-dimethyl-4-cyclopentanone, a colourless, mobile liquid, b. p.  $48^\circ/14$  mm. (corr.),  $152.5^\circ/770$  mm. (corr.),  $D_4^{19}$  0.8914,  $n_D^{19}$  1.4308,  $[\alpha]_D^{19} + 126^\circ 43'$ . This ketone readily undergoes successive methylation in dry ether in the presence of sodamide, yielding successively: 1:2:4-trimethyl-3-cyclopentanone, a colourless, mobile liquid, b. p.  $158$ — $159^\circ/770$  mm. (corr.),  $D_4^{19}$  0.8778,  $n_D^{19}$  1.4316,  $[\alpha]_D^{19} + 103^\circ 41'$ , 1:2:4:4-tetramethyl-3-cyclopentanone, a colourless, mobile liquid, having a strong odour of camphor, b. p.  $165$ — $166^\circ/765$  mm. (corr.),  $D_4^{19}$  0.8668,  $n_D^{19}$  1.4321,  $[\alpha]_D^{19} + 70^\circ 8'$ , and 1:2:2:4:4-pentamethyl-3-cyclopentanone, a colourless, mobile liquid, with a pronounced odour of camphor, b. p.  $170$ — $171^\circ/770$  mm. (corr.),  $D_4^{20}$  0.8619,  $n_D^{20}$  1.4335,  $[\alpha]_D^{20} + 32^\circ 53'$ .

Comparing the physical constants of these homologues, it is of interest to note that the boiling point increases on ascending the series, as does the refractive index, if 1-methyl-3-cyclopentanone is

omitted. The density and specific rotatory power, on the other hand, diminish with increase in the number of the methyl groups.

1:2:2:4:4-Pentamethyl-3-cyclopentanone is decomposed by soda-mide in boiling toluene, yielding a *tetramethylhexoamide*, b. p. 152—153°/14 mm. (corr.),  $[\alpha]_D^{20} + 46.6'$ , in which the four methyl groups occupy the positions  $\alpha\alpha\gamma\delta$ ,  $\alpha\alpha\beta\delta$ . The amide is decomposed by sulphuric acid and sodium nitrite, giving *tetramethylhexoic acid*, b. p. 138—141°/19 mm.,  $[\alpha]_D^{17} + 45.54'$ .

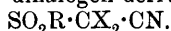
1:3-Dimethyl-4-cyclopentanone readily undergoes successive allylation under conditions similar to those for methylation, yielding:

1:3-Dimethyl-5-allyl-4-cyclopentanone, a colourless, mobile liquid, with an odour of menthone, b. p. 84—85°/14 mm. (corr.),  $D_4^{20}$  0.8968,  $n_D^{20}$  1.4550,  $[\alpha]_D^{20} + 71.44'$ ; 1:3-dimethyl-3:5(or 5:5)-diallyl-4-cyclopentanone, a colourless, mobile liquid, b. p. 116—119°/15 mm. (corr.),  $D_4^{20}$  0.8994,  $n_D^{20}$  1.4676,  $[\alpha]_D^{20} + 74.07'$ ; and 1:3-dimethyl-3:5:5-triallyl-4-cyclopentanone, a colourless, slightly viscous liquid, b. p. 140—141°/15 mm.,  $D_4^{20}$  0.9179,  $n_D^{20}$  1.4841,  $[\alpha]_D^{20} + 73.11'$ .

In this series the boiling point rises with increase in the number of allyl groups, but not regularly, as do the density and refractive index, whilst the specific rotatory power remains practically constant after the introduction of the first allyl group.

W. G.

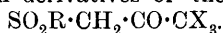
**Influence of Electronegative Complexes on the Halogenation of Certain Methylene Derivatives.** J. TROEGER and W. MÜLLER (*Arch. Pharm.*, 1914, 252, 32—55. Compare A., 1913, i, 630).—Attempts have been made to prepare monohalogen derivatives of arylsulphonylacetonitriles,  $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{CN}$ , by the action of the theoretical amount of halogen on the unsubstituted nitriles. These attempts, however, were unsuccessful, the direct action of halogens leading to the formation of dihalogen derivatives of the type



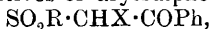
Thus benzenesulphonylacetonitrile reacts with bromine in molecular proportions yielding *aa*-dibromobenzenesulphonylacetonitrile, part of the original nitrile being recovered unchanged.

Reduction of the dihalogen derivatives by means of sodium benzenesulphinate in alcoholic solution (compare A., 1913, i, 169) also failed to yield the monohalogen compounds, the dihalogen derivatives being completely reduced to the unsubstituted arylsulphonylacetonitriles.

Arylsulphonylacetones,  $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{COMe}$ , readily react with halogens, yielding trihalogen derivatives of the type



The introduction of halogen proceeds so readily that all attempts to prepare mono- and di-halogen derivatives proved fruitless. On the other hand, monohalogen derivatives of arylsulphonylacetophenones,



can be readily obtained both by the direct action of halogens on the unsubstituted ketones, and also by reducing the dihalogen derivatives,  $\text{SO}_2\text{R}\cdot\text{CX}_2\cdot\text{COPh}$ , with sodium benzenesulphinate.

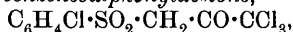
The *p*-cyanobenzylarylsulphones ( $\omega$ -arylsulphonyl-*p*-toluonitriles),  $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ , differ from the arylsulphonyl derivatives of acetonitrile, acetone, and acetophenone in that neither the mono- nor

the dihalogen derivatives can be obtained by the direct action of halogen on the unsubstituted sulphonyl compound. A monohalogen derivative has, however, been prepared indirectly by the interaction of *p*-cyanobenzylidene dichloride and sodium benzenesulphinate in hot alcoholic solution.

The *ω*-chloro-*ω*-benzenesulphonyl-*p*-toluonitrile  $\text{SO}_2\text{Ph}\cdot\text{CHCl}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ , thus formed crystallises in lustrous leaflets, m. p.  $162\cdot5$ — $163\cdot5^\circ$ .

*p*-Chlorobenzenesulphonylacetone,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COMe}$ , prepared by heating chloroacetone with sodium benzenesulphinate in alcoholic solution, crystallises in lustrous, pale yellow plates, m. p.  $82\cdot5$ — $83^\circ$ ; the *oxime* forms stout, white needles, m. p.  $163$ — $164^\circ$ ; the *semi-carbazone*, rhombic crystals, m. p.  $205\cdot5^\circ$ . On treatment with bromine (3 mols.) in acetic acid solution, it yields *aaa*-tribromo- $\gamma$ -*p*-chlorobenzene-sulphonylacetone,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CBr}_3$ , which crystallises in stout, white needles, m. p.  $125\cdot5^\circ$ . Attempts to prepare the mono- and di-bromo-derivatives resulted in the formation of the tribromo-compound, part of the original ketone being recovered unchanged.

*aaa*-*p*-Tetrachloro-*p*-benzenesulphonylacetone,



prepared by the addition of bleaching powder to a glacial acetic acid solution of *p*-chlorobenzenesulphonylacetone, forms white needles, m. p.  $119\cdot5^\circ$ .

*aaa*-Trichloro- $\gamma$ -benzenesulphonylacetone,  $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CCl}_3$ , is obtained in an impure condition from benzenesulphonylacetone in a similar manner.

$\omega$ -Dichloro- $\omega$ -benzenesulphonylacetophenone,  $\text{SO}_2\text{Ph}\cdot\text{CCl}_2\cdot\text{COPh}$ , forms stout, white crystals, m. p.  $104^\circ$ , and when heated with sodium benzenesulphinate (1 mol.) in alcoholic solution is converted into *ω*-chloro-*ω*-benzenesulphonylacetophenone,  $\text{SO}_2\text{Ph}\cdot\text{CHCl}\cdot\text{COPh}$ , which crystallises in felted, slender, white needles, m. p.  $126^\circ$ , and is reduced by the further action of sodium benzenesulphinate to *ω*-benzenesulphonylacetophenone.

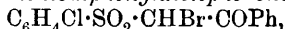
The last-named compound reacts with bromine (1 mol.) in glacial acetic acid solution, yielding *ω*-bromo-*ω*-benzenesulphonylacetophenone,  $\text{SO}_2\text{Ph}\cdot\text{CHBr}\cdot\text{COPh}$ , which has m. p.  $138^\circ$  and is reduced by sodium benzenesulphinate to the original ketone; with an excess of bromine, it yields *ωω*-dibromo-*ω*-benzenesulphonylacetophenone, stout, white needles, m. p.  $119\cdot5$ — $120^\circ$ . Attempts to prepare the monobromo-derivative from the dibromo-compound by reduction with sodium benzenesulphinate resulted in the formation of the unsubstituted ketone. On treatment with bleaching powder, *p*-toluenesulphonylacetophenone in glacial acetic acid solution gives rise to *ω*-chloro-*ω*-*p*-toluenesulphonylacetophenone,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CHCl}\cdot\text{COPh}$ , slender, white needles, m. p.  $139^\circ$ .

*ω*-Bromo-*ω*-*p*-toluenesulphonylacetophenone has m. p.  $158^\circ$ ; *ω*-*p*-dichloro-*ω*-benzenesulphonylacetophenone,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{CHCl}\cdot\text{COPh}$ , m. p.  $145\cdot5$ — $146\cdot5^\circ$ .

*ωω*-*p*-Trichloro-*ω*-benzenesulphonylacetophenone,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{CCl}_2\cdot\text{COPh}$ , prepared by the gradual addition of bleaching powder to *ω*-*p*-chlorobenzenesulphonylacetophenone in acetic acid solution, forms pale yellow crystals, m. p.  $98$ — $99^\circ$ , and differs from all the analogously

constituted mono- and di-halogen compounds in that it is not reduced by sodium benzenesulphinate in alcoholic solution to the original ketone, but is converted into *p*-chlorophenyldichloromethylsulphone,  $C_6H_4Cl \cdot SO_2 \cdot CHCl_2$ , which has m. p.  $121.5^\circ$ , and is also obtained, instead of  $\omega\omega$ -*p*-trichloro- $\omega$ -benzenesulphonylacetophenone, when the chlorination of  $\omega$ -*p*-chlorobenzenesulphonylacetophenone is carried out too rapidly or if an excess of bleaching powder is employed.

$\omega$ -Bromo- $\omega$ -*p*-chlorobenzenesulphonylacetophenone,



has m. p.  $163-164^\circ$ ;  $\omega\omega$ -dibromo- $\omega$ -*p*-chlorobenzenesulphonylacetophenone, m. p.  $121-121.5^\circ$ . F. B.

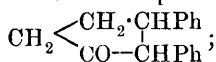
**The Two Stereoisomeric Forms of Benzoylphenylacetylene Dibromide.** CHARLES DUFRAISSE (*Compt. rend.*, 1914, 158, 1691—1694).—The author has isolated the two stereoisomeric forms of *benzoylphenylacetylene dibromide* from the products of the action of bromine on the acetylene in chloroform solution. The product on crystallisation from light petroleum by very slow evaporation yields two sets of large crystals, of which one (*A*) has m. p.  $113-114^\circ$ , and the other (*B*) has m. p.  $79-80^\circ$ . In general, (*B*) forms about 5% of the mixture. The two forms undergo reciprocal transformation: *A* into *B* on heating to  $250^\circ$ , and *B* into *A* on warming with a trace of iodine. In sunlight each of the two isomerides is converted into a mixture rich in *A*. Judging from its properties and the fact that it forms by far the greater proportion of the product, the author considers that *A* is the *cis*-isomeride and *B* the *trans*-isomeride. *A* crystallises in white regular, hexagonal prisms, and *B* in hexagonal pyramids or dodecahedra, which are pale yellow whether obtained from the original preparation or from the transformation of *A*. Under the influence of alcoholic potassium hydroxide both isomerides yield benzoic acid, hydrogen bromide, and phenylacetylene. In the case of *A*, an intermediate product, m. p.  $-11^\circ$  to  $-10^\circ$ , isomerising rapidly in sunlight, has been isolated, and is apparently one of the two isomeric forms of phenylacetylene dibromide. W. G.

**Conversion of Distyryl Ketone into Derivatives of Diphenylcyclopentane.** H. J. VON LIEBIG (*Annalen*, 1914, 405, 188—211).—The behaviour towards oxidising and reducing agents of the keto-enol,  $C_{17}H_{14}O_2$ , obtained by the action of acetic anhydride and sulphuric acid on distyryl ketone, indicates that the substance is a derivative of diphenylcyclopentane (Vorländer and Schrödter, A., 1903, i, 496; Vorländer and von Liebig, A., 1905, i, 426). The  $C_5$ -ring must be present in the keto-enol itself, not produced during the oxidation or reduction of the substance, because distyryl ketone does not yield benzil or desylacetic acid by oxidation with potassium permanganate and does not yield 1:2-diphenylcyclopentane by reduction with hydriodic acid and phosphorus.

The whole behaviour of the keto-enol is in accord with its formulation as 1:2-diphenylcyclopentane-3:4-dione (1:2-diphenyl- $\Delta^2$ -cyclopenten-3-ol-4-one), except that it does not react with *o*-diamines. It

reacts with benzoyl chloride and an excess of 8% potassium hydroxide in the cold to form a *benzoyl* derivative,  $C_{24}H_{18}O_3$ , m. p.  $124^\circ$ , large, colourless prisms, and with benzoyl chloride alone at  $100^\circ$  to form an isomeric *benzoyl* derivative, m. p.  $173^\circ$ , colourless needles; these derivatives do not develop a coloration with ferric chloride, and are converted into benzoic acid and diphenylcyclopentanedione by hydrolysis. The various methods of acetylation all yield Vorländer and Schrödter's acetyl derivative, m. p.  $143-144^\circ$ . The diphenylcyclopentenolone forms an *anilide*, m. p.  $133^\circ$ , and benzylidene derivative (compare Gray, T., 1909, **95**, 2144); the latter is soluble in alkali hydroxides or carbonates, develops a brownish-black coloration with alcoholic ferric chloride and forms an acetyl derivative, m. p.  $149^\circ$  (compare Gray, *loc. cit.*, p. 2146), almost colourless plates, which does not exhibit these two properties.

[With G. METGE].—The potassium hydrogen sulphite compound of the acetylated diphenylcyclopentenolone is reduced to 1:2-diphenylcyclopentane by boiling hydriodic acid and amorphous phosphorus, but is converted by 3% sodium amalgam and water in an atmosphere of carbon dioxide into a *ketone*,  $C_{17}H_{16}O$ , m. p.  $175^\circ$ , colourless crystals, which is also produced by the action of the same reducing agent on diphenylcyclopentenolone and therefore probably has the formula



the ketone is reduced to 1:2-diphenylcyclopentane by hydriodic acid and phosphorus. C. S.

**2-Benzoylcyclopentanone and 2-Benzoylcyclohexanone.** ÉDOUARD BAUER (*Ann. Chim.*, 1914, [ix], 1, 393—437).— $\delta$ -Benzoylvaleric and  $\epsilon$ -benzoylhexoic acids are obtained as secondary products in the preparation of  $\alpha\delta$ -dibenzoylbutane and  $\alpha\epsilon$ -dibenzoylpentane by the action of adipyl and pimelyl chlorides on benzene in the presence of aluminium chloride. The conversion of these acids into cyclic compounds has been studied (compare Blaise and Kœhler, A., 1909, i, 287, 478; 1910, i, 561, 626).

$\delta$ -Benzoylvaleric acid,  $CH_2Bz \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , forms thin leaflets, m. p.  $78^\circ$ , and yields a *semicarbazone*,  $C_{13}H_{17}O_3N_3$ , m. p.  $183^\circ$ , a *methyl* ester, m. p.  $36.5^\circ$ , b. p.  $189^\circ/15$  mm., an *ethyl* ester, m. p.  $30-30.5^\circ$ , b. p.  $189^\circ/11$  mm., and an *isoamyl* ester, b. p.  $213-214^\circ/12$  mm.

**2-Benzoylcyclopentanone**,  $CHBz \begin{array}{l} \swarrow CO - CH_2 \\ \searrow CH_2 \cdot CH_2 \end{array}$ , prepared by the action of sodamide on  $\delta$ -benzoylvaleric esters, forms yellow leaflets, m. p.  $41-42^\circ$ , b. p.  $172-173^\circ/12$  mm., and has the following refractive indices: in toluene solution at  $25.2^\circ$ ,  $n_a$  0.3023,  $n_D$  0.3079,  $n_B$  0.3209; in alcoholic solution at  $25.2^\circ$ ,  $n_a$  0.3089,  $n_D$  0.3140,  $n_B$  0.3290. Thus, alcohol exerts a considerable, and toluene a somewhat less, exalting effect. The formation by 2-benzoylcyclopentanone of a blood-red ferric salt and a greyish-green *copper* salt,  $(C_{12}H_{11}O_2)_2Cu$ , and the magnitudes of the refractive indices indicate that it has the enolic

structure  $\begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{OH}) \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array} \gg \text{CBz}$ . The closed ring is readily opened by the action of alkali, even in the cold,  $\delta$ -benzoylvaleric acid being obtained. The diketone does not react with phenylcarbimide, but readily forms a *disemicarbazone*,  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_6$ , m. p.  $235^\circ$  (decomp.), in a mercury bath heated at that temperature.

$\epsilon$ -Benzoylhexoic acid forms nacreous leaflets, m. p.  $85^\circ$  (Kipping and Perkin, T., 1889, 55, 350, give m. p.  $81$ – $82^\circ$ ), and yields a *semicarbazone*,  $\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}_3$ , m. p.  $180$ – $181^\circ$ ; a *methyl* ester, m. p.  $24^\circ$ , b. p.  $202$ – $204^\circ/17$  mm., which gives a *semicarbazone*,  $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}_3$ , m. p.  $96^\circ$ ; and an *ethyl* ester, b. p.  $199$ – $200^\circ/13$  mm., which forms a *semicarbazone*,  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}_3$ , m. p.  $125^\circ$ . The action of sodamide on  $\epsilon$ -benzoylhexoic esters does not give satisfactory yields of 2-benzoylcyclohexanone, which can, however, be obtained by the action of benzoyl chloride on the sodium derivative of cyclohexanone.

2-Benzoylcyclohexanone,  $\text{CHBz} \llcorner \begin{array}{c} \text{CO} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \gg \text{CH}_2$ , forms needles, m. p.  $92$ – $93^\circ$ , and has the following refractive indices: in alcohol at  $24.8^\circ$ ,  $n_a$  0.2918,  $n_D$  0.2953,  $n_B$  0.3031; in toluene at  $25^\circ$ ,  $n_a$  0.28693–0.2871,  $n_D$  0.2891–0.2892,  $n_B$  0.2934–0.2937. It forms a greyish-green copper salt,  $(\text{C}_{13}\text{H}_{13}\text{O}_2)_2\text{Cu}$ , and by the action of cold sodium hydroxide solution is converted through the intracyclic enolic form,  $\text{CH}_2 \llcorner \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{OH}) \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array} \gg \text{CBz}$ , into  $\epsilon$ -benzoylhexoic acid.

Dibenzoylcyclohexanone,  $\text{OBz} \cdot \text{C} \llcorner \begin{array}{c} \text{CBz} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \gg \text{CH}_2$ , also formed by the action of benzoyl chloride on the sodium derivative of cyclohexanone, forms large, colourless prisms, m. p.  $46^\circ$ , b. p.  $240$ – $242^\circ/16$  mm. By alcoholic potassium hydroxide it is converted into  $\epsilon$ -benzoylhexoic and benzoic acids, by sodium ethoxide into ethyl benzoate, ethyl  $\epsilon$ -benzoylhexoate and 2-benzoylcyclohexanone, and by alcohol and dry hydrogen chloride into 2-benzoylcyclohexanone and ethyl benzoate.

From 2-benzoylcyclohexanone are obtained: (1) 1-acetoxy-2-benzoyl- $\Delta^1$ -cyclohexene,  $\text{CH}_2 \llcorner \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{OAc}) \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array} \gg \text{CBz}$ , b. p.  $197$ – $200^\circ/20$  mm.; (2) the *oxime*,  $\text{CH}_2 \llcorner \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \gg \text{CH} \cdot \text{CPh} \cdot \text{NOH}$ , m. p.  $115^\circ$ , which yields an internal *anhydride*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CPh} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} - \text{O} \end{array} \gg \text{N}$ , m. p.  $67^\circ$ ; (3) the *phenylhydrazone*,  $\text{CH}_2 \llcorner \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \gg \text{CH} \cdot \text{CPh} \cdot \text{N} \cdot \text{NHPh}$ , melting at  $140^\circ$  with a loss of water and formation of the internal *anhydride*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CPh} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NPh} \end{array} \gg \text{N}$ , m. p.  $111.5^\circ$ ; (4) the internal *anhydride* of the *hydrazone*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CPh} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH} \end{array} \gg \text{N}$  (?), m. p.  $133^\circ$ , which forms a yellow *picrate*,  $\text{C}_{19}\text{H}_{17}\text{O}_7\text{N}_5$ , m. p.  $180$ – $181^\circ$ ; a *hydrochloride*,  $\text{C}_{13}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$ , m. p.  $205$ – $220^\circ$  (decomp.), which is insoluble in water or cold dilute hydrochloric acid, and is converted by boiling with water into a soluble modification, the latter undergoing gradual change into the



insoluble form; a *platinichloride*,  $(C_{13}H_{14}N_2)_4 \cdot H_2PtCl_6$ ; a *phenyl-carbamyl* derivative,  $\begin{array}{c} CH_2 \cdot CH_2 \cdot C \\ | \\ CH_2 \cdot CH_2 \cdot C \cdot N(CO \cdot NHPh) \end{array} \begin{array}{c} \text{---} \\ \text{---} \end{array} \begin{array}{c} CPh \\ \text{---} \\ N \end{array}$ , m. p. 115—116°, and an *acetyl* derivative,  $\begin{array}{c} CH_2 \cdot CH_2 \cdot C \\ | \\ CH_2 \cdot CH_2 \cdot C \cdot NAc \end{array} \begin{array}{c} \text{---} \\ \text{---} \end{array} \begin{array}{c} CPh \\ \text{---} \\ N \end{array}$ , m. p. 68·5°. In its reactions with organo-magnesium compounds, this compound (4) acts as a pyrazole, corresponding with the above structure, and not as an isopyrazole derivative; with magnesium ethyl bromide it gives ethane, and by subsequent treatment of the residual product with water, the original base.

In alcoholic solution, the action of semicarbazide yields the *semicarbazone*,  $CH_2 \begin{array}{c} \text{---} CH_2 \cdot CH_2 \\ \text{---} CH_2 \cdot CO \end{array} \text{---} CH \cdot CPh \cdot N \cdot NH \cdot CO \cdot NH_2$ , m. p. 225°, which was not obtained quite pure owing to its partial conversion into the corresponding internal *anhydride*,  $C_{14}H_{15}ON_3$ , m. p. 164°. In acetic acid solution, the action gives the pyrazole derivative, m. p. 133° (see above) and hydrazodicarbonamide, which are apparently formed by decomposition of an unstable disemicarbazone.

The action of organo-magnesium derivatives on 2-benzoylcyclohexanone yields the whole of the latter in its enolic form, together with the hydrocarbon corresponding with the halogen derivative employed. T. H. P.

**Action of Sodamide on Some  $\alpha\epsilon$ -Diketones.** ÉDOUARD BAUER (*Compt. rend.*, 1914, 158, 1680—1683. Compare A., 1913, i, 724).—The two  $\alpha\epsilon$ -diketones studied were  $\alpha\gamma$ -dibenzoylpropane and  $\alpha\gamma$ -dibenzoyl- $\beta$ -phenylpropane.

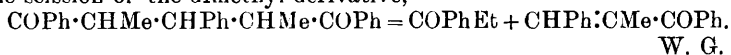
On addition of sodamide (2 mols.) to a solution of  $\alpha\gamma$ -dibenzoylpropane in ether, benzene or toluene, ammonia is evolved and a brick-red precipitate is formed, which on treatment with water regenerates the original diketone. The brick-red precipitate is therefore the disodium derivative. On adding methyl iodide to this precipitate suspended in toluene, a violent reaction occurs, sodium iodide is precipitated, and the product of the reaction on treatment with ice yields an oil, which on distillation gives three fractions: (1) b. p. 225°/12 mm., (2) b. p. 232—235°/12 mm., (3) b. p. above 300°. Fraction (2) by analysis is shown to be  $\beta\delta$ -dibenzoylpentane,



an oil, which neither crystallises nor forms a semicarbazone, b. p. 230—233°/12 mm. Fraction (3) is resinous, and forms the major portion of the product.

$\alpha\gamma$ -Dibenzoyl- $\beta$ -phenylpropane behaves similarly towards sodamide, giving a disodium derivative, which reacts with methyl iodide. After decomposition with ice, small, white needles are deposited from the toluene solution. These are insoluble in toluene, alcohol, acetone and ether, and are not acted on by hot or cold sulphuric acid or sodium hydroxide, and do not combine with bromine. They have m. p. 331°, and are probably a polymeride of the original diketone, since analysis gives the formula  $C_{23}H_{20}O_2$ . After filtration and evaporation of the toluene an oil is left, which on fractionation yields (1) phenyl ethyl ketone, b. p.

75°/3 mm., (2) a little benzoic acid, (3) a viscid oil, b. p. 165—170°/3 mm., which is phenyl  $\alpha$ -methylstyryl ketone,  $\text{CHPh}:\text{CMe}\cdot\text{COPh}$ , (4) an oily residue, soluble in ether, yielding two sets of crystals, one, m. p. 137°, consisting of a *compound*,  $\text{C}_{23}\text{H}_{18}\text{O}$ , probably a dehydrated form of the original diketone, and the other, m. p. 160°, which is the *dimethyl* derivative of the original diketone. The principal products are phenyl ethyl ketone and phenyl  $\alpha$ -methylstyryl ketone arising from the scission of the dimethyl derivative,



W. G.

***p*-Benzoquinone and Sodium Sulphite.** JOH. PINNOW (*J. pr. Chem.*, 1914, [ii], 89, 536—546).—The interaction of *p*-benzoquinone and sodium sulphite in aqueous solution yields as main product sodium quinolmonosulphonate, small amounts of quinol and hydroxyquinol being also formed in the reaction. The formation of the latter compounds is due to the simultaneous oxidation and reduction of the quinone under the influence of the alkali produced by the hydrolysis of the sulphite. Both the formation of the *p*-benzoquinonemonosulphonate and also the production of *p*-benzoquinone and hydroxyquinol proceed with great rapidity, and are independent of the colour changes which the solution undergoes.

The sodium quinolmonosulphonate further reacts with sodium sulphite to form sodium quinoldisulphonate, and with *p*-benzoquinone to form sodium *p*-benzoquinonesulphonate and quinol. The extent of the latter reactions, however, is diminished if the hydrolysis of the sodium sulphite is suppressed by the addition of acetic acid or by increasing the concentration of the sulphite.

Only a small amount of sulphuric acid is formed in the interaction of *p*-benzoquinone and sodium sulphite, the amount being insufficient to exert any influence on the main reaction.

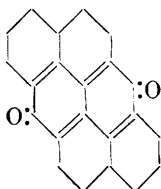
F. B.

**Characteristic Behaviour of 1-Chloro-4-methylantraquinone Towards Concentrated Nitric Acid.** II. O. FISCHER and A. SCHWECKENDIEK, (*Ber.*, 1914, 47, 1576—1578).—In an earlier paper (Fischer and Rebsamen, this vol., i, 419) it has been shown that 3-nitro-1:2-dihydroxy-4-methylantraquinone and 3-nitro-1-hydroxy-4-methylantraquinone can be obtained by treating 1-chloro-4-methylantraquinone with concentrated nitric acid. It is now shown that by leaving 1-hydroxy-4-methylantraquinone dissolved in nitric acid (D 1.52) for twenty-four hours this substance is converted into 3-nitro-1:2-dihydroxy-4-methylantraquinone, whilst 1-methoxy-4-methylantraquinone is converted by similar acid into 3-nitro-1-hydroxy-4-methylantraquinone, which, by warming with concentrated nitric acid, is further changed into 3-nitro-1:2-dihydroxy-4-methylantraquinone.

D. F. T.

**Anthanthrone.** I. LUDWIG KALB (*Ber.*, 1914, 47, 1724—1730).—Anthanthrone is the name given by the author to the quinone of

the given structure (annexed formula), which is obtainable by intramolecular condensation of 1:1'-dinaphthyl-8:8'-dicarboxylic acid and of 1:1'-dinaphthyl-2:2'-dicarboxylic acid.



[With ARNULF LECHNER and JULIUS RENNING.]—8-Chloro-1-naphthylamine was converted by the diazo-reaction into 8-chloro-1-naphthonitrile. For the hydrolysis of the resistant 8-chloro-1-naphthonitrile it was found most convenient to effect a conversion into the corresponding amide (needles, m. p. 203.5°) by heating with a mixture of sulphuric acid, acetic acid, and water, and then to treat with nitrous acid, when the desired 8-chloro-1-naphthoic acid was obtained. This was converted into the corresponding ester by successive treatment with phosphorus pentachloride and an alcoholic solution of sodium ethoxide. When heated with copper bronze and a trace of iodine for three-quarters of an hour at 290° the ester loses its halogen with formation of *ethyl 1:1'-dinaphthyl-8:8'-dicarboxylate*,  $\text{CO}_2\text{Et} \cdot \text{C}_{10}\text{H}_6 \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO}_2\text{Et}$ , pale yellow tablets, m. p. 183°, which on heating with sulphuric acid passes into *anthanthrone*, orange-yellow needles, m. p. above 300°. In this final condensation reaction the colour passes through a brownish-red before reaching a permanent green, and the intermediate colour is ascribed to the presence of a product in which only one of the new rings has formed.

1-Chloro-2-naphthoic acid was prepared by treating 1-hydroxy-2-naphthoic acid successively with phosphorus pentachloride and water, and could be made to yield *ethyl 1:1'-dinaphthyl-2:2'-dicarboxylate* by heating its ethyl ester with copper powder. The last-named acid can be obtained more conveniently from 2:2'-diamino-1:1'-dinaphthyl, which can be converted through the corresponding bisdiazo-compound into 1:1'-dinaphtho-2:2'-dinitrile; this is hydrolysable by alcoholic potassium hydroxide at 175° with the formation of 1:1'-dinaphthyl-2:2'-dicarboxylic acid, m. p. 266°, which can be condensed to anthanthrone by conversion into the corresponding acid chloride and warming with aluminium chloride.

The constitution of anthanthrone is determined by its formation from the above two acids. Anthanthrone is surprisingly stable towards alkalis and oxidising agents; it is reducible by stannous chloride to the corresponding hydro-compound, it can be readily nitrated, although it resists sulphonation, and it gives an orange-coloured vat which dyes cotton orange-yellow. D. F. T.

**Pinacolin Transformations. III. Mechanism of the Reaction whereby Borneol is Converted into Camphene.** HANS MEERWEIN (*Annalen*, 1914, 405, 129—175. Compare A., 1910, i, 856; 1913, i, 485).—The transformation of borneol into camphene (Wagner's formula) is in some respects parallel to the conversion of  $\beta\beta$ -dimethylbutan- $\gamma$ -ol into  $\beta\gamma$ -dimethyl- $\Delta^2$ -butene, but is of course much more complicated since a profound change of the cyclic structure occurs. Borneol may be regarded as a  $\text{C}_5$ -cyclic pinacolin alcohol containing an extracyclic hydroxyl group, or as a  $\text{C}_6$ -cyclic pinacolin

alcohol containing an intracyclic hydroxyl group. To secure an insight into the mechanism of its conversion into camphene, therefore, it is necessary to examine monocyclic pinacolin alcohols containing an intra- or extra-cyclic hydroxyl group, and to ascertain whether or not the elimination of water is accompanied by a change in the ring structure. The two monocyclic pinacolin alcohols which most nearly resemble borneol in structure are 1:1-dimethylcyclohexan-2-ol and 1-methyl-1- $\alpha$ -hydroxyethylcyclopentane; the latter, however, is very difficult to prepare, so 1-methyl-1- $\alpha$ -hydroxyethyl-3-isopropylcyclopentane, which is easily obtained in quantity, has been examined instead. The results obtained by the elimination of water from each of these two pinacolin alcohols show that the ring changes which also occur are quite analogous to those obtaining during the conversion of borneol into camphene.

[With H. PROBST.]—1:1-Dimethylcyclohexan-2-one (A., 1910, i, 856), which has been purified through its semicarbazone in order to free it from 1-acetyl-1-methylcyclopentane (see below), has b. p. 172.4—172.5° or 59.4°/14 mm.,  $D_4^{20}$  0.9134,  $n_D^{20}$  1.44864, and yields a semicarbazone, m. p. 200—201°. An ethereal solution of the ketone is reduced by sodium and saturated aqueous potassium carbonate almost quantitatively to 1:1-dimethylcyclohexan-2-ol, b. p. 72.2°/13 mm., freezing point 8°, which has an intense odour of peppermint and forms a *phenylcarbamate*, m. p. 84—85°, flattened needles; a by-product of the reduction is the *pinacone*,  $C_{16}H_{30}O_2$ , m. p. 85°, large plates.

The elimination of water from 1:1-dimethylcyclohexan-2-ol is effected by potassium hydrogen sulphate or oxalic acid, or, best, by zinc chloride at about 190°, whereby a mixture, b. p. 131.5—137.5°,  $D_4^{20}$  0.8162,  $n_D^{20}$  1.45534, of two hydrocarbons is obtained. By bromination in cold chloroform the mixture yields 1:2-dibromo-1:2-dimethylcyclohexane,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CMeBr} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CMeBr} \end{array}$ , m. p. about 150°, colourless needles, which is identical with the dibromide obtained from 1:2-dimethyl- $\Delta^1$ -cyclohexene. By heating with quinoline at 190°, the dibromoderivative is converted into 1:2-dimethyl- $\Delta^{2:5}$ -cyclohexadiene, b. p. 134—137°,  $D_4^{20}$  0.8373,  $n_D^{20}$  1.46928 (compare Haworth, T., 1913, 103, 1242), which is readily oxidised to *o*-toluic acid by dilute nitric acid at 140—150°.

The second constituent of the hydrocarbon mixture is isolated in the form of the sparingly soluble *nitrosochloride*, m. p. 88°, colourless needles with a blue shimmer (*nitrolpiperidide*,  $C_{13}H_{24}ON_2$ , m. p. 93.5°, slender needles), which is transformed by warm acetic acid and sodium acetate into an oxime, the hydrolysis of which by dilute sulphuric acid yields an unsaturated *ketone*,  $C_8H_{12}O$  (*semicarbazone*, m. p. 203—204°). Behaviour identical in all respects with the preceding is exhibited by the nitrosochloride of isopropyl- $\Delta^1$ -cyclopentene (prepared by the elimination of water from the cyclopentanol obtained from cyclopentanone and magnesium isopropyl iodide).

The mixture of hydrocarbons obtained by the elimination of water from 1:1-dimethylcyclohexan-2-ol consists, therefore, of about 75% of 1:2-dimethyl- $\Delta^1$ -cyclohexene and about 25% of isopropyl- $\Delta^1$ -cyclo-

pentene. This statement is confirmed by the results obtained by oxidising the hydrocarbon mixture with ozone in glacial acetic acid; the products are  $\beta\eta$ -diketo-octane and  $\gamma$ -isobutyrylbutyric acid (*semicarbazone*, decomp.  $185.5^\circ$ ) formed from 1:2-dimethyl- $\Delta^1$ -cyclohexene and isopropyl- $\Delta^1$ -cyclopentene respectively.

[With W. MÜHLENDYK.]—Fencholyl chloride (Wallach, A., 1911, i, 310) and zinc methyl react in ether in an atmosphere of carbon dioxide to form, after the usual decomposition of the initial product with water and dilute sulphuric acid, 1-acetyl-1-methyl-3-isopropylcyclopentane, b. p.  $103\text{--}104^\circ/18$  mm. (*semicarbazone*, m. p.  $130^\circ$ , large prisms), in 88% yield. An ethereal solution of the ketone is reduced by sodium and aqueous potassium carbonate to 1-methyl-1- $\alpha$ -hydroxyethyl-3-isopropylcyclopentane, b. p.  $108^\circ/16$  mm., the *pinaccone*,  $C_{22}H_{42}O_2$ , m. p.  $85\text{--}86^\circ$ , prismatic needles, being obtained as a by-product.

By the elimination of water by zinc chloride at about  $190^\circ$ , 1-methyl-1- $\alpha$ -hydroxyethyl-3-isopropylcyclopentane yields a mixture of hydrocarbons, b. p.  $84\text{--}87^\circ/19$  mm. Since crystalline derivatives cannot be isolated from the mixture, it is oxidised by ozone in glacial acetic acid. The products of decomposition of the ozonides are an unsaturated ketone,  $C_{11}H_{18}O$ , b. p.  $116^\circ/11$  mm.,  $D_4^{20}$  0.914,  $n_D^{20}$  1.47722 (*semicarbazone*, m. p.  $186^\circ$ ), an unidentified aldehyde, a substance which is very probably  $\beta\eta$ -diketo- $\delta$ -isopropyloctane, and a ketonic acid,  $C_{11}H_{20}O_3$ , b. p.  $180\text{--}186^\circ/16$  mm. The unsaturated ketone,  $C_{11}H_{18}O$ , yields bromoform by warming with sodium hypobromite. The substance which is supposed to be  $\beta\eta$ -diketo- $\delta$ -isopropyloctane also yields bromoform by the same treatment, and is converted into the ketone,  $C_{11}H_{18}O$ , by warming with dilute alcoholic sulphuric acid. The authors claim from the preceding evidence that the hydrocarbon mixture obtained from 1-methyl-1- $\alpha$ -hydroxyethyl-3-isopropylcyclopentane consists of 1:3-diisopropyl- $\Delta^1$ -cyclopentene and 1:2-dimethyl-4-isopropyl- $\Delta^1$ -cyclohexene.

The chloride of 1-methylcyclopentane-1-carboxylic acid reacts with zinc methyl to give ultimately an extremely small yield of 1-acetyl-1-methylcyclopentane, b. p. about  $56\text{--}60^\circ/13$  mm. (*semicarbazone*, m. p.  $141\text{--}142^\circ$ , needles). C. S.

**Derivative of Cineole containing Iodine.** EMIL FROMM and HERMANN FLUCK (*Annalen*, 1914, 405, 175—180).—Well-cooled cineole reacts with concentrated hydriodic acid free from iodine to form dipentene dihydriodide. When the acid contains free iodine, the reaction results in the formation of a substance,  $C_{20}H_{37}O_2I_3$ , dark green crystals, which is apparently *cineole di-iodide hydriodide*. The same substance is produced from cineole and hydrochloric acid, and a solution of  $N/10$ -iodine in potassium iodide so easily that the reaction serves for the estimation of cineole in fractions containing more than 60%; 1 mol. of cineole combines with 1 atom of iodine. C. S.

**The Total Synthesis of Camphenilone.** GUST. KOMPPA and S. V. HINTIKKA (*Ber.*, 1914, 47, 1550—1552).—The synthesis of camphenecamphoric acid (Lipp, this vol., i, 542) and the preparation of

$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \end{array}$ 
 camphenilone by the dry distillation of the lead salt of this acid (Komppa, this vol., i, 556) supply a complete synthesis of camphenilone, and this together with the recent confirmation (Hintikka, this vol., i, 409) of Aschan's formula (A., 1910, i, 709; 1911, i, 797) for camphenecamphoric acid is decisive for the annexed constitution for camphenilone.

The identity of two specimens of camphenilone, one prepared from camphenecamphoric acid and the other from camphene, was proved by direct comparison as also by the identity of the semicarbazones, leaflets, m. p. 224°.

D. F. T.

**New Investigations of Santenone.** II. E. RIMINI (*Gazzetta*, 1914, 44, i, 568—574. Compare this vol., i, 65).—When an aqueous-alcoholic solution of santenone is exposed to light for several months, it undergoes to a small extent (2—3%) the aldehydic decomposition observed with camphor under similar conditions. The aldehyde formed yields an *hydroxamic acid*,  $\text{C}_9\text{H}_{15}\text{O}_2\text{N}$ , which crystallises in colourless, silky needles, m. p. 144—145° (decomp.), and on hydrolysis yields a mixture of  $\pi$ -norcampholenic acids as well as a lactone identical with *dihydro- $\pi$ -norcampholenic lactone*,  $\text{C}_9\text{H}_{14}\text{O}_2$ . This lactone, obtained also from  $\pi$ -norcampholenic acid prepared from santenoneoxime, is a colourless liquid, b. p. 142—144°/27 mm., and can be obtained in crystals, m. p. 36—37°. The *aldehyde* probably has the formula  $\text{CMe} \begin{array}{c} \text{CH} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CHMe} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CHO}$ . By treatment of the reaction product from which the aldehyde has been separated with semicarbazide, a *semicarbazone*,  $\text{C}_{10}\text{H}_{17}\text{ON}_3$ , crystallising in needles, m. p. 156—158°, can be obtained. This on decomposition yields a liquid, b. p. 193—194°,  $n_D^{20}$  1.475, which shows the reactions of an aldehyde and has the formula,  $\text{C}_9\text{H}_{14}\text{O}$ , of the aldehyde already mentioned.

R. V. S.

[**Essential Oils.**] SCHIMMEL & Co. (*Semi-Annual Report*, April, 1914, pp. 48—102. Compare this vol., i, 67).—African copaiba balsam oil contains a *l-sesquiterpene*, b. p. 246—251°,  $D^{15}$  0.9077,  $[\alpha]_D - 13.21'$ ,  $n_D^{20}$  1.48943, which differs considerably from cadinene in physical properties, but nevertheless yields cadinene hydrochloride.

The presence of *l*-sylvestrene in *Dacryodes hexandra* oil (More, T., 1899, 75, 718) has been confirmed.

*Eryngium foetidum* oil (this vol., i, 68) yields an *acid*, m. p. 165—166°, acid number 327.1—332.4 (*Jaarb. dep. Landb. Ned. Ind.*, 1912, 57).

Frankincense oils (olibanum oils) of commerce were formerly lævorotatory, but are now generally dextrorotatory. A recent sample had  $D^{15}$  0.8775,  $\alpha_D + 19.18'$ ,  $n_D^{20}$  1.47245, acid number 1.8, ester number 7.5, ester number after acetylation 106.0, and was soluble in 2 vols. or less of 90% alcohol, but became turbid on addition of a further quantity. The terpene fraction of this oil consisted mainly (99%) of  $\alpha$ -pinene and camphene, and also contained small quantities of dipentene and cymene, but no phellandrene.

*Helichrysum angustifolium* oils from Dalmatia gave the following constants: (1)  $D_{15}^{20}$  0.8923,  $\alpha_D - 9^\circ 40'$ ,  $n_D^{20}$  1.48490, acid number 2.8, ester number 39.2, ester number after acetylation 65.8, soluble in 8—9 vols. of 90% alcohol; (2)  $D_{15}^{20}$  0.8964,  $\alpha_D - 9^\circ 38'$ ,  $n_D^{20}$  1.48422, acid number 1.9, ester number 56.2, soluble in 10 vols. of 90% alcohol (compare A., 1911, i, 893).

Mastix (*Pistacia Lentiscus*) leaves yielded an oil with an odour recalling those of rue and savin; it had  $D$  0.887,  $\alpha_D + 3^\circ$ , and contained 5.8% of esters, 13.5% of acetylisable constituents, together with pinene and other terpenes, and sesquiterpenes (*Perf. Record*, 1913, 4, 403).

*Mentha sylvestris* oil from Cyprus had  $D_{15}^{15}$  0.9687,  $\alpha_D + 31^\circ 58'$ , saponification number 24.9, saponification number after acetylation 175.5, and was soluble in 2.5 vols. of 70% alcohol (*Bull. Imp. Inst.*, 1913, 11, 432).

*Myrtus communis* oil from Cyprus had  $D_{15}^{15}$  0.9166 and 0.9302,  $\alpha_D + 8^\circ 14'$  and  $+ 8^\circ$ , saponification number 25.1, saponification number after acetylation 61.5, and was soluble in 5 vols. of 70% alcohol (*Bull. Imp. Inst.*, 1913, 11, 433).

Neroli oil contains farnesol (Kerschbaum, A., 1913, i, 739) in quantity probably not exceeding 2%.

Pagsainguin oil, derived from the oleo-resin of *Canarium villosum*, contains *l*- $\beta$ -pinene as principal constituent together with *p*-cymene and probably camphene (compare Bacon, A., 1911, i, 73).

Peru balsam oil contains nerolidol; it is probable that Thoms' peruvial (A., 1899, i, 715) consisted, wholly or in part, of this compound.

Petit grain oil contains *l*- $\beta$ -pinene (compare A., 1903, i, 186).

Rasamala oil, obtained in 80.4% yield from the resin of *Canarium microcarpum*, boiled mostly between  $250^\circ$  and  $285^\circ$ , and had  $D^{27}$  0.930,  $\alpha_D + 0^\circ 28'$ , and saponification number 2.8 (*Jaarb. dep. Landb. Ned. Ind.*, 1912, 57).

*Salvia cyprica* oils from Cyprus had  $D_{15}^{15}$  0.9263 and 0.925,  $\alpha_D^{20} - 6^\circ 31'$  and  $- 22^\circ 23'$ , saponification number 13.9 and 8, saponification number after acetylation 38.9 and 36, and were soluble in 0.8 and in 1 vol. of 80% alcohol respectively (*Bull. Imp. Inst.*, 1913, 11, 429).

Two samples of Ashanti pepper (*Piper guineense*) oil, obtained in yields of 11.5 and 10.96%, had the following constants: (1)  $D_{15}^{15}$  0.8733,  $\alpha_D - 3^\circ 43'$ ,  $n_D^{20}$  1.48905, acid number 0.6, ester number 5.5; (2)  $D_{15}^{15}$  0.8788,  $\alpha_D - 5^\circ 34'$ ,  $n_D^{20}$  1.48847, acid number 0.9, ester number 4.2, ester number after acetylation 22.1. Both samples were soluble in 8 vols. of 90% alcohol and gave a reaction for phellandrene.

Machilus oil from Japan, distilled from *Machilus Thunbergii* (*Laurus indica*) (?), was a yellow, solid mass, which melted above  $58^\circ$  to a yellow liquid with  $D^{50}$  0.9482,  $[\alpha]_D + 27^\circ 50'$  (in 10% alcoholic solution), acid number 1.2, ester number 5.4, ester number after acetylation 155.5, and soluble in 3 vols. of 70% alcohol. The solid constituent, m. p.  $82^\circ$ ,  $[\alpha]_D + 38^\circ 26'$  (in 10% alcoholic solution), forms white, silky needles, and is probably a sesquiterpene alcohol. E. G.

**Galingale Oil.** EMIL FROMM and HERMANN FLUCK (*Annalen*, 1914, 405, 181—187).—About a kilogram of galingale oil has been distilled,

fractions at 157—159°, 171—173°, 208—210°, 250—260°, and 260—270°, being collected. The first fraction is small and consists probably of *d*- $\alpha$ -pinene. The main fraction, b. p. 171—173°, contains more than 60% of cineole, which is precipitated as the di-iodide hydriodide (this vol., i, 852). The cineole regenerated from the di-iodide hydriodide by means of cold dilute aqueous sodium hydroxide is pure to the extent of 99.7%.

The fraction, b. p. 208—210°, is very small and contains a substance,  $C_{10}H_{16}O$ , which has not been identified. The fractions, b. p. 250—260° and 260—270°, yielded by further distillation a fraction, b. p. 260—263°, containing two *sesquiterpenes*. One of these, b. p. 150—155°/18 mm., is not attacked by hydrogen chloride in ether, whilst the other, which is present in very small amount, is converted into a *dihydrochloride*,  $C_{15}H_{24} \cdot 2HCl$ , m. p. 118°, fine needles, which is isomeric with cadinene hydrochloride. C. S.

**The Insoluble Constituents of Raw Caoutchouc, their Isolation, and Characterisation.** D. SPENCE and G. D. KRATZ (*Kolloid. Zeitsch.*, 1914, 14, 262—277).—By the addition of small quantities of acid to solutions of caoutchouc in benzene, the viscosity of the colloidal solution is greatly reduced and the insoluble constituents can then be readily separated from the solution by filtration. One hundred grams of caoutchouc are dissolved in a litre of benzene containing 0.3 to 0.5% of trichloroacetic acid; the solution is then exposed to the action of sunlight or heated gently on a water-bath. If the solution is well shaken from time to time, forty-eight hours' exposure to sunlight suffices for the complete separation of the insoluble constituents in such a form that the mother liquor can be poured off from the insoluble residue. This may be purified by extraction with a further quantity of benzene containing trichloroacetic acid.

The insoluble constituent of fine Para- and plantation Para-caoutchouc contains about 10% of nitrogen, which is considerably smaller than the nitrogen content of normal vegetable proteins. It not only gives the reactions characteristic of proteins, but in addition those for carbohydrates; in this respect it resembles the glucoproteins. In view of the above value for the nitrogen content of the insoluble constituent, it is probable that the factor, 6.25, which is usually employed in the deduction of the proportion of the insoluble constituent from the nitrogen content of caoutchouc samples is much too small. This is certainly the case for Para- and plantation-caoutchouc.

The protein obtained from the sap of *Kickxia elastica* is very similar in its properties to the insoluble constituent of plantation-caoutchouc; it contains the same proportion of nitrogen and gives the reactions characteristic of both proteins and carbohydrates.

The insoluble constituent of balata has also been found to be of the same character, but the proportion of carbohydrate is much larger than that in the insoluble constituent of Para-caoutchouc.

H. M. D.

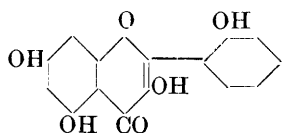


**Cerebrosides of the Brain.** VI. H. THIERFELDER (*Zeitsch. physiol. Chem.*, 1914, **91**, 107—114).—The cerebrone fraction of the cerebrosides (A., 1913, i, 747) contains in addition to cerebrone a cerebroside, which the author has termed phrenosin; this differs from cerebrone in certain respects. It forms a *hexa-acetyl* compound, which has  $[\alpha]_D -5.4^\circ$  [in 10.06% solution in chloroform (75%) and methyl alcohol]. On hydrolysis it yields the same products as cerebrone (cerebronic esters, dimethylsphingosine sulphate and galactose), but in different amounts.

After removal of cerebrone and kersin from the cerebroside mixture (this vol., i, 339) two fractions were obtained: the less soluble, which contains 18—19% of sugar and has about the composition of kersin, has now been further investigated. From the results of hydrolysis with 7.5% methyl-alcoholic solution of sulphuric acid, it appears to contain kersin, as well as another cerebroside, which yields sphingosine, galactose and an *acid* which is probably different from those previously found in the cerebrosides.

R. V. S.

**Constitution of Datiscetin.** J. LESKIEWICZ and L. MARCHLEWSKI (*Ber.*, 1914, **47**, 1599—1600. Compare A., 1907, i, 435).—Datiscetin has been hydrolysed by alkalis under various conditions, with the hope



of isolating the polyhydric phenol which is condensed with salicylic acid in the molecule. Qualitative tests showed the presence of phloroglucinol in the products. When bromine was added to a boiling solution of the colouring matter in acetic acid, however, tribromophloroglucinol could actually be separated in a pure form. Datiscetin is therefore, probably, 1:3:1'-trihydroxyflavonol (above formula).

J. C. W.

**Digitalinum verum.** H. KILIANI (*Arch. Pharm.*, 1914, **252**, 26—32).—The author has shown previously (A., 1892, 1482) that digitalin, on hydrolysis with aqueous alcoholic hydrogen chloride, yields digitaligenin, digitalose, and dextrose, but the latter sugar could not be obtained in a pure condition. The hydrolysis has now been repeated with larger quantities of material, and the dextrose isolated in a crystalline condition.

Full details of the hydrolysis and the purification of digitalin are given.

F. B.

**The Saponin from *Styrax japonica* (Siebold and Zuccarini).** I. Y. ASAHINA and M. MOMOYA (*Arch. Pharm.*, 1914, **252**, 56—69).—The outer covering of the fruit of *Styrax japonica* contains a crystalline saponin which occurs in the form of a calcium salt, and is best extracted by means of methyl alcohol (compare Keimatsu, *J. Chem. Soc. Tokyo*, 1903, **25**, 1052). After purification by extraction with ether and crystallisation from methyl alcohol, it is obtained in stellar aggregates of slender, white prisms, m. p. 254—257°. The calcium-free saponin, which the authors term *jegosaponin*, is prepared by shaking the calcium salt with hydrochloric acid (0.5%) at the ordinary

temperature. It separates from methyl alcohol in lustrous, white needles, m. p.  $238^{\circ}$ ,  $[\alpha]_D -39.15^{\circ}$  in 90% alcohol, and gives with sulphuric acid a yellow coloration, passing into red on warming. With cholesterol in methyl-alcoholic solution it yields a white, amorphous precipitate, m. p.  $260^{\circ}$ . Analyses and molecular-weight determinations indicate that it has the formula  $C_{55}H_{80}O_{25}$ , and not  $C_{38}H_{66}O_{18}$  assigned to it by Keimatsu.

On treatment with aqueous calcium hydroxide, its solution in methyl alcohol yields a calcium salt, crystallising in prisms, m. p.  $255-258^{\circ}$ , identical with the naturally occurring saponin salt. The jegosaponin is slowly hydrolysed by hot 5% sulphuric acid to dextrose, glycuronic acid, tiglic acid, and a mixture of sapogenins, which are separated by fractional extraction with light petroleum. The less soluble  $\beta$ -sapogenin receives provisionally the formula  $C_{33}H_{52}O_7$ , and forms an almost white powder, m. p.  $225-228^{\circ}$ , whilst the more readily soluble  $\alpha$ -sapogenin probably has the formula  $C_{33}H_{52}O_6$ , and separates in white, wart-like granules, m. p.  $150^{\circ}$ . On hydrolyses with alcoholic potassium hydroxide, the  $\alpha$ -sapogenin yields tiglic acid and two *alcohols*, which crystallise in short, lustrous leaflets, m. p.  $298^{\circ}$ , and long, thin plates, m. p. above  $300^{\circ}$  respectively. F. B.

"Gitalin": a Mixture. H. KILIANI (*Arch. Pharm.*, 1914, 252, 13-26).—By treatment with water and with a mixture of methyl alcohol, chloroform, and ether, gitalin can be separated into fractions, which differ in their physiological action, in their solubility in water, and in their behaviour on hydrolysis with acids. The author therefore concludes that gitalin is a mixture and not a single chemical individual, as has hitherto been imagined. F. B.

Formula of Bixin. J. F. B. VAN HASSELT (*Rec. trav. Chim.*, 1914, 33, 192-194).—In previous papers (A., 1909, i, 598; 1911, i, 550) the author has suggested the formula  $C_{29}H_{34}O_5$  for bixin in preference to the older formula  $C_{28}H_{34}O_5$ , which, however, has been recently defended by Heiduschka and Riffert (A., 1911, i, 315). Fresh analyses of bixin and of the crystalline methylbixin confirm the formula  $C_{29}H_{34}O_5$ . The discrepancy is attributed to the fact that bixin is readily oxidised with the production of amorphous products, the removal of which is not guaranteed by the method of purification adopted by Heiduschka and Riffert. Actually, specimens of bixin prepared by the latter process give analytical figures closely in accordance with those required by a substance,  $C_{28}H_{34}O_5$ .

Further, the analytical data obtained by Marchlewski and Matejo for hydrobixin (A., 1906, i, 760) are readily explained on the assumption of the formula  $C_{29}H_{34}O_5$  for bixin, whilst they are inexplicable if the older formula is adopted. H. W.

Bile Pigments. VII. Action of Ferric Chloride on Bilirubin, and the Preparation of Substances from Gall-stones. W. KÜSTER, K. REIHLING, and R. SCHMIEDEL (*Zeitsch. physiol. Chem.*, 1914, 91, 58-77).—Oxidation of bilirubin in acetic acid solution with ferric chloride yields a green substance of the probable

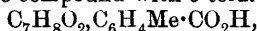
formula  $C_{92}H_{24}O_7N_4$ , which is termed *dehydro-oxybilirubin*. An acetic acid solution of the substance gives a red coloration with nitric acid, and the substance also gives the diazo-reaction, but does not seem to condense with formaldehyde. Alkaline solutions kept in the air do not change in colour; on boiling, about a quarter of the total nitrogen is split off in the form of ammonia and hæmatic acid is also produced. Dehydro-oxybilirubin in acetic acid solution is reduced by zinc dust or sulphur dioxide with the formation of a red substance which is not identical with bilirubin. The *silver* salt,  $C_{32}H_{31}O_7N_4Ag_3$ , was prepared.

The oxidation of bilirubin with ferric chloride yields also a second substance of the probable formula  $(C_{16}H_{15}O_5N_2)_x$ , termed *bilinigrin*. This product is characterised by the insolubility of its salts, of which the *sodium* salt,  $C_{16}H_{15}O_5N_2Na$ , the *potassium* salt,  $C_{16}H_{15}O_5N_2K$ , and the *silver* salt,  $C_{16}H_{15}O_5N_2Ag$ , were prepared. Bilirubin, dehydro-oxybilirubin and bilinigrin form a compound, which may appear during the preparation of the last two substances; from its behaviour with solvents here described, it is uncertain whether the union is chemical or physical in character.

In the extraction of the constituents of gall-stones, extraction with chloroform after treatment with acetic acid yields a bright orange-red bilirubin. If choleprasin is then removed with concentrated acetic acid, subsequent extraction with chloroform gives a reddish-brown coloured bilirubin. When neither chloroform nor glacial acetic acid dissolves anything more, a substance is left ("bilihumin") which resembles bilinigrin in the insolubility of its alkali salts. Details are given of the extraction and purification of these substances from gall-stones.  
R. V. S.

**Additive Compounds of Dimethylpyrone with Organic Acids.** JAMES KENDALL (*J. Amer. Chem. Soc.*, 1914, 36, 1222-1243). —Maass and McIntosh (*A.*, 1912, i, 825) have studied the additive compounds of ethers and alcohols with the halogen hydrides by means of the f.p. method. This method has now been applied to the investigation of the additive compounds formed by dimethylpyrone with monobasic organic acids and phenols. The substances investigated were formic, acetic, chloroacetic, dichloroacetic, trichloroacetic, trichlorobutyric, trichlorolactic,  $\beta$ -iodopropionic, crotonic, chlorocrotonic, benzoic, *o*-, *m*- and *p*-toluic, phenylacetic, salicylic, *o*-nitrobenzoic, cinnamic,  $\beta$ -phenylpropionic and mandelic acids, and phenol, *o*-, *m*- and *p*-cresol, *o*-, *m*- and *p*-nitrophenol, 2:4-dinitrophenol, picric acid, trinitrotoluene, and  $\alpha$ - and  $\beta$ -naphthol. The existence has been demonstrated of a large number of additive compounds which are of three types:  $C_7H_8O_2 \cdot HX$ ;  $2C_7H_8O_2 \cdot 3HX$ , and  $C_7H_8O_2 \cdot 2HX$ . These compounds, as a rule, are well crystallised, and have m. p.'s usually much lower than those of their components.

It was found that the compound with *o*-toluic acid,



crystallises only from solutions containing excess of acid; the corresponding *m*-toluic acid compound is stable at its maximum, and the *p*-toluic acid compound crystallises only from solutions containing an

excess of dimethylpyrone. *o*-Nitrophenol does not form an additive compound; *m*-nitrophenol yields the compound  $C_7H_8O_2 \cdot NO_2 \cdot C_6H_4 \cdot OH$ , and *p*-nitrophenol gives two compounds:  $C_7H_8O_2 \cdot NO_2 \cdot C_6H_4 \cdot OH$  and  $C_7H_8O_2 \cdot 2NO_2 \cdot C_6H_4 \cdot OH$ .  $\alpha$ -Naphthol furnishes the compounds

$C_7H_8O_2 \cdot C_{10}H_7 \cdot OH$   
and  $2C_7H_8O_2 \cdot 3C_{10}H_7 \cdot OH$ , whilst  $\beta$ -naphthol yields the compounds  $2C_7H_8O_2 \cdot 3C_{10}H_7 \cdot OH$  and  $C_7H_8O_2 \cdot 2C_{10}H_7 \cdot OH$ .

A consideration of the results of this work leads to the view that the reaction is ionic and that the compounds formed are true oxonium salts. E. G.

**The Chemical Activity of Xanthhydrol and its Application to the Estimation of Carbamide.** R. FOSSE (*Compt. rend.*, 1914, 158, 1432—1435).—The author has prepared a number of condensation products of xanthhydrol with substances occurring more or less frequently in biochemical work. The conditions of preparation of the following compounds will be described later.

*Xanthylphenylurethane*,  $O \langle C_6H_4 \rangle CH \cdot NH \cdot CO \cdot NHPh$ , microscopic crystals, m. p. about 220° (decomp.) according to the rate of heating.

*Methyl xanthylcarbamate*,  $O \langle C_6H_4 \rangle CH \cdot NH \cdot CO_2Me$ , slender needles, m. p. 193°; *isobutyl xanthylcarbamate*, long, slender needles, m. p. 148°; *isoamyl xanthylcarbamate*, m. p. 145°.

*Dixanthylbiuret*,

$O \langle C_6H_4 \rangle CH \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH \cdot CH \langle C_6H_4 \rangle O$ ,  
m. p. 260°.

*Dixanthylmalonamide*,

$C_{12}H_8O : CH \cdot NH \cdot CO \cdot CH_2 \cdot CO \cdot NH \cdot CH : C_{12}H_8O$ ,  
m. p. about 270°, according to rate of heating.

*Dixanthylsuccinamide*,

$C_{12}H_8O : CH \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH : C_{12}H_8O$ ,  
decomposing at 275°.

*Xanthylsuccinimide*,  $O \langle C_6H_4 \rangle CH \cdot N \begin{smallmatrix} \diagup CO \cdot CH_2 \\ \diagdown CO \cdot CH_2 \end{smallmatrix}$ , brilliant crystals,  
m. p. 245—247°.

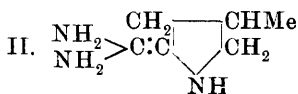
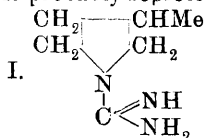
*Xanthylsuccinamic acid*,  $C_{12}H_8O : CH \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , colourless crystals, m. p. 192—196°, prepared by the action of potassium hydroxide on the preceding substance and giving a *silver* salt crystallising in white, silky needles, blackened by exposure to light.

*Dixanthylpyrrole*,  $C_4H_5N(CH : C_{12}H_8O)_2$ , colourless crystals, decomposing at 195—200°; *dixanthylindole*,  $C_8H_5N(CH : C_{12}H_8O)_2$ , decomposing at 205—214°.

*p*-*Xanthyldimethylaniline*,  $C_{12}H_8O : CH \cdot C_6H_4 \cdot NMe_2$ , colourless needles, m. p. 157—158°, giving a *hydrochloride*, needles, soluble in and dissociated by water. W. G.

**The Constitution of Galegine.** GEORGES TANRET (*Compt. rend.*, 1914, 158, 1426—1429; *Bull. Soc. chim.*, 1914, [iv], 15, 613—625. Compare this vol., i, 721).—The alkaloid galegine,  $C_6H_{13}N_3$ , as obtained from *Galega officinalis*, possesses the following

properties, which throw light on its constitution. It is devoid of optical activity and cannot be resolved, through its tartrate, into optical isomerides. It is unsaturated, since it absorbs bromine and decolorises acid permanganate. On heating until dry distillation commences it gives the pyrrole reaction. On distilling the hydrated base, 3-methylpyrrolidone is obtained. From these facts its constitution is probably represented by one of the two formulæ :



Formula II. is probably the correct one, since it explains the formation of the following compounds :

*Benzoylgalegin*,  $\text{C}_5\text{H}_9\text{N} : \text{C} \begin{smallmatrix} \text{NH} \cdot \text{COPh} \\ \text{NH} \cdot \text{COPh} \end{smallmatrix}$ , needles, m. p. 95—96°.

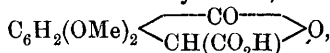
*Galeginedimethylpyrimidine*,  $\text{C}_5\text{H}_{10}\text{N} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} \cdot \text{CMe} \end{smallmatrix} \text{CH}$ , m. p. 74°, resulting from the condensation of galegine (1 mol.) with acetylacetone (1 mol.).

*Oxalylgalegine*,  $\text{C}_5\text{H}_9\text{N} : \text{C} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , crystallising with  $2\text{H}_2\text{O}$ , m. p. 203—206°, obtained by the action of ethyl oxalate on galegine hydrogen carbonate. At the same time there is formed the *oxamic ester*,  $\text{C}_5\text{H}_9\text{N} : \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}, \frac{1}{2}\text{H}_2\text{O}$ , prisms, m. p. 88°.

*Benzilgalegine*,  $\text{C}_5\text{H}_9\text{N} : \text{C}(\text{NH}_2) \cdot \text{N} : \text{CPh} \cdot \text{CO} \cdot \text{Ph}$ , m. p. 228—230°.

Finally on heating galegine with a solution of barium hydroxide at 100° in sealed tubes it is decomposed, giving 3-methylpyrrolidone and carbamide, the reaction being quantitative. W. G.

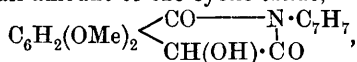
**Meconinecarboxylic Acid.** P. FREUNDLER (*Bull. Soc. chim.*, 1914, [iv], 15, 465—470. Compare Fritsch, A., 1898, i, 663).—The author has prepared meconinecarboxylic acid,



and a number of its derivatives. On condensing opianic acid with potassium cyanide,  $\alpha$ -cyanomeconine is obtained (compare Robinson and Robinson, P., 1913, 29, 267), which on hydrolysis with hydrochloric acid yields, in the cold, the corresponding *amide*, and on warming, meconinecarboxylic acid. The acid crystallises from water in white plates, m. p. 110—111°, containing  $\frac{1}{3}\text{H}_2\text{O}$ , and from concentrated hydrochloric acid in prisms, m. p. 152—153°. At 180—190°, it decomposes, giving a quantitative yield of meconine.

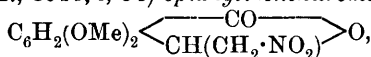
The *amide* crystallises from benzene in white prisms, m. p. 174·5°, or from the solution of its hydrochloride in water; the crystals have m. p. 86—87° and contain  $\frac{3}{4}\text{H}_2\text{O}$ . The following derivatives of meconinecarboxylic acid have been prepared: the *methyl ester*, white needles, m. p. 98·5°; the *benzylamine salt*,  $\text{C}_{11}\text{H}_{10}\text{O}_6, \text{C}_7\text{H}_7 \cdot \text{NH}_2$ , white needles, m. p. 146°; the *homopiperonylamine salt*, m. p. 175° (decomp.); the

benzylamide,  $\text{C}_6\text{H}_2(\text{OMe})_2 \langle \begin{array}{c} \text{CO} \\ \text{CH}(\text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}) \end{array} \rangle \text{O}$ , m. p. 157—158°, together with a small amount of the cyclic imide,



m. p. 290°; the *homopiperonylamide*, m. p. 147—148°, and the *quinine* salt,  $C_{11}H_{10}O_8 \cdot C_{20}H_{24}O_2N_2$ , m. p. 184—185° (decomp.).

In the course of the work, the author has prepared by Rosenmund's method (compare A., 1911, i, 34) *opianylidenenitromethane*,



yellow plates, m. p. 164°.

W. G.

**Strychnos Alkaloids. XXII. The Oxidation of Acetylstrychninolone and the Discovery of an Isomeric Strychninolone.** HERMANN LEUCHS and GEORG SCHWAEBEL (*Ber.*, 1914, 47, 1552—1560).—It has recently been shown (Leuchs and Rauch, this vol., i, 317) that crude brucinolone contains two isomeric substances, for whilst oxidation of the acetyl derivative yielded acetylbrucinolonic acid,  $C_{23}H_{24}O_9N_2$ , and an acid,  $C_{23}H_{24}O_{10}N_2$ , the purified substance gave only the former product.

Strychninolone can be obtained analogously to brucinolone by the action of *N*-sodium hydroxide solution on strychninolic acid, but the reaction proceeds much more rapidly than with brucinolic acid. The main product is strychninolone, which separates, but the filtrate from this contains a small quantity of an isomeride which can be extracted by chloroform, of dihydrostrychninonic acid, and a substance,

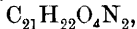
$\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}_2$ ,  
prisms, m. p. 280—290° (decomp.), with previous sintering at 260°.

The formation of the isomeric strychninolone, which is designated *strychninolone-b*, appears to be favoured somewhat by longer contact of the precipitate of ordinary strychninolone with the alkaline liquid. Strychninolone-*b*,  $C_{19}H_{18}O_3N_2 \cdot H_2O$ , forms lustrous, prismatic crystals; when anhydrous it has m. p. 228—230°, and gives a marked depression of the m. p. when mixed with strychninolone-*a*; it is more easily soluble than the latter, and has  $[\alpha]_D^{20} = -37.0^\circ$  (in acetic acid), whilst the value for strychninolone-*a* is  $-112.4^\circ$ .

In the investigation of brucinolone, it was found that treatment with a hot methyl-alcoholic solution of ammonia converted the crude substance containing the isomeric impurity (brucinolone-*a*) into a homogeneous substance (brucinolone-*b*). There is thus an analogy between the isomerism observed with brucinolone and strychninolone and in both cases the phenomenon is attributed to a different position of a double bond.

Acetylstrychninolone-*a*, obtained by heating with acetic anhydride and a little sodium acetate, has m. p. 241—243° (not 126—128° as earlier published; Leuchs and Reich, A., 1910, i, 768). On oxidation in acetone solution with potassium permanganate it gave an acid substance,  $C_{21}H_{20}O_8N_2$ , a yellow syrup (*barium* salt, needles), together with a small quantity of a neutral substance,  $C_{21}H_{22}O_6N_2$ , hexagonal

prisms, m. p.  $232^{\circ}$ , with previous sintering at  $220^{\circ}$ , probably *dihydroxyacetylstrychninolone*, and another neutral substance,



colourless prisms or polyhedra, m. p.  $254\text{--}256^{\circ}$ ,  $[\alpha]_{\text{D}}^{20} - 56.9^{\circ}$  (in acetic acid), possibly acetyldihydrostrychninolone.  
D. F. T.

**Identity of Yohimbine and Quebrachine.** E. FOURNEAU and HAROLD J. PAGE (*Bull. Sci. Pharmacol.*, 1914, **21**, 7—16).—The identity of the two alkaloids has been established by the following comparisons. The bases crystallise from alcohol in elongated, prismatic needles, have m. p.  $247\text{--}248^{\circ}$  (Maquenne block), and  $[\alpha]_{\text{D}}^{20} 56.0^{\circ}$  and  $56.1^{\circ}$  in alcohol, and exhibit the same colour reactions with various reagents. The hydrochlorides,  $\text{C}_{24}\text{H}_{26}\text{O}_3\text{N}_2\cdot\text{HCl}$ , are anhydrous, and have m. p.  $302\text{--}303^{\circ}$  and  $[\alpha]_{\text{D}}^{20} 106.4^{\circ}$  and  $106.0^{\circ}$  in water. The sulphates contain  $8\text{H}_2\text{O}$ , have m. p.  $281\text{--}282^{\circ}$  (anhydrous), and  $[\alpha]_{\text{D}}^{20} 100^{\circ}$  and  $100.3^{\circ}$  in water. The tartrates contain  $6\text{H}_2\text{O}$ , have m. p.  $278^{\circ}$  (anhydrous; the hydrated salts melt at  $213^{\circ}$  and resolidify), and  $[\alpha]_{\text{D}}^{20} 104.9^{\circ}$  and  $105.0^{\circ}$  in water. The oxalates have the same crystalline form, anhydrous needles, and the same slight solubility in water.  
C. S.

**Pyrrole.** HANS FISCHER (*Zeitsch. physiol. Chem.*, 1914, **91**, 308).—The condensation product from 5-acetyl-2:4-dimethylpyrrole with formaldehyde or acetaldehyde recently described (Fischer and Zimmermann, this vol., i, 319) is ethyl 5-acetyl-2:4-dimethylpyrrole-3-carboxylate.  
R. V. S.

**Distillation of Some Pyrrolecarboxylic Acids.** HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1914, **91**, 184—193).—When 2:4-dimethylpyrrole-5-acetic acid is distilled, carbon dioxide is eliminated and trimethylpyrrole is produced.

Distillation of 2:4-dimethylpyrrole-5-propionic acid causes the loss of the propionic acid residue, and 2:4-dimethylpyrrole is chiefly formed. A substance crystallising in colourless needles, m. p. about  $60^{\circ}$ , is also produced. This resembles the result of the distillation of bilirubic ester, which leads to the production of isophonopyrrolecarboxylic ester and phonopyrrolecarboxylic ester.

Trimethylpyrrole-3-propionic acid yields on distillation chiefly tetramethylpyrrole, acetic acid being eliminated.

Trimethylpyrrolepropionic acid can be prepared from hæmin which has been reduced with hydrogen iodide and glacial acetic acid. The mixture of esters, after saponification, is heated with an alcoholic solution of potassium ethoxide for three and a-half hours at  $210^{\circ}$  in a closed vessel, a pressure of 87 atmospheres being reached.

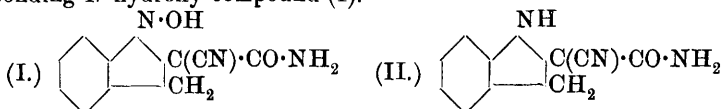
Oxidation of bilirubin with sodium nitrite in particular conditions, an excess of nitrite being avoided, yields a small quantity of a colourless, crystalline substance, m. p. about  $87\text{--}88^{\circ}$ .  
R. V. S.

**The Hydroxylamine Derivatives of  $\alpha\delta$ -Diketones and 1-Hydroxy-2:5-dimethylpyrrole.** E. E. BLAISE (*Compt. rend.*, 1914, 158, 1686—1688).—Hydroxylamine reacts with  $\alpha\delta$ -diketones

in the normal manner giving either a mixture of the monoxime with a trace of the dioxime or the dioxime according to the amount of hydroxylamine used. Of the two diketones used, acetonylacetone yields a *monoxime*, b. p.  $130^{\circ}/11$  mm., and *s*-dipropionylethane a *monoxime*, b. p.  $137\text{--}140^{\circ}/15$  mm., and a *dioxime*, m. p.  $155^{\circ}$ . The author has repeated Knorr's work on the condensation of hydroxylamine with diacetylsuccinic ester, and finds certain differences in the stages of the reaction. The product of condensation is ethyl 1-hydroxy-2:5-dimethylpyrrole-3:4-dicarboxylate, which on saponification yields successively an acid ester, the monoester and finally 1-hydroxy-2:5-dimethylpyrrolecarboxylic acid. Contrary to the results of Knorr the monoester is a solid, m. p.  $61^{\circ}$ , and gives a *sodium* derivative, long needles stable in aqueous solution. The product obtained by Knorr on heating the mono-acid on an oil-bath is not 1-hydroxydimethylpyrrole, but a product of polymerisation. 1-Hydroxy-2:5-dimethylpyrrole is, however, readily obtained by boiling the acid with water for a few minutes, saturating the solution with ammonium sulphate, and extracting with ether. It crystallises in needles, m. p.  $44\text{--}45^{\circ}$ , b. p.  $126\text{--}127^{\circ}/19\text{--}20$  mm., and slowly liquefies to a reddish-brown, viscous, product. Its constitution has been proved by reducing it with zinc and hydrochloric acid, obtaining 2:5-dimethylpyrroline, identical in every respect with that obtained by Knorr on reducing 2:5-dimethylpyrrole. The aurichloride of the base has m. p.  $102^{\circ}$  (compare A., 1902, i, 54).

W. G.

***N*-Hydroxydihydroindoles and Their Transformation Products.** GUSTAV HELLER and PAUL WUNDERLICH (*Ber.*, 1914, 47, 1617—1629).—When *o*-nitrobenzylidenecyanoacetamide (Issoglio, A., 1904, i, 526) is reduced by zinc dust and acetic acid, the products are 2-cyano-2:3-dihydroindole-2-carboxylamide (II) and the corresponding *N*-hydroxy-compound (I).



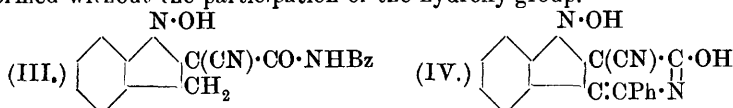
The hydroxy-derivative represents an intermediate stage in the reduction. It gives a deep blue coloration with ferric chloride, is insoluble in alkalis, and is neutral to litmus, whereas the hydroindole (II) which it yields on reduction is alkaline. In common with the corresponding carboxylic acid it forms well-defined salts without the elimination of water. These salts are dissociated by water and represent the first of such derivatives of cyclic *N*-hydroxy-compounds. Similar derivatives of indole are not basic, from which it appears that the dihydroindole ring influences the basicity of the *N*-hydroxy-group.

When the above *N*-hydroxy compound was oxidised by chromic acid, the only product which could be isolated, and this to the extent of 50%, was the hydroindole, the curious result representing a reduction by an oxidising agent. The two compounds were hydrolysed to the corresponding 2-cyano-2-carboxylic acids by sodium hydroxide or hydrochloric acid, and in this case, also, chromic acid "reduced" the hydroxy-derivative.



Attempts were made to hydrolyse the 2-cyano-2:3-dihydroindole-2-carboxylamide by Bouveault's method, but the product was 2-hydroxy-quinoline-3-carboxylamide, an interesting result from the point of view of the natural synthesis of alkaloids with pyridine nuclei, for it is an example of the transformation of a pyrrole ring into a pyridine ring by the participation of a carbonyl group.

The 2-cyano-1-hydroxy-2:3-dihydroindole-2-carboxylamide was also benzoylated in pyridine solution. The product (III) contained the hydroxy-group intact, for it still responded to the ferric chloride reaction. When dissolved in sodium hydroxide, it soon deposited a sodium salt of another compound (IV), in which a new ring was formed without the participation of the hydroxy-group.



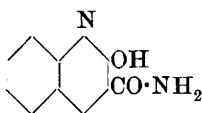
The corresponding acetyl derivative could not be crystallised, but it also dissolved in alkali to give the well-defined methyl compound analogous to IV.

*o*-Nitrobenzaldehyde condenses with malononitrile in warm alcohol, yielding *ω*-dicyano-*o*-nitrostyrene,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CN})_2$ , in the form of colourless needles, m. p. 137.5—138°, which strongly irritate the mucous membrane. Only one cyano-group is hydrolysed when the compound is dissolved in concentrated sulphuric acid, the product being *o*-nitrobenzylidenecyanoacetamide. Issoglio (*loc. cit.*) prepared this by condensing *o*-nitrobenzaldehyde with cyanoacetamide in presence of ammonia, but it is better to use a few drops of diethylamine. The compound was reduced by zinc dust and glacial acetic acid at 60° when the product was cooled, diluted slightly to dissolve zinc acetate, filtered, and diluted still further, when 2-cyano-1-hydroxy-2:3-dihydroindole-2-carboxylamide (I) separated. This compound crystallises in long, yellow needles from hot water (75 parts), m. p. above 290°, and forms sparingly soluble salts with most acids, the *hydrochloride* being described. The filtrate from the hydroxy-compound was evaporated and nearly neutralised with ammonia, when 2-cyano-2:3-dihydroindole-2-carboxylamide (II) gradually separated. This also crystallised from water in yellow, interlocked spikelets, m. p. 237—238°, and forms a pale yellow *chromate*. The compound was also prepared by reducing the hydroxy-derivative with zinc dust and ammonia, or by adding chromic acid to a solution of the substance in 5% sulphuric acid. Reduction with zinc dust and acetic acid on the water-bath yielded another base,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_3$ , some re-arrangement having taken place.

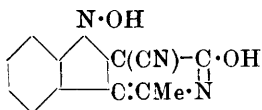
The above hydroxy-compound was hydrolysed by 50% potassium hydroxide or by 23% hydrochloric acid at 220°, when 2-cyano-1-hydroxy-2:3-dihydroindole-2-carboxylic acid,  $\text{C}_{10}\text{H}_8\text{O}_3\text{N}_2$ , was obtained in yellow needles which scarcely dissolve in organic media, but may be recrystallised from hot, dilute solutions of sodium acetate. The same acid may be obtained by reducing *o*-nitro-*α*-cyanocinnamic acid by zinc dust and acetic acid at 25°, but the reduction proceeds farther at 80°, and leads to the formation of 2-cyano-2:3-dihydroindole-2-carboxylic acid,  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$ , in colourless crystals. The latter acid was also prepared

by hydrolysing the corresponding amide, by reducing the hydroxy-amide (I) with zinc and sodium hydroxide and by the action of chromic acid on the above corresponding hydroxy-acid.

Nitrous fumes, from arsenious oxide, were passed into a 1% aqueous solution of 2-cyano-2:3-dihydroindole-2-carboxylamide at 60°, when yellow crystals of 2-hydroxyquinoline-3-carboxylamide (annexed formula), m. p. 290—291°, gradually separated. The constitution was proved by hydrolysis with dilute sodium hydroxide to the known acid.

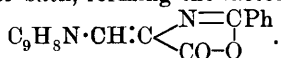


2-Cyano-1-hydroxy-2:3-dihydroindole-2-carboxybenzamide (III) forms colourless leaflets from acetic acid and benzene, but sparkling, yellow leaflets from alcohol, and the compound IV crystallises in hygroscopic, yellow needles, which are hydrolysed by 15% sulphuric acid at 180° to benzoic acid and the sulphate of 2-cyano-1-hydroxy-2:3-dihydroindole-2-carboxylic acid. The corresponding methyl compound (annexed formula) was obtained by dissolving the crude acetyl derivative, prepared by the action of acetic anhydride and sulphuric acid, in sodium hydroxide, when the yellow sodium salt crystallised.

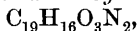


J. C. W.

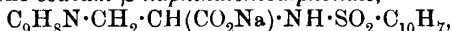
**Preparation of  $\alpha$ -Methyltryptophan and Its Behaviour in the Animal Organism.** A. ELLINGER and Z. MATSUOKA (*Zeitsch. physiol. Chem.*, 1914, 91, 45—57).—2-Methylindole-3-aldehyde condenses with hippuric acid in the presence of sodium acetate and acetic anhydride on the water-bath, forming the lactone,



When this is heated with 1% sodium hydroxide until ammonia is evolved, filtered, and the undissolved portion treated in the same way, an alkaline solution is obtained from which, by the action of dilute sulphuric acid, 2-methylindole- $\alpha$ -benzoylaminoacrylic acid,



is precipitated; it forms colourless prisms, m. p. 205° (decomp.). This acid on reduction with sodium and boiling alcohol yields  $\alpha$ -methyltryptophan,  $\text{C}_9\text{H}_8\text{N}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , which crystallises in needles, and on heating becomes coloured at 215° and is completely melted at about 234°. The sodium  $\beta$ -naphthalenesulphonate,



crystallises in needles, m. p. 172—173°.  $\alpha$ -Methyltryptophan on oxidation with ferric chloride yields 2-methylindole-3-aldehyde, identical with that of Plancher and Ponti (A., 1907, i, 341).

After injection of  $\alpha$ -methyltryptophan into rabbits, no kynurenic acid could be found in the urine.

$\alpha$ -Methyltryptophan does not give colorations either with bromine water or with glyoxylic acid and sulphuric acid. This makes it probable that the  $\alpha$ -C-atom of the pyrrole nucleus is concerned in these reactions (compare Homer, A., 1913, ii, 451).

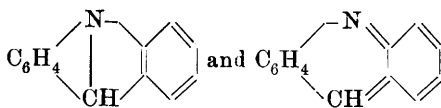
R. V. S.

**Colourless Additive Products of Quinoline and Pyridine with Fluorescein.** O. FISCHER and W. HOFFMANN (*Ber.*, 1914, 47, 1578—1579).—On recrystallising fluorescein from quinoline and pyridine, colourless compounds,  $C_{20}H_{12}O_5, 3C_9H_7N$  (prisms) and  $C_{20}H_{12}O_5, 3C_5H_5N$  (needles or prisms), are respectively obtained; separation of the crystals is aided by the addition of ether and a little light petroleum to the solutions. The quinoline compound is decidedly the more stable, but, on keeping, both slowly lose the added base with assumption of a yellow colour. It is believed that the compounds contain the lactonic modification of fluorescein.

Oddo has recently described additive compounds of fluorescein with 1—3 molecules of pyridine (*A.*, 1913, i, 1110), but these were yellow.

D. F. T.

**The Homologues of Acridine Resulting from the Nuclear Methylation of Aromatic Bases.** C. LIEBERMANN and M. KARDOS (*Ber.*, 1914, 47, 1563—1576).—In the course of a recent investigation, the authors have noticed the formation of a certain amount of homologues of acridine in the nuclear methylation of homologues of aniline (*A.*, 1913, i, 276). The experiments have now been repeated on a larger scale with 1 to  $1\frac{1}{2}$  kilos. of the hydrochlorides of the respective bases, which were heated with methyl alcohol in an autoclave for five hours at  $250$ — $260^\circ$ . In all cases the products were tarry, more so than those obtained on a smaller scale in a glass tube; for the method of separating the resulting complicated mixtures, reference must be made to the original. The acridine derivatives were found in the less volatile portions, and formed colourless or yellow, crystalline solids of high m. p., which gave feebly fluorescent solutions. They dissolved in hydrochloric and sulphuric acids to yellow solutions, which, when treated with ammonia, gave emulsions which subsequently deposited colourless needles. To explain the change in colour, it is suggested that the acridine molecules can exist in the annexed tauto-



meric forms, the latter representing the coloured compounds.

In the methylation of *m*-toluidine in this way, the portion of the product, b. p. above  $360^\circ$ , contained some *tetramethylacridine*,

$C_{13}H_9NMe_4$ , yellow needles, m. p.  $252$ — $257^\circ$ ; *platinichloride*, sparingly soluble; *dichromate*, an orange-yellow, crystalline precipitate; *methiodide*, orange needles. Reduction of tetramethylacridine by heating with dilute hydrochloric acid and zinc dust gave *tetramethyldihydroacridine*,

$C_{13}H_7NMe_4$ , colourless leaflets, m. p.  $279$ — $281^\circ$ , which does not fluoresce either in alcoholic or acidic solution, but gradually oxidises in solution, regenerating the tetramethylacridine. A trimethylacridine,  $C_{13}H_6NMe_3$ , yellow prisms, m. p.  $203$ — $206^\circ$ , and a dimethylacridine, m. p.  $112$ — $113^\circ$ , were also separated from the reaction product.

From the product obtained with *m*-4-xylylidine were isolated two *hexamethylacridines*, one forming yellow needles, m. p.  $208$ — $210^\circ$ , the other also consisting of yellow needles, m. p.  $120$ — $123^\circ$ ; *hydrochloride*,

deep yellow and sparingly soluble. A colourless *tetramethylacridine* (possibly 1:3:7:9) was also separated, m. p. 93—99° (compare Senior and Compton, T., 1907, 91, 1927); *dichromate*; *persulphate*, yellow, crystalline precipitate. *isoDuridine* was also detected in the fraction, b. p. 250—310°, being separated in the form of its acetyl derivative.

*m*-5-Xylidine gave a mixture of products from which an almost colourless *tetramethylacridine* (probably 2:4:6:8), m. p. 200—210°, was obtained; *hydrochloride* gives solution with a deep green fluorescence. A small quantity of a hexamethylacridine was also separated as the *platinichloride*; *methiodide*, orange-red needles.

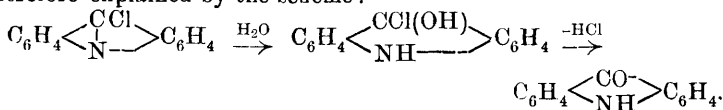
In the reaction product obtained with  $\psi$ -cumidine, a *hexamethylacridine* (probably 1:3:4:6:7:9), yellow needles, m. p. 213—215°, was obtained; *hydrochloride* and *sulphate*, orange-red; *dichromate*, orange; *platinichloride*, red. This was converted by reduction into the corresponding *hexamethyldihydroacridine*, colourless leaflets, m. p. 201°. *isoDuridine* was also present in good amount (compare Limpach, A., 1888, 464).

D. F. T.

**10-Hydroxyacridone and "Acridol."** A. KLIEGL and ALFRED FEHRLE (*Ber.*, 1914, 47, 1629—1640).—A few years ago, it was discovered that *o*-nitrobenzaldehyde condenses with benzene to form phenylanthranil, and a yellow substance,  $C_{13}H_9O_2N$ , which gives orange alkali salts (A., 1908, i, 549). The latter compound has now been investigated. Its formation might be due to the oxidation of phenylanthranil,  $C_{13}H_9ON$ , or to the elimination of water from *o*-nitrobenzhydrol,  $C_{13}H_{11}O_3N$ . The substance contains a hydroxyl group, and, assuming that it is an acridine derivative, since arylanthranils are readily transformed into such compounds, it seemed probable that it is 10-hydroxyacridone,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{N}(\text{OH}) \end{smallmatrix} C_6H_4$ . That the hydroxyl group has not migrated to a carbon atom is shown by comparing the substance and its methyl ether with the four *C*-hydroxyacridones and their ethers. The assumption that the compound does belong to the acridine series is justified by the formation of dihydroacridine on complete reduction.

When 10-hydroxyacridone is reduced by mild agents, the products are acridine and another base, isomeric with acridone, which is considered to be the supposed unstable and somewhat hypothetical

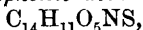
"acridol,"  $C_6H_4 \begin{smallmatrix} \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6H_4$ . It has been assumed that this compound would immediately isomerise to acridone, and Graebe and Lagodzinski (A., 1893, i, 649) used this theory to explain the formation of acridone, rather than acridol, during the replacement of chlorine by hydroxyl in 5-chloroacridine. The compound is stable in hot hydrochloric or concentrated sulphuric acids, however, and is only rearranged by acetic anhydride. The above reaction of Graebe's is therefore explained by the scheme:



The authors had hoped to postpone publication until they were able to prepare more of the hydroxyacridone, but the announcement of a paper by Drechsler, in which, unknowingly, acridol is described, has led them to make the present record of their results.

The yield of 10-hydroxyacridone, obtained by the condensation of *o*-nitrobenzaldehyde with benzene, is only about 5% of the amount of the aldehyde employed. The compound forms deep yellow needles, m. p. 255–256°, and is converted by methyl sulphate into 10-methoxyacridone, which crystallises in pale yellow, sparkling needles, m. p. 153°, and exhibits a marked violet fluorescence in alcoholic solution. A solution of the substance in very dilute sodium hydroxide was gradually treated with sodium amalgam at room temperature, with shaking, when a mixture of acridone, acridol, and dihydroacridine was obtained. The former two bases were extracted by 5% hydrochloric acid, and then dissolved in boiling light petroleum. *Acridol* (5-hydroxyacridine) crystallised, on cooling, in long, slender, yellow needles, m. p. 169°. The solutions in alcohol, concentrated sulphuric acid or hydrochloric acid exhibit green fluorescence. The sulphate, picrate, and dichromate are very sparingly soluble. On reduction with sodium amalgam in boiling alcohol, it is reduced to dihydroacridine, and when treated with phosphoryl chloride, it is converted into 5-chloroacridine.

For the preparation of 4-methoxyacridone, 2:6-dinitrotoluene was converted into 2-chloro-6-methoxybenzoic acid (Ullmann and Panchaud, A., 1907, i, 63) and this condensed with aniline to form 3-methoxydiphenylamine-2-carboxylic acid (I), which crystallises in colourless needles, m. p. 110–111°. When this is dissolved in cold concentrated sulphuric acid, it forms a *sulphonic acid* of 4-methoxyacridone,



in yellow needles, m. p. 240–245° (decomp.), the *sodium*, *barium* and *silver* salts of which were prepared. When the carboxylic acid is treated successively with phosphorus pentachloride and aluminium chloride, however, the desired condensation to 4-methoxyacridone (II) is achieved.



The latter compound was purified through the yellow *picrate*, m. p. about 200°, and forms a pale yellow, microcrystalline powder, m. p. 346–348°. It is remarkable in that it dissolves readily in dilute acids. It is known that acridone is basic (compare A., 1909, i, 255), but the proximity of the methoxy-group to the carbonyl group increases the basicity considerably.

J. C. W.

**Constitution and Colour of Azine, Azoxine, and Thiazine Dyes.** III. **Quinoneimide Dyes.** F. KEHRMANN, E. HAVAS, and E. GRANDMOUGIN (*Ber.*, 1914, 47, 1881–1903).—The authors give a tabular summary of the colours and absorption spectra of the dyes of these three classes in aqueous sulphuric acid solution, the sulphates being preferably

examined, since hydrochloric and hydrobromic acid often introduce halogen and exert a reducing action at the same time. The results obtained lead to a large number of deductions, some of the most important of these being as follows.

In all concentrations of acid phenazthionium salts give the same colour and the same spectrum, characterised by six sharp and two indistinct maxima. 1-Aminophenazthionium, however, gives two series of salts, the mono-acid ones being green and giving spectra with three sharp maxima. The greenish-orange solutions corresponding with the diacid salts give a spectrum virtually identical with that of phenazthionium salts. Hence the orange solutions of the amine contain only ortho-quinonoid salt, and the same is the case with the green solutions. 3-Aminophenazthionium salts are differently constituted, and are hence probably para-quinonoid. The para-quinonoid imine-base is orange; addition of acid to the imino-group gives a violet mono-acid salt and thus results in deepening of the colour, which is enhanced by further addition of acid to the azine nitrogen, the diacid salt being green. The 1:3-diamine gives three series of salts, mono-, di- and tri-acid, all of them showing dichroism; the mono-acid salt consists of an equilibrated mixture of ortho- and para-quinonoid salt, and this is probably also the case with the di- and tri-acid salts. The violet mono-acid salt of the 3:6-diamine (Lauth's violet) gives bands very near to those of the corresponding 3-monoamine salt, but are partly of shorter wave-length and so result in brightening of the colour, which is also more intense; this double effect is to be ascribed to the symmetrical position of the 6-amino-group. The relations of the 3:6-diamine to the 3-amine become quite clear if a paraquinonoid constitution is attributed to its three series of salts. Optically, methylene-blue is a normal methylated Lauth's violet, but apparently it gives only two series of salts, possibly because the diacid salt resembles closely the mono-acid salt in its subjective colour.

In all concentrations of sulphuric acid, phenazoxonium gives only one series of reddish-violet salts. 1-Aminophenazoxonium behaves exactly as 1-aminophenazthionium and is ortho-quinonoid in both mono- and di-acid salts. 3-Aminophenazoxonium is analogous to 3-aminophenazthionium and, like its mono- and di-acid salts, is of para-quinonoid structure. With the diamines the relations are far more complicated and less clear. Like the isologous sulphur derivative, the 1:3-diamine probably forms three series of salts, the mono-acid salt being greenish-orange-yellow and the diacid cherry-red; the latter is, however, really a mixture of a para-quinonoid, yellowish-red diacid salt with an ortho-quinonoid violet triacid salt. The 3:6-diamine shows three distinct series of salts, and the tetramethyl-3:6-diamine is characterised optically as its methyl homologue.

The parent substances of the azine-dyes, phenazine, methylphenazonium, and phenylphenazonium give two series of salts, and can only be ortho-quinonoid. With 1-aminophenylphenazonium the results are in accord with the assumption of an ortho-quinonoid constitution for its three series of salts. The various observations for and against the different constitutions for *aposafranine* (3-aminophenylphenazonium) salts are fully discussed, the weight of the evidence being in

favour of the para-quinonoid configuration for the red mono-acid salts; as regards the brownish-red triacid salts, the almost complete identity of their behaviour with that of phenylphenazonium scarcely allows a doubt of their ortho-quinonoid structure, whilst the green diacid salts are evidently mixtures of much para-quinonoid and little yellow ortho-quinonoid di-salts. Here, also, more complicated relations are met with the diamines. In the case of phenosafranine (3 : 6-diaminophenylphenazonium), the spectrometric data indicate that the mono-, di-, and tri-acid salts are para-quinonoid and the tetra-acid salt ortho-quinonoid. With the 1 : 3-diamine, the mono- and di-acid salts are para-quinonoid, and the tri- and tetra-acid salts orthoquinonoid. With the 2-6-diamine the mono-, di-, and tri-acid salts are para-quinonoid, and the tetra-acid salt ortho-quinonoid. As has been shown by Havas and Bernhard (A., 1913, i, 1245), the 3 : 11-diamine exhibits all the behaviour of an *aposafranine* with an external amino-group; its first three series of salts are hence para- and the last ortho-quinonoid. The 2 : 13-diamine differs from all its isomerides in that it contains no amino-group in the para-position to the tervalent nitrogen, and cannot therefore exhibit any relations with *aposafranine*; the fundamental 2-aminophenylphenazonium, from which it differs only in the external amino-group, is, however, insufficiently known, especially as regards its spectroscopic behaviour, to admit of discussion of the relationships between the two compounds.

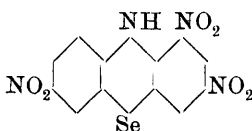
The above conclusions contradict, in certain respects, the results of Pummerer and Gassner (A., 1913, i, 991). T. H. P.

**Selenazine Colouring Matters.** HUGO BAUER (*Ber.*, 1914, 47, 1873—1881).—For the preparation of selenazine colouring matters the author uses a method analogous to that employed by Kehrmann (A., 1900, i, 61; 1913, i, 1383) for obtaining 1 : 3-diaminophenazonium and phenazthionium salts.

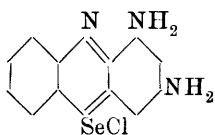
*o*-Picrylamino-phenylselenol,  $\text{SeH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$ , prepared by the action of picryl chloride on the zinc salt of *o*-aminophenylselenol (compare A., 1913, i, 263), forms a brownish-red powder, and is converted by alcoholic alkali hydroxide into 3 : 5-dinitrophenselenazine (annexed formula), which forms almost black, shining needles, m. p. 195—196°, and exhibits properties analogous to those of 3 : 5-dinitrophenothiazine (compare Kehrmann and Schild (A., 1900, i, 62). By careful

nitration or by the action of sodium nitrite and glacial acetic acid, this compound is converted into 3 : 5 : 9-trinitrophenselenazine (annexed formula), which forms a crystalline powder composed of opaque prisms, m. p. 220—223°. Like the corresponding substituted nitrophen-oxazines and -thiazines, these compounds form intensely-coloured sodium salts soluble in alcohol, that of the dinitrophenselenazine being violet and that of the trinitro-derivative blue.

Reduction of the above nitro-compounds by means of stannous chloride and hydrochloric acid leads to the double tin salts of amino-



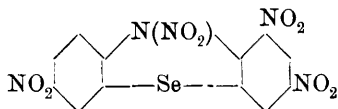
selenazines, which are converted by oxidation with ferric chloride into the selenazine colouring matters, and must be regarded as phenaz-selenonium salts of ortho-quinonoid structure.



3:5-Diaminophenazselenonium chloride (annexed formula) forms long, dark green needles (+ 3H<sub>2</sub>O), giving a greenish-brown aqueous solution. The corresponding *nitrate*, *dichromate*, and *platinichloride* are sparingly soluble. Sodium hydroxide precipitates the base in red flocks,

dissolving in ether to an orange solution. Concentrated sulphuric acid dissolves the colouring matter with formation of a brown coloration, red by transmitted light; addition of a trace of water gives a deep green solution, whilst more water yields a brown, discoloured liquid. Tannin-mordanted cotton is dyed olive-brown.

3:5:9-Triaminophenazselenonium chloride, C<sub>12</sub>H<sub>11</sub>N<sub>4</sub>SeCl, 1½H<sub>2</sub>O, forms metallic-green needles, giving a violet solution in hot water. Tannin-mordanted cotton is dyed violet of a bluer tint than that given by the corresponding thionium chloride. Sodium hydroxide precipitates the base in reddish-brown flocks, sparingly soluble in ether to a reddish-brown solution. The colouring matter dissolves in concentrated sulphuric acid with development of a dark blue coloration, changing to brownish-green and then to violet on continued addition of water, the colouring matter being ultimately precipitated. The corresponding



*nitrate*, *dichromate*, and *platinichloride* are only sparingly soluble.

3:5:9-Trinitrophenazselenazine (annexed formula), obtained on nitrating 3:5-dinitrophenazselenazine in glacial acetic acid with excess of nitric acid, forms dark red, indistinct crystals, m. p. 182° with previous sintering, and on reduction and subsequent oxidation gives 3:5:9-triaminophenazselenonium chloride.

Like the corresponding oxazines and thiazines, the selenazine colouring matters rendered the trypanosomes blepharoplast-free.

T. H. P.

**Hydrazides and Azoimides of Organic Acids. XXVII.** Hydrazide and Azoimide of *m*-Nitro- and *p*-Bromo-hippuric Acid. THEODOR CURTIUS (*J. pr. Chem.*, 1914, [ii], 89, 481—507).—A continuation of previous work (compare A., 1902, i, 302, and earlier papers).

[With ROBERT RAILTON HALLAWAY.]—Ethyl *m*-nitrohippurate, prepared by esterifying the acid by the hydrogen chloride method (compare Franzen, A., 1909, i, 576), has m. p. 75°, and reacts with hydrazine hydrate in hot alcoholic solution, yielding *m*-nitrohippurylhydrazide, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO·NH·CH<sub>2</sub>·CO·NH·NH<sub>2</sub>, which crystallises with 1H<sub>2</sub>O in long, colourless needles and in the anhydrous condition has m. p. 159°. When shaken with benzaldehyde in hot aqueous solution the hydrazide forms a *benzylidene* derivative,

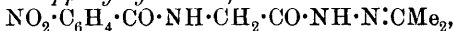


m. p. 189·5°; the *o*-hydroxybenzylidene derivative crystallises in slender,



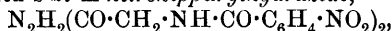
yellowish-white needles, m. p. 244°; the *cinnamylidene* derivative in slender, pale yellow needles, m. p. 233°.

*Acetone-m-nitrohippurylhydrazide*,



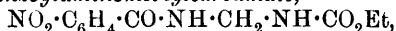
prepared by heating the hydrazide in acetone solution, has m. p. 192°.

When heated with benzophenone and alcohol at 120° the hydrazide yields *benzophenone-m-nitrohippurylhydrazide*, white leaflets, m. p. 129°, together with *s-di-m-nitrohippurylhydrazide*,



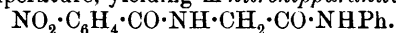
crystallising in slender leaflets which become brown at 240° and char at 270°. The latter compound is also produced by the addition of iodine to a hot alcoholic solution of *m-nitrohippurylhydrazide*. *m-Nitrohippurylazoimide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CON}_3$ , prepared by adding a solution of the hydrazide and sodium nitrite in aqueous sodium hydroxide to dilute acetic acid at a low temperature, separates as a yellow powder which suddenly decomposes at 74°, and explodes when rapidly heated. It slowly decomposes when kept, and dissolves in aqueous sodium hydroxide, yielding blood-red solutions.

*Ethyl m-nitrobenzoylaminomethylcarbamate*,



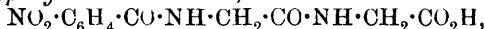
obtained by boiling an alcoholic solution of the preceding azoimide, crystallises in small, white leaflets, m. p. 170°, and is hydrolysed by acids to *m-nitrobenzoic acid*, ammonia, formaldehyde, carbon dioxide, and alcohol. The *methyl ester*, prepared in a similar manner, crystallises in leaflets, m. p. 181.5°; the *benzyl ester* forms slender, snow-white needles, m. p. 172.5°.

When boiled with water, the azoimide is converted into *s-di-m-nitrobenzoylaminomethylcarbamide*,  $\text{CO}(\text{NH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , m. p. 237°, which is accompanied by a small amount of a substance, m. p. 212—213°. The azoimide reacts with aniline in benzene solution at the ordinary temperature, yielding *m-nitrohippuranilide*,



This has m. p. 233—234°, and is also formed by heating *m-nitrohippuric acid* with aniline. If the interaction of the azoimide and aniline is carried out in boiling benzene solution, *phenyl-m-nitrobenzoylaminomethylcarbamide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , m. p. 213.5°, is produced. In a similar manner, *p-toluidine* gives rise to *m-nitrohippur-p-toluidide*, m. p. 206°, and *p-tolyl-m-nitrobenzoylaminomethylcarbamide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ .

*m-Nitrohippurylaminoacetic acid*,

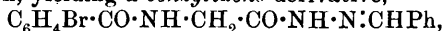


prepared by slowly adding aqueous sodium hydroxide to an alcoholic solution of *m-nitrohippurylazoimide* and aminoacetic acid, crystallises in slender, white needles, which become brown at 188°, m. p. 196° (decomp.).

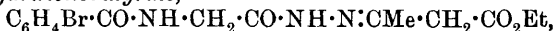
Hippuric acid may be obtained from benzoylazoimide and aminoacetic acid in a similar manner.

[With HEINRICH HEIL.]—*p*-Bromohippurylhydrazide (A., 1913, i, 897), prepared from ethyl *p*-bromohippurate and hydrazine hydrate in alcoholic solution, forms a *hydrochloride*, crystallising in lustrous,

silvery leaflets, m. p.  $261^{\circ}$ , and reacts with benzaldehyde in hot aqueous solution, yielding a *benzylidene* derivative,

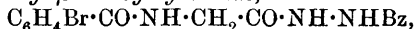


which crystallises in elongated leaflets, m. p.  $223^{\circ}$ . With acetone it yields *acetone-p-bromophenylhippurylhydrazide*, leaflets, m. p.  $215^{\circ}$ . When heated with ethyl acetoacetate, it gives rise to *ethyl  $\beta$ -p-bromohippurylhydrazonobutyrate*,



crystallising in slender, yellow needles (decomp.  $240\text{--}250^{\circ}$ , with previous sintering at  $175^{\circ}$ ). The latter compound is accompanied by a *substance*, m. p.  $118^{\circ}$ , together with *s-di-p-bromohippurylhydrazide*,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br})_2$ , which crystallises in small needles (decomp. above  $250^{\circ}$ ), and is also obtained by the addition of iodine to a hot alcoholic solution of *p-bromohippurylhydrazide*.

*$\alpha$ -p-Bromohippuryl- $\beta$ -benzoylhydrazide*,

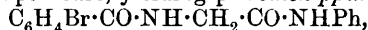


prepared by benzoylating the hydrazide in the presence of aqueous sodium hydroxide, forms microscopic needles, m. p.  $244^{\circ}$ . When boiled with alcohol, *p-bromohippurylazoimide* (*loc. cit.*) yields *thyl p-bromobenzoylaminomethylcarbamate*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , which crystallises in felted, silvery leaflets, m. p.  $171^{\circ}$ , and is also obtained by the interaction of alcohol and *p-bromobenzoylaminomethylcarbimide* (*loc. cit.*).

*Methyl p-bromobenzoylaminomethylcarbamate* forms lustrous, silvery needles, m. p.  $212^{\circ}$ .

*Di-p-bromobenzoylaminodimethylcarbamide*, prepared by heating *p-bromobenzoylaminocarbimide* with water, has m. p.  $261^{\circ}$ , and is hydrolysed by sulphuric acid to formaldehyde, carbon dioxide, ammonia, and *p-bromobenzoic acid*.

*p-Bromohippurylazoimide* reacts with aniline in benzene solution at the ordinary temperature, yielding *p-bromohippuranilide*,

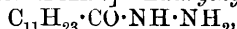


leaflets, m. p.  $233^{\circ}$ ; *p-bromohippur-p-toluidide* has m. p.  $220^{\circ}$ . If the interaction of aniline and the azoimide is carried out in boiling benzene solution and excess of aniline employed, *phenyl-p-bromobenzoylaminomethylcarbamide*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , is produced. This crystallises in slender, colourless needles, m. p.  $226\text{--}227^{\circ}$ .

F. B.

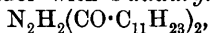
**Hydrazides and Azoimides of Organic Acids. XXVIII.** Hydrazide and Azoimide of Lauric, *p*-Nitro- and *p*-Chlorobenzoic Acids. THEODOR CURTIUS (*J. pr. Chem.*, 1914, [ii], 89, 508—535. Compare preceding abstract).—An account of the preparation of undecylamine, *p*-nitro- and *p*-chloro-benzylamine from lauric, *p*-nitrobenzoic and *p*-chlorobenzoic acids by the method indicated in the following scheme:  $\text{R}\cdot\text{CO}_2\text{Et} \rightarrow \text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 \rightarrow \text{R}\cdot\text{CO}\cdot\text{N}_3 \xrightarrow{\text{Et}\cdot\text{OH}} \text{R}\cdot\text{NH}\cdot\text{CO}_2\text{Et} \rightarrow \text{R}\cdot\text{NH}_2$ .

[With CHRISTIAN SCHÄTZLEIN.]—*Laurylhydrazide*,

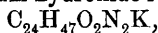


prepared by heating ethyl laurate (b. p.  $163^{\circ}/25\text{ mm.}$ ) with hydrazine

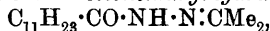
hydrate at  $130^{\circ}$ , crystallises in fatty leaflets of a silvery lustre, m. p.  $104.5^{\circ}$ , and forms with ethereal hydrogen chloride a *hydrochloride*, crystallising in long needles which sinter at  $140^{\circ}$ , m. p. about  $165^{\circ}$  (decomp.). When heated with benzaldehyde in alcoholic solution it yields a *benzylidene* derivative,  $C_{11}H_{23} \cdot CO \cdot NH \cdot N : CHPh$ , white needles, m. p.  $79^{\circ}$ , together with *s-dilaurylhydrazide*,



which separates from alcohol in small needles, m. p.  $149^{\circ}$ , and on treatment with alcoholic potassium hydroxide forms a *potassium salt*,

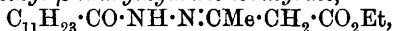


small needles, m. p.  $225^{\circ}$  (not sharp). The dilaurylhydrazide is best obtained by the action of iodine on the monohydrazide in hot aqueous-alcoholic solution. *Acetonelaurylhydrazone*,



prepared from the hydrazide and acetone, crystallises in spherical aggregates of small needles, sintering at  $75^{\circ}$ , m. p.  $88^{\circ}$ .

When heated with ethyl acetoacetate in alcoholic solution, laurylhydrazide yields *ethyl  $\beta$ -laurylhydrazonobutyrate*,



microscopic needles, m. p.  $75^{\circ}$ , together with 1-amino-2:5-diundecyl-1:3:4-triazole, m. p.  $142^{\circ}$ , which is readily obtained by heating laurylhydrazide at  $160^{\circ}$ , and has been previously described by Stollé and Schätzlein (A., 1904, i, 697) as a diundecyldihydrotetrazine.

*Benzoyl-laurylhydrazide*,  $C_{11}H_{23} \cdot CO \cdot NH \cdot NHBz$ , prepared by heating laurylhydrazide with benzoyl chloride, forms fatty flakes, m. p.  $95^{\circ}$ , with previous sintering at  $80^{\circ}$ . It is accompanied by dibenzoylhydrazide and *s-dilaurylhydrazide*.

*Laurylazoimide*,  $C_{11}H_{23} \cdot CO \cdot N_2$ , is obtained as an oil by the action of nitrous gases on an aqueous suspension of the hydrazide. In ethereal solution it reacts with ammonia and aniline, yielding the corresponding amide and anilide respectively. When boiled with methyl alcohol it is converted into methyl undecylcarbamate, m. p.  $45^{\circ}$  (compare Jeffreys, A., 1899, i, 730), which is hydrolysed by concentrated hydrochloric acid at  $110^{\circ}$  to undecylamine; *ethyl undecylcarbamate*,  $C_{11}H_{23} \cdot NH \cdot CO_2Et$ , has b. p.  $178^{\circ}/13$  mm., m. p. about  $30^{\circ}$ .

*s-Diundecylcarbamide*,  $CO(NH \cdot C_{11}H_{23})_2$ , prepared by slowly adding an ethereal solution of laurylazoimide to boiling water, crystallises in small, lustrous needles, m. p.  $105^{\circ}$ .

Undecylamine is most readily prepared by distilling the preceding carbamide or methyl undecylcarbamate with calcium hydroxide; the *hydrochloride*, *platinichloride*, yellow spangles (decomp.  $190^{\circ}$ ), and white amorphous *additive compound* with mercuric chloride are described.

[With FRIEDRICH WIENGREEN.]—Methyl *p*-nitrophenylacetate reacts with hydrazine hydrate at  $100^{\circ}$ , yielding *p-nitrophenylacetylhydrazide*,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$ , which crystallises in yellow needles having a magnificent satin lustre, m. p.  $167^{\circ}$ , and forms a *hydrochloride*, yellowish-white needles, m. p.  $251^{\circ}$  (decomp.); the *benzylidene* derivative,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH \cdot N : CHPh$ , crystallises in lustrous, white leaflets, m. p.  $202^{\circ}$  (decomp.); the *p-hydroxybenzylidene* derivative in yellowish-white needles, m. p.  $216^{\circ}$ .

*Ethyl β-p-nitrophenylacetylhydrazonobutyrate,*

prepared by shaking the hydrazide with ethyl acetoacetate in aqueous solution, has m. p. 148—149°, and when boiled with water loses nitrogen with the formation of a *substance*, m. p. 163°.

*s-Di-p-nitrophenylacetylhydrazide*,  $\text{N}_2\text{H}_2(\text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , obtained by the action of iodine on the monohydrazide in hot alcoholic solution, crystallises in yellow needles, m. p. 267—271°.

The monohydrazide is converted by the action of nitrous acid into *p-nitrophenylacetylazoimide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_3$ , m. p. 45° (decomp.), which reacts with boiling alcohol to form ethyl *p-nitrobenzylcarbamate*, m. p. 115—116°, and *s-di-p-nitrobenzylcarbamide* respectively.

The two last-named substances are hydrolysed by hydrochloric acid to *p-nitrobenzylamine* (compare Hafner, A., 1890, 486).

[With WILHELM KRAUTH.]—*p-Chlorophenylacetylhydrazide*, prepared from ethyl *p-chlorophenylacetate*, b. p. 253°/749 mm., and hydrazine hydrate in alcoholic solution, crystallises in long, colourless needles, m. p. 170°, and forms a *hydrochloride*, crystallising in long, slender needles, which begin to decompose at 100°, m. p. 150° (complete decomp.); the *benzylidene* derivative separates from dilute alcohol in rosettes of slender, white needles, m. p. 164°; the *p-hydroxybenzylidene* derivative crystallises in yellow needles, m. p. 224°. *Acetone-p-chlorophenylacetylhydrazone*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe}$ , forms lustrous, white leaflets, m. p. 143°; *ethyl β-p-chlorophenylacetylhydrazonobutyrate*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , minute, colourless needles, m. p. 128°.

The hydrazide reacts with iodine in hot alcoholic solution, yielding *s-di-p-chlorophenylacetylhydrazide*,  $\text{N}_2\text{H}_2(\text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Cl})_2$ , slender needles, m. p. 255°, and with nitrous acid to form *p-chlorophenylacetylazoimide*, which is converted by boiling with 85% alcohol into *ethyl p-chlorobenzylcarbamate*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , slender leaflets, m. p. 62°, and *s-di-p-chlorobenzylcarbamide*,  $\text{CO}(\text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Cl})_2$ , small, colourless needles, m. p. 225°. *p-Chlorobenzylamine*, prepared by hydrolysing the two last-named compounds with concentrated hydrochloric acid, has b. p. 215°/734 mm.; the hydrochloride and carbonate have m. p. 259° and 120° respectively (Jackson and Field, A., 1881, 804, give 239—241° and 114—115°); the *platinichloride*, crystallises in minute, pale yellow leaflets, m. p. 244°; the *aurichloride*, in lustrous, golden leaflets, m. p. 160°; the *benzoyl* derivative forms colourless needles, m. p. 140°.

F. B.

**Mode of Oxidation of Indigotin.** HUGO E. WAGNER (*J. pr. Chem.*, 1914, [ii], 89, 377—414).—In the estimation of indigotin by the titration of its disulphonic acid with potassium permanganate, the amount of the latter used is always less than the theoretical. In order to discover the cause of this discrepancy the author has undertaken a systematic examination of the oxidation of indigotindisulphonic acid under various conditions. He confirms the results of previous observers that the amount of permanganate used is, on the average, 12.6% less than the theoretical, and this remains constant up to dilutions of 1 : 4000—5000.

Addition of manganese sulphate to the indigotin solution slightly increases the amount of permanganate used. Experiments carried out in an atmosphere of carbon dioxide and of oxygen show that the results cannot be attributed to atmospheric oxidation of the indigotin solution.

The divergence from the theoretical value is less marked if a large amount of sulphuric acid is added, and the conclusion is therefore drawn that the water plays a part in the oxidation.

Addition of the indigotin solution drop by drop to the feebly acid permanganate solution gives almost theoretical results; rapid addition, however, yields too high values. Addition of isatin or isatinsulphonic acid to the indigotin solution also causes the amount of permanganate used to be in excess of the theoretical value.

The author attributes these discrepancies to the formation of an unstable oxide, derived from isatinsulphonic acid during the titration.

F. B.

**Some New Derivatives of Indigotin.** HERBERT LEVINSTEIN (*J. Soc. Chem. Ind.*, 1914, **33**, 574—575).—When indigotin (15 parts) is suspended in nitrobenzene and treated with bromine (32 parts) and sulphur (1·8 parts), or the equivalent amount of selenium, arsenic, arsenious or arsenic oxides, for several hours at 180°, combination takes place. A bromoindigotin sulphide was thus prepared by Cassella & Co. (A., 1910, i, 438) and accorded the formula



which the author confirms, but the figures for selenium or arsenic were found to be considerably lower. Arsenic oxide is the most active of these agents. The shades of the dyes do not differ much from those of the corresponding simple brominated indigotins.

When 5-hydroxy-7-sulpho-2-naphthylglycine is slowly added to concentrated sulphuric acid at 100° and then heated to 170°, it is transformed into 5:5'-*dihydroxy*-7:7'-*disulphonaphthylindigotin*, which has a bronzy lustre and is dichroic. It absorbs four atoms of bromine in glacial acetic acid. It imparts a green shade to wool in a faintly acid bath, and also has an affinity for vegetable fibres. J. C. W.

**Indigo-like Colouring Matters.** P. FRIEDLÄNDER and F. RISSE (*Ber.*, 1914, **47**, 1919—1929).—The action of isatin chloride on *a*-naphthol yields 1-oxy-2:(2')-indoxyl-naphthalene and an isomeric dye, different only in the length of the chain of conjugated double linkings and not in its typical properties (compare Bezdzik and Friedländer, A., 1908, i, 673). This and similar phenomena with other dyes render probable the existence of a compound differing from indigotin by the insertion of the group :CH·CH: between the two symmetrical halves of the molecule, but possessing the typical colouring properties of the mother substance. Such a compound has been obtained by the condensation of indoxyl and glyoxal, and its sulphur and oxygen analogues are formed similarly by the action of glyoxal on oxythionaphthen and on cumaranone. These compounds resemble closely those without the C<sub>2</sub>H<sub>2</sub> group, and the first two are normal vat dyes giving tints differing little from those of indigotin and "thioindigo." A compound similar to "thioindigo," but containing a still longer

chain of conjugated linkings is obtained by condensation of oxythionaphthen and maleic dialdehyde, and this also resembles "thio-indigo," but is appreciably less stable.

The dye previously obtained by Friedländer and Kielbasinski by the condensation of oxythionaphthen and oxythionaphthaldehyde (A., 1911, i, 1021), has also been prepared by treating thiosalicylic acid in alkaline solution with dichloroacetone, condensing the acetonyl-bis-*o*-thiolbenzoic acid thus formed to 3:3'-dihydroxydithionaphthen ketone and reducing the latter, the carbinol probably yielded in this way losing the elements of water spontaneously and giving the dye mentioned. The same compound is obtained on treating oxythionaphthen with sodium hydroxide and chloroform. Unsuccessful attempts were made to convert the connecting carbon atom chain, C·CH·C, of this compound into C:C:C, the only oxidation product obtained being "thioindigo."

The colours given by such dyes containing increasingly long chains of conjugated double linkings are displaced more and more towards the yellow. The absorption spectra measured in xylene solution by Formánek fail to indicate any relation between the position of the sharp absorption bands of the visible spectrum and the constitution. The insertion of C<sub>2</sub>H<sub>2</sub> or ·CH·C<sub>6</sub>H<sub>4</sub>·CH· into the molecule of "thio-indigo" displaces the bands considerably towards the violet, whilst that of C<sub>4</sub>H<sub>2</sub> leaves their position almost unchanged. Spectroscopically the dye obtained from indoxyl and glyoxal differs inappreciably from indigotin, but as a vat dye it yields a redder colour.

With the exception of the cumaronone derivatives, which undergo profound decomposition, these dyes form normal vats with alkaline reducing agents, such as sodium hyposulphite and hydroxide. In these reduction products, as in indigo-white, the conjugated double linking is probably displaced, but they yield intense orange-yellow to orange-red solutions, so that the group ·CH·CH· intensifies the colour in the same way as ·CO· does.

The compound, C<sub>6</sub>H<sub>4</sub>  $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix}$  C:CH·CH:C  $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix}$  C<sub>6</sub>H<sub>4</sub>, prepared from indoxyl and glyoxal, forms compact, quadratic crystals of pronounced metallic lustre. Cold concentrated sulphuric acid dissolves it unchanged with formation of an olive-green coloration, which changes to greenish-blue on heating, when a sulphonic acid giving a blue solution in water is formed. Fuming sulphuric acid dissolves it to a turbid, reddish-violet solution, presumably with formation of a polysulphonic acid, which also yields a blue aqueous solution. With alkaline hyposulphite it gives an intense orange-yellow vat, which dyes textile fibres bluish-violet. Unlike indigotin, the dye is very sensitive to halogens, its solution in nitrobenzene being discoloured and finally decolorised by bromine vapour. It melts at a very high temperature and later sublimates and undergoes profound decomposition into purple vapour.

The compound, C<sub>6</sub>H<sub>4</sub>  $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix}$  C:CH·CH:C  $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix}$  C<sub>6</sub>H<sub>4</sub>, obtained from oxythionaphthen and glyoxal, forms red needles, and gives a bluish-violet solution in concentrated sulphuric acid, from which

water precipitates orange-red flocks; these are readily dissolved by alkaline hyposulphite to an intensely yellow solution, which in the air becomes covered with a cherry-red bloom. In solvents of high boiling points it gives orange-red solutions showing, unlike those of "thioindigo," no fluorescence.

The compound,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C:CH \cdot CH:C \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C_6H_4$ , prepared from cumaranone and glyoxal, forms needles, and begins to decompose at about  $120^\circ$ .

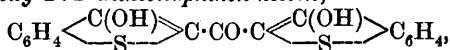
The compound,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} C:CH \cdot CH:CH \cdot CH:C \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} C_6H_4$ , obtained from oxythionaphthen and maleic dialdehyde, forms hair-like, reddish-brown needles. In concentrated sulphuric acid it forms a brownish-olive-green solution, becoming green on absorption of moisture, and depositing the unchanged dye in reddish-brown flocks on further dilution.

Indoxyl and maleic dialdehyde readily interact with formation of a dye, but no crystalline product could be separated.

The compound,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} C:CH \cdot C_6H_4 \cdot CH:C \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} C_6H_4$ , obtained from indoxyl and terephthalaldehyde, forms dark brownish-red needles, dissolving in concentrated sulphuric acid with an olive-brown coloration. Alkaline hyposulphite dissolves it, yielding an almost colourless solution, which in the air becomes covered with a cherry-red bloom. The isomeric *product* obtained from indoxyl and *o*-phthalaldehyde has similar properties.

The compound,  $C_{24}H_{14}O_2S_2$ , obtained from oxythionaphthen and terephthalaldehyde, forms orange-red needles, m. p. about  $220^\circ$  (decomp.), and yields an almost colourless vat dye, which colours paper pale blue and then orange-red. The dye,  $C_{24}H_{14}O_4$ , from cumaronone and terephthalaldehyde, forms lemon-yellow needles, and dyes paper an intense sky-blue, gradually changing to yellow in the air.

3 : 3'-Dihydroxy-2 : 2'-dithionaphthen ketone,



forms lemon-yellow needles, m. p.  $229^\circ$ , and its *diacetyl* derivative,  $C_{21}H_{14}O_5S_2$ , almost colourless needles, m. p.  $182^\circ$ .

The compound,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} C:CH \cdot C \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} C_6H_4$ , prepared by condensing indoxyl and oxythionaphthalenaldehyde in dilute alcohol by means of hydrochloric acid, forms brownish-red needles and its *sodium* salt, lustrous, cantharides-green needles.

*Acetylonylbis-o-thiolbenzoic acid*,



forms compact, colourless needles, m. p.  $217.5^\circ$  (decomp.), and its *ethyl* ester,  $C_{21}H_{22}O_5S_2$ , slender, white needles, m. p.  $102^\circ$ . T. H. P.

**Pyrimidines. LXX. Isomerism of 4-Phenylisocytosine.** TREAT B. JOHNSON and ARTHUR J. HILL (*J. Amer. Chem. Soc.*, 1914, 36, 1201—1209).—It has been shown by Jaeger (A., 1891, 1007) that guanidine carbonate reacts with ethyl benzoylacetate in alcoholic

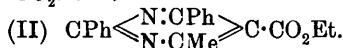
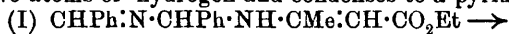
solution with production of 2-amino-4-phenyldihydro-6-pyrimidone (4-phenylisocytosine),  $\text{NH} \begin{smallmatrix} \text{C}(\text{NH}_2):\text{N} \\ \text{CO}-\text{CH} \end{smallmatrix} \text{CPh}$ , m. p. 294°. Warmington (A., 1893, i, 369) has stated that, in addition to this compound, an isomeric modification, m. p. 272°, is simultaneously formed, and that the two bases yield different hydrochlorides, but are both converted into 4-phenyluracil by hydrolysis with hydrochloric acid; he also found that the modification, m. p. 294°, can be transformed into that of m. p. 272° by heating it with alcohol or alcoholic ammonia at 180°.

This work has now been repeated, and the two isomerides were obtained. The product of higher m. p. (now designated the  $\gamma$ -modification) has been found to melt at 303°, instead of 294°, and the other (the  $\delta$ -modification) at 279–280°, instead of 272°. It has been found that both isomerides yield the same hydrochloride,  $\text{C}_{10}\text{H}_9\text{ON}_3\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , m. p. 266° (decomp.). The  $\gamma$ -modification is the stable form, and is obtained by decomposing the hydrochloride with alkali hydroxide. The  $\delta$ -form is transformed into the  $\gamma$ -form by the action of hydrochloric acid, and a mixture of the two modifications melts at the same temperature as the  $\gamma$ -modification, namely, 303°.

When the reaction between guanidine and ethyl benzoylacetate takes place in presence of sodium ethoxide, an entirely different modification of 4-phenylisocytosine is obtained. This  $\alpha$ -form, m. p. 279–280°, on recrystallisation from alcohol, is transformed into a fourth modification, the  $\beta$ -form, m. p. 303°. The  $\alpha$ - and  $\beta$ -forms are both stable in presence of alkali hydroxide, and can be reprecipitated from alkaline solutions by addition of hydrochloric acid. They both furnish the same hydrochloride as is given by the  $\gamma$ - and  $\delta$ -forms, or, in other words, they are both converted by hydrochloric acid into the hydrochloride of the  $\gamma$ -modification. On decomposing the hydrochloride with ammonia the  $\gamma$ -form is produced.

It is considered not improbable that the existence of the four isomerides is a unique case of physical isomerism. E. G.

**A Synthesis of Substituted Pyrimidines.** YASUHIKO ASAHINA and ETSUO KURODA (*Ber.*, 1914, 47, 1815–1820).—Lachowicz (A., 1897, i, 118) isolated as the primary product in the condensation of ethyl acetoacetate with benzaldehyde and ammonia, “ethyl hydrobenzimidooacetoacetate” (I.). The same compound separates at once when ethyl benzylideneacetoacetate and alcoholic ammonia are mixed, hydrolysis of the former being the first step in the process. When the compound is treated with permanganate in cold acetone it loses two atoms of hydrogen and condenses to a pyrimidine derivative (II.).



The primary product in the condensation of ethyl benzoylacetate with benzaldehyde and ammonia behaves similarly.

The compound (I) forms a *picrate*,  $\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3\cdot\text{H}_2\text{O}$ , m. p. 220–225° (decomp.). *Ethyl 2:4-diphenyl-6-methylpyrimidine-5-carboxylate* (II.) forms white needles, m. p. 76°, and is but feebly basic. The free *acid* crystallises in colourless, hexagonal leaflets, m. p. 207–209° (decomp.),

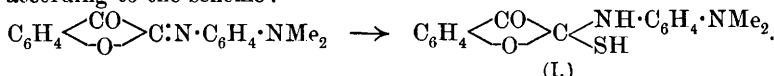


and loses carbon dioxide on distillation, yielding 2 : 4-diphenyl-6-methylpyrimidine,  $N \begin{smallmatrix} \text{CPh} \text{---} \text{N} \\ \text{CMe} \text{:} \text{CH} \end{smallmatrix} \text{CPh}$ , which forms rhombic leaflets, m. p. 94°.

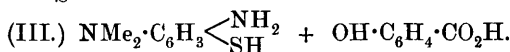
A mixture of ethyl benzoylacetate, benzaldehyde, and ammonia gradually deposits the compound,  $C_{25}H_{24}O_2N_2$ , which crystallises from alcohol in slender prisms, m. p. 136°, another form of the same substance, m. p. 194°, separating from the mother liquor on keeping. The *picrate* has m. p. 275—278°. The oxidation product, namely, ethyl 2 : 4 : 6-triphenylpyrimidine-5-carboxylate, forms pale yellow, prismatic needles, m. p. 99—100°, and the free acid,  $C_{23}H_{16}O_2N_2$ , slender, glistening needles, m. p. 229°, yields 2 : 4 : 6-triphenylpyrimidine, which crystallises in colourless, slender needles, m. p. 185—186°.

J. C. W.

**Derivatives of 1-Coumaran-2-dihydrobenzthiazolespiran.** K. FRIES, A. HASSELBACH, and L. SCHRÖDER (*Ber.*, 1914, **47**, 1640—1645).—The failure to obtain "oxindigo" by the action of ammonium sulphide on 1-*p*-dimethylaminoanilcoumaran-2-one (A., 1911, i, 150) has led the authors to try the effect of hydrogen sulphide. This agent is absorbed with the formation of a mercaptan, according to the scheme :



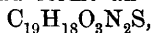
The new compound is easily oxidised to a bright red substance, which cannot be a disulphide or have a quinonoid character, since it cannot be reduced, and forms an acetyl derivative. The molecular weight and analysis agree with the spiran structure (II), and the formation of salicylic acid and 2-thiol-*as*-dimethyl-*p*-phenylenediamine (III), on hydrolysis, confirms this constitution :



Hydrogen sulphide was passed into the hot, dark red solution of 1-*p*-dimethylaminoanilcoumaran-2-one, when the colour faded and a mass of reddish-yellow crystals separated. 1-thiol-1-*p*-dimethylaminoanilincoumaran-2-one (I) has m. p. 148°, dissolves easily in dilute sodium hydroxide and slowly in sodium carbonate, and forms a *hydrochloride*. When an alkaline solution is shaken with methyl sulphate, the products are methylmercaptan and the original anil. The alkaline solutions are slowly oxidised in the air, quickly by potassium ferrieyanide, when 2[2-coumaranone]2-[6-dimethylamino-dihydrobenzthiazole]spiran (II) separates in brilliant red flocks. The latter compound crystallises in long, red, sparkling needles, m. p. 175°, and forms a sulphate, *hydrochloride* and *methiodide*,  $C_{17}H_{17}O_2N_2IS$ , all of which are yellow.

Starting with the anil of 6-methylcoumaranone, analogous derivatives were prepared by the same means. 1-thiol-5-methyl-1-*p*-dimethylaminoanilincoumaran-2-one,  $C_{17}H_{18}O_2N_2S$ , forms yellow needles, m. p. 173° (decomp.). 2-[5-Methyl-2-coumaranone]2-[6-dimethylamino-

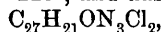
*dihydrobenzthiazole*]spiran,  $C_{17}H_{16}O_2N_2S$ , crystallises in soft, glistening, red needles, m. p. 197°, and forms an *acetyl* derivative,



which exists in labile yellowish-red leaflets and stable dark red needles, m. p. 155°, and a golden-yellow *methiodide*. The products of hydrolysis by alcoholic potassium hydroxide at 170—180° were  $\gamma$ -cresotic acid and aminodimethylanilinomercaptan (Bernthsen, A., 1889, i, 775).

J. C. W.

**Tri-indylmethane Dyes. IV.** ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1914, 91, 15—20. Compare A., 1912, i, 587; Scholtz, A., 1913, i, 1227).—The dye from indolealdehyde and chloromethylindole previously described can be obtained from its leuco-compound by treating the *sulphate* (m. p. about 215°) with ammonia; it has m. p. 222—225°, and has the composition



corresponding with the carbinol-base of a tri-indylmethane dye. This makes it probable that the dye similarly prepared from methylindolealdehyde and methylindole is of analogous constitution (compare Scholtz, *loc. cit.*). It is possible that the dyes obtained by Scholtz and by König are not identical with those of the present authors, especially as the conditions of their preparation are not the same.

R. V. S.

**Preparation of Phenylglycocycamidines and Their Behaviour Towards Alkalis, as Well as Experiments on the Changes Produced in Creatinine by Dilute Alkali.** ALEXANDER ELLINGER and ZENJI MATSUOKA (*Zeitsch. physiol. Chem.*, 1914, 89, 441—455).—When an alcoholic solution of phenylglycine and cyanamide is heated on the water-bath, 2:5-diketo-1:4-diphenylpiperazine is formed, and, in small quantity, *phenylglycocycamine*,  $HN:C \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NPh} \cdot \text{CH}_2 \end{smallmatrix}$ , which crystallises in colourless leaflets, becomes coloured at 220° and melts at 227—228° (decomp.) when slowly heated, at 235—236° (decomp.) when rapidly heated. The substance gives reactions like creatinine with sodium nitroprusside and with alkali and picric acid. The *picrate*,  $C_9H_9ON_3 \cdot C_6H_3O_7N_3$ , has m. p. 203°. The cycamine forms a crystalline salt with zinc chloride. Efforts to prepare phenylglycocycamine either directly or from the cycamine were unsuccessful. In the latter case hydantoins were formed however cautiously hydrolysis was effected. Colorimetric experiments showed that the same change takes place, but to a much smaller extent, when creatinine is treated with alkalis. A repetition of Ackermann's experiment (A., 1913, i, 1049) in the absence of bacteria led to the formation of methylhydantoin, so that the decomposition is not necessarily bacterial.

Phenylglycocycamine subcutaneously administered is excreted, like creatinine, unchanged.

Repeating Ramsay's experiment with guanidine and phenylbromoacetic acid, the authors obtained, not the acid stated by that author,

but its *lactam*,  $HN:C \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CHPh} \end{smallmatrix}$ , which forms colourless needles,

m. p. 314—315° (becoming slightly brown at about 300°). It does not give Jaffe's reaction. The *nitrate* has m. p. 160°. The substance is identical with that prepared by fusion of guanidine carbonate with phenylaminoacetic acid.

R. V. S.

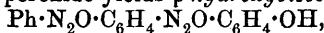
**Preparation of Triphenyltriazole.** M. BUSCH (*J. pr. Chem.*, 1914, [ii], 89, 552).—In a recent paper (this vol., i, 585) Busch and Schneider have stated that 3:4:5-triphenyl-1:2:4-triazole is not produced when dibenzoylhydrazide is heated with aniline under the conditions given by Pellizzari and Alciatore (A., 1901, i, 571). It is now found that a small amount of the triazole is formed if the mixture is heated for six hours at 250°. If the hydrazide is heated with excess of aniline in the presence of phosphoric oxide a 90% yield of the triazole is obtained.

F. B.

**Azoxyphenols.** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 557—570).—When the acetyl derivative of *p*-hydroxyazobenzene,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ , is heated on the water-bath with hydrogen peroxide in glacial acetic acid solution, a product is obtained which crystallises in yellowish-white needles, m. p. about 81°, and has the composition of the *acetyl* derivative of *p*-hydroxyazoxybenzene,  $\text{Ph}\cdot\text{N}_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ . On saponification it yields *p*-hydroxyazoxybenzene, m. p. 148°, but this can be separated by recrystallisation into the two possible isomerides, of which  $\alpha$ -*p*-hydroxyazoxybenzene has m. p. 156°, identical with that of Bamberger (A., 1902, i, 506), and  $\beta$ -*p*-hydroxyazoxybenzene has m. p. 107°. The *acetyl* derivatives of the two substances have m. p. 89° and 73°, and the *ethyl ethers*, m. p. 72° and 75°, respectively. Direct oxidation of *p*-hydroxyazobenzene yields identical products.

Oxidation of 4'-bromo-4-hydroxyazobenzene with hydrogen peroxide yields the corresponding *azoxy*-compound,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , a yellow, crystalline powder, m. p. 156°, as well as a yellow *substance*, decomposing at about 260°. The *ethyl ether* of the *azoxy*-compound,  $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_2\text{Br}$ , forms small, yellow needles, m. p. 123°. When the *ethyl ether* is reduced with aluminium amalgam and the product oxidised with mercury oxide, the *ethyl ether*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , is formed; it crystallises in golden-yellow laminæ, m. p. 136°, and is identical with that obtained by ethylating 4'-bromo-4-hydroxyazobenzene.

Oxidation of *p*-hydroxybisbenzeneazobenzene (Angeli, A., 1913, i, 658) with hydrogen peroxide yields *p*-hydroxybisbenzeneazoxybenzene,



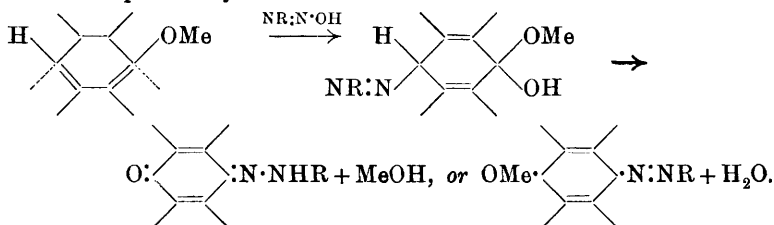
which forms lemon-yellow crystals, m. p. 185°. The *ethyl ether* of this compound, m. p. 125°, is identical with that obtained (as previously described) by oxidation of the ether,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ . From the mother-liquor of the compound of m. p. 185°, a *substance*, also of the formula  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_4$ , m. p. 200°, and also a *substance*,  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_4$ , crystallising in yellow needles, m. p. about 175°, can be isolated; both are soluble in alkalis.

R. V. S.

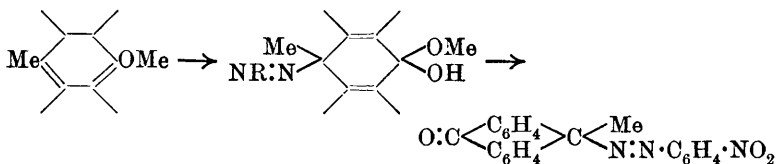
**The Coupling of Phenols and Phenolic Ethers with Diazo-compounds.** KURT H. MEYER, ALFRED IRSCHICK, and HANS SCHLÖSSER (*Ber.*, 1914, 47, 1741—1755).—It has recently been shown

(Meyer and Lenhardt, A., 1913, i, 723) that contrary to the generally accepted idea (compare Dimroth, A., 1907, i, 662), not only phenols, but phenolic ethers, can couple with diazo-compounds, the products being alkyloxyazo-compounds. Investigation now proves that, generally speaking, the introduction of negative substituents into the diazo-compounds increases their activity towards coupling with phenolic ethers; thus the diazo-compound derived from 2:4-dinitroaniline couples readily with anisole and phenetole, and immediately with the ethers of resorcinol and  $\alpha$ -naphthol, whilst the nitrobenzenediazonium compounds do not couple with the latter class of substance, although they do so easily with the former class, and benzenediazonium salts couple still less readily. On the other hand, the introduction of negative groups into the phenolic ethers diminishes their tendency to coupling, whilst positive radicles, especially alkyloxy- and alkyl groups, in the meta-position, increase the tendency (compare Auwers and Michaelis, this vol., i, 744).

In some cases the coupling of diazo-compound and alkyloxy-compound leads, not only to the alkyloxyazo-derivative, but also to the free hydroxyazo-substance, for example, the diazo-compound of dichloroaniline and  $\beta$ -naphthol ether gave approximately 20% of the alkyloxy-compound, the chief product being the hydroxyazo-compound, whilst in other cases the hydroxyazo-substance formed the sole product. This result is explained by the scheme :



In accordance with this view, which regards the coupling as a case of addition at a double bond, it is found that 2:4-dinitrodiazobenzene condenses with furyl alcohol, and also that the methyl ether of 9-methylanthranol, which possesses no "active" hydrogen in the ortho- or para- positions, can couple with *p*-nitrobenzenediazonium hydroxide according to the representation :



the product being the first example of a new type of azo-compound.

Although the above view as to the course of the coupling of diazo-compounds is developed only with alkyloxy-compounds, the change is almost certainly of the same nature for the hydroxy-compounds, because the relative reactivity of the hydroxy-compounds falls in the same order as that of the corresponding alkyloxy-derivatives. Finally, it is

shown that unsaturated hydrocarbons, such as styrene, which can scarcely be regarded as containing active hydrogen, are also able to condense with diazo-compounds, although the reaction is not smooth and the products could not be obtained pure.

*p*'-2:4-Dinitrobenzeneazoisole forms orange-red needles, m. p. 178°; it was also prepared by methylating 2:4-dinitrobenzeneazophenol.

*p*'-2:4-Dinitrobenzeneazophenetole forms orange-red needles, m. p. 165°.

2:4-Dinitrobenzeneazoresorcinol diethyl ether forms deep red needles, m. p. 172°.

*m*-Nitrobenzeneazoresorcinol dimethyl ether, orange-red needles, m. p. 188.5° (decomp.).

4-*m*-Nitrobenzeneazo- $\alpha$ -naphthyl ethyl ether had m. p. 145—146° (decomp.); in its preparation it was accompanied by a smaller quantity of 4-*m*-nitrobenzeneazo- $\alpha$ -naphthol, m. p. 288° (decomp.).

*p*-Bromobenzeneazo- $\alpha$ -naphthyl ethyl ether formed yellow crystals, m. p. 155°.

4-*m*-Bromobenzeneazo- $\alpha$ -naphthyl ethyl ether, brown needles, m. p. 115°.

2:4-Dichlorobenzeneazoresorcinol dimethyl ether, orange-yellow crystals, m. p. 126°.

2:4-Dichlorobenzeneazo- $\alpha$ -naphthyl ethyl ether, m. p. 138—139°.

2:4:6-Tribromobenzeneazoresorcinol dimethyl ether, red crystals, m. p. 147°.

2:4:6-Tribromobenzeneazo- $\alpha$ -naphthyl ethyl ether, deep red needles with bluish glance, m. p. 129—130°.

2:4-Dinitrobenzeneazo- $\alpha$ -naphthol, obtained by coupling diazotised dinitroaniline with either naphthyl phenyl ether or naphthol, forms yellow crystals, m. p. 278°, giving a deep blue solution in alkalis, and a bluish-red in sulphuric acid; 2:4-dinitrobenzene-4'-azo- $\alpha$ -naphthyl phenyl ether, which accompanies the preceding substance, when prepared by the first method forms red needles with a bluish lustre, m. p. 212°, soluble in sulphuric acid to a deep blue colour.

Anthranol methyl and ethyl ethers reacted with *p*-nitrobenzene-diazonium hydroxide, giving only nitrobenzeneazanthranol, the alkyl groups having undergone scission. 9-Methylanthranol methyl ether, m. p. 147°, when treated in acetic acid with an acetic acid solution of sodium nitrophenylnitrosoamine gave 9-*p*-nitrobenzeneazo-9-methylanthrone,

$$\text{O}:\text{C} < \begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C} < \begin{matrix} \text{Me} \\ \text{N}:\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{matrix}$$
 orange-coloured leaflets, m. p. 99° (decomp.). The corresponding ethyl derivative forms monoclinic prisms ( $a:b:c = 1.2304:1:0.9850$ ;  $\beta = 96.2^\circ$ ), m. p. 121° (decomp.).

The additive compound of dinitrobenzenediazonium hydroxide and furyl alcohol, which contained equimolecular proportions of the components, formed a yellowish-brown powder, m. p. 167° (decomp.).

When treated with diazotised nitroaniline, isoprene gave a mixture of two substances, one brown, m. p. 145°, the other black, m. p. 251°. Substances were also obtained by the action of dinitrobenzenediazonium sulphate on anthracene, mesitylene, pinene, limonene, and acenaphthene.

The general method of procedure in the preparation of the preceding substances was to work with solutions of the reagents in acetic acid.

It was found that, on keeping, the acetic acid solution of diazotised 2:4-dinitroaniline deposits a red, crystalline substance,  $C_{18}H_{12}O_{10}N_{10}$ , prisms, m. p. above  $280^{\circ}$ .

In boiling toluene solution, styrene and nitrosodimethylaniline slowly condense together, giving a brown substance,  $C_{24}H_{26}ON_4$ , m. p.  $110^{\circ}$  (decomp.).  
D. F. T.

**Constitution of the Bisazophthaleins and of the Coloured Salts of Phenolphthalein.** P. SCHESTAKOV and TH. NOCKEN (*Ber.*, 1914, 47, 1903—1907).—Reply to Oddo's criticisms (this vol., i, 601) of the authors' results (this vol., i, 335).  
T. H. P.

**The Combination of Proteins with Metallic Salts. The Behaviour of Protein Solutions in a Magnetic Field.** A. BENEDICENTI (*Biochem. Zeitsch.*, 1914, 63, 276—286).—The diminution of the diamagnetic value of solutions produced by the addition of ferric chloride to water and serum (5 c.c. of serum + 5 c.c. of water) was measured. When added to water the gradual addition of iron produces a continual diminution of this value, which is almost a linear function of the amount of the metal added. The first additions of iron to the protein solutions, produce, however, only a small fall; larger additions produce a gradual fall, which, when plotted graphically, falls nearly on a straight line, parallel with that representing the diamagnetic change when the iron salt is added to pure water. It is suggested that by the measurement of diamagnetic changes, the combination of proteins with metals can be studied.  
S. B. S.

**The Relationship of the Oxydones to the Proteins.** F. BATTELLI and L. STERN (*Biochem. Zeitsch.*, 1914, 63, 369—378).—In the case of the majority of anæsthetics, there is a very marked parallelism between their capacity of precipitating nucleoproteins and their power of producing an irreversible destruction of the phenylene-diamine oxydone, which is more complete at  $40^{\circ}$  than at  $15^{\circ}$ . At the higher temperature the concentrations necessary to produce these actions is smaller than at the lower temperature. The authors do not agree with the suggestion that the anæsthetics destroy the oxydones owing to their action on the lipoids; the action, they assume, is due rather to their effect on the insoluble proteins.  
S. B. S.

**Oxyproteic Acids.** P. GLAGOLEV (*Zeitsch. physiol. Chem.*, 1914, 89, 432—440).—These substances are of the nature of polypeptides, for they possess a definite number of amino-groups which increases on hydrolysis. The amino-acid nitrogen (estimated by van Slyke's method) amounts to 44.3% of the total nitrogen. Most (80%) of the nitrogenous products obtained on hydrolysis of oxy- or alloxy-proteic acid are not precipitated by phosphotungstic acid. Both acids contain arginine and cystine. The hydrolysis with 25% hydrofluoric acid (Hugounenq and Morel, A., 1909, i, 195, 685) has the advantages that melanines are not produced, and the formation of ammonia is less than when hydrochloric acid is employed.  
R. V. S.

**The Blood Pigment.** HANS FISCHER and K. EISMAYER (*Ber.*, 1914, 47, 1820—1828).—The authors have submitted a relatively large quantity of crude hæmopyrrole oil to fractional precipitation by picric acid (compare Willstätter and Asahina, A., 1912, i, 41), and have obtained as the only constituent pyrroles, hæmopyrrole, phyllopyrrole, cryptopyrrole, and Piloty and Stock's "hæmopyrrole-a" (A., 1912, i, 924), the latter being the only one which does not form a picrate. The yields obtained, calculated on the original hæmin, were 8·8%, 1%, 2·7%, and 0·75% respectively. The last-named pyrrole was established as 3-methyl-4-ethylpyrrole by conversion into 3-methyl-2:4:5-triethylpyrrole, which was also synthesised. The constitution of the main constituents of hæmopyrrole oil is therefore firmly established.

The first fraction obtained by adding a 10% ethereal solution of picric acid to 64·5 grams of the mixed bases gave 60 grams of pure hæmopyrrole (2:3-dimethyl-4-ethylpyrrole) picrate, m. p. 124°. The next fraction yielded nearly 20 grams of pure cryptopyrrole (2:5-dimethyl-4-ethylpyrrole) picrate, m. p. 138—139°, and 15·6 grams of the above picrate, m. p. 124°. The third fraction, obtained by evaporating the ether and adding light petroleum, could not be purified by crystallisation, but the base was liberated and distilled, when 3·2 grams of pure phyllopyrrole (2:3:5-trimethyl-4-ethylpyrrole), b. p. 95—96°/15 mm., was obtained. The distillate solidified and was pressed between filter papers until Ehrlich's reaction for tri-substituted pyrroles was negative. The remaining base (1·7 gram) had b. p. 75—80°/15 mm., and yielded methylethylmaleimide on oxidation. It was heated with potassium and alcohol in a sealed tube, when the new base gave a picrate, m. p. 102—103°, and was identified with 3-methyl-2:4:5-triethylpyrrole (below). Success was also achieved by this method of separation when working on only 20 grams of hæmin.

[*Synthesis of 3-methyl-2:4:5-triethylpyrrole.*]—Dipropionylmethane (A., 1912, i, 646) and oximinomethyl propyl ketone were dissolved in glacial acetic acid and stirred with zinc dust, when 4-propionyl-3-methyl-2:5-diethylpyrrole was obtained, in colourless prisms, m. p. 100—101°. This was heated to 100° with about 70% sulphuric acid, and thus converted into 3-methyl-2:5-diethylpyrrole, b. p. 94—95°/15 mm., which coupled with diazobenzenesulphonic acid to give a 2-azo-dye,  $C_{15}H_{20}O_3N_3S$ , pale brownish-red needles, and also formed a picrate, m. p. 90—91°. Finally, a third ethyl group was introduced by the action of alcohol and potassium in an autoclave. 3-Methyl-2:4:5-triethylpyrrole,  $NH < \begin{matrix} CET:CM_e \\ CET:C\acute{E}t \end{matrix}$ , has b. p. 104—110°/15 mm., and the picrate has m. p. 103°.

J. C. W.

**Iron in Blood. III. Iron Absorption Bands.** H. W. FISCHER and GISEBERT (FREIHERR) VON ROMBERG (*Zeitsch. physikal. Chem.*, 1914, 87, 589—598. Compare A., 1912, ii, 269, 924).—A number of absorption spectra of iron sulphide sols in alkaline glycerol-water solution have been photographed and compared qualitatively with the absorption spectrum of hæmoglobin which has been treated in alkaline

solution with dilute ammonium sulphide. From the similarity of the absorption spectra of the two substances, the authors draw the conclusion that the sulphur in hæmoglobin is similarly bound to the iron as the sulphur is to the iron in the red iron sulphide glycerol sol.

J. F. S.

**Bromohæmins. I.** WILLIAM KÜSTER and KARL REIHLING (*Zeitsch. physiol. Chem.*, 1914, 91, 115—150. Compare Küster and Greiner, A., 1913, i, 1005).—A bromodimethylacethæmin,  $C_{36}H_{36}O_4N_4FeBr$ , can be prepared from bromoacethæmin, dehydrobromoacethæmin and from chlorodimethylhæmin, but it is doubtful whether the dimethylated substance is a direct derivative of unmethylated hæmin. When chloroacethæmin is treated with methyl alcohol and hydrogen bromide, the chlorine is completely displaced by bromine, but a dimethyl-derivative is not obtained.

The employment of Mörner's process with ox blood yields chiefly a mixture of bromodimethylhæmin and bromomonomethylhæmin which crystallises in cubes. Horse blood yields unmethylated hæmin, which also crystallises in cubes. These substance cannot be treated by the acetic acid method without losing bromine, and they cannot be completely dimethylated. When this is attempted an unstable compound or mixture of bromodimethyl- and bromomonomethyl-hæmin is formed. If in the methylation hydrogen bromide is replaced by hydrogen chloride, the bromine is displaced by chlorine, but complete methylation is not obtained. Similar observations are made in the methylation of bromoacethæmin by means of methyl alcohol and hydrogen chloride.

Dehydrobromohæmin, prepared from Mörner's bromohæmin, can be dimethylated by the alcohol method. The product differs from bromoacethdimethylhæmin in that it loses bromine when treated with 1% sodium hydroxide.

Dehydrobromoacethæmin ( $\alpha$ -hæmin) forms a colloidal solution in 5% sodium carbonate, and may be converted by the acetic acid method into chloroacethæmin, but not into bromoacethæmin. Mörner's dehydrobromohæmin ( $\beta$ -hæmin) dissolves in 5% sodium carbonate solution, and when treated by the acetic acid method does not combine either with hydrogen chloride or with hydrogen bromide.

$\alpha$ -Dehydrobromohæmin when treated with alkalis appears to take up water with more difficulty than the  $\beta$ -form.

From ox blood two bromomonomethylhæmins can be prepared; one is soluble, the other insoluble, in 5% sodium carbonate solution.

In regard to nomenclature, the authors propose Mörner's original term  $\beta$ -hæmin for the hæmin prepared by his process, whilst for that prepared by Schalféev's method, instead of the term acethæmin the name  $\alpha$ -hæmin should be employed. The analytical results obtained in respect of the products described in this paper all concord with the formula  $C_{34}H_{32}O_4N_4BrFe$  for both  $\alpha$ - and  $\beta$ -bromohæmins. R. V. S.

**Bromomesoporphyrin and the Reduction of Blood and Bile Pigments in the Presence of Colloidal Palladium.** H. FISCHER and A. HAHN (*Zeitsch. physiol. Chem.*, 1914, 91, 174—183).



—When mesoporphyrin is treated with hydrogen bromide and bromine in acetic acid solution, a *bromomesoporphyrin* is deposited in violet crystals. It readily loses bromine, so that the analytical results lie between those required by the tri- and tetra-bromomesoporphyrins, but it is probably similar to the tetrachloro-compound previously described (Fischer and Röse, A., 1913, i, 1006). A *bromo-derivative of mesoporphyrin diethyl ester* was also prepared.

Hæmin prepared from the blood of carp yields hæmatoporphyrin, so that there is no reason to suppose that mesohæmin occurs in fishes.

Hæmin is reduced by hydrogen in the presence of colloidal palladium, the unsaturated side-chains being attacked, for, after subsequent oxidation, methylethylmaleinimide can be isolated. Bilirubin, when treated in the same way, yields the same product, as well as a yellow, crystalline *substance* which does not give the Ehrlich aldehyde reaction.

Hæmin, mesohæmin, hæmatoporphyrin and porphyrinogen kill frogs when injected subcutaneously. This is remarkable, because the protein part of the blood pigment molecule is also poisonous, whilst hæmoglobin is not. R. V. S.

*b*-Nucleic Acid. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1914, 91, 165—173).—Sodium *b*-nucleate is best prepared by keeping sodium *a*-nucleate, first for some hours at 60°, then for twenty-four hours at 100°, and finally for four days at 110°. From it, free *b*-nucleic acid can be prepared with the aid of crystal-violet (A., 1913, i, 661). It is shown that the best criterion of purity for the nucleic acids, which are apt to be contaminated with their own decomposition products, lies in the determination of the ratio of total nitrogen to total phosphorus, which is always lower than the theoretical value (1.70) in such cases.

The conversion of sodium *a*-nucleate into *b*-nucleate can be followed by observations of the melting point of the gelatinised solution of known strength (5%). Such a gel of *a*-nucleate melts at 60° or 70°, and the m. p. gradually falls until it lies below room temperature, when *b*-salt is chiefly present. The conversion can be brought about by heating with water, normal sodium carbonate solution or 20% sodium acetate solution, and the change is associated with a loss of water. When it is effected, as above described, by mere heating, a continuous loss of water takes place, both before and after the transformation begins. R. V. S.

The Degradation of Chondroitin-sulphuric Acid to Crystalline Products. I. Chondridin and Chondrosin Ethyl Ester Hydrochloride. JOSEF HEBTING (*Biochem. Zeitsch.*, 1914, 63, 353—358).—Chondroitin-sulphuric acid was hydrolysed by oxalic acid solution in the presence of barium oxalate. The concentrated solution of the product was then thrown into alcohol. A white precipitate containing a mixture of substances is thereby obtained. On treating this with hydrochloric acid and alcohol, *chondrosin ethyl ester hydrochloride*,  $C_{14}H_{26}O_{11}NCl$ , is obtained, having  $[\alpha]_D + 34.8^\circ$ . It is very

hygroscopic and reduces Fehling's solution. On addition of ether to the filtrate from the above-mentioned white precipitate, a further precipitate is obtained, which can be recrystallised from hot aqueous alcohol. This substance darkens on heating to  $125^{\circ}$  and decomposes at  $180-185^{\circ}$ ; it corresponds with the formula  $C_{12}H_{23}O_{12}N$ , and has  $[\alpha]_D + 41^{\circ}$ . It has only very weak basic properties, and reduces Fehling's solution. It is designated *chondridin*. S. B. S.

**Chondroitin-Sulphuric Acid.** III. P. A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1914, **18**, 123—130. Compare A., 1913, i, 917, 1006).—The hexosamine formerly described as glucosamine is not identical with that substance, but isomeric with it. The physical properties of the new hexosamine (termed *chondrosamine*) described in this paper differ from those of the corresponding glucosamine derivatives. The *hydrochloride*,  $C_6H_{13}O_5N \cdot HCl$ , remains unmelted above  $200^{\circ}$ ; its solution shows mutarotation, the initial value of  $[\alpha]_D^0$  being  $129.5^{\circ}$ , the final  $93.82^{\circ}$ . The *osazone*,  $C_{18}H_{24}O_4N_4$ , prepared either from chondrosamine or deaminochondrosamine, has m. p.  $180-185^{\circ}$  (decomp.). On oxidation with nitric acid deaminochondrosamine yields a dibasic hexonic acid, *chondrosic acid* (calcium salt,  $C_6H_8O_8Ca \cdot 2H_2O$ ); it has initially  $[\alpha]_D 0.45^{\circ}$ , finally  $0.37^{\circ}$ . The monocarboxylic acid (*chondronic acid*) from the new sugar gives a *brucine* salt,  $C_{29}H_{36}O_{10}N_2 \cdot H_2O$ , m. p.  $213^{\circ}$ ,  $[\alpha]_D^{20} 16.85^{\circ}$ . R. V. S.

**Theory of Wool Dyeing. I. The Composition and the Dyeing Capacity of Wool.** K. GEBHARD (*Zeitsch. angew. Chem.*, 1914, **27**, 297—307).—From an investigation of the products obtained by the action of alkaline solutions on wool, it is found that the insoluble residual substances are essentially responsible for the fixing of dyes. A comparison of the chemical-dyeing properties of wool with those of the decomposition products of proteins has shown that phenylglycine and anthranilic acid behave in several respects similarly to wool. In the expectation that an increase in the molecular weight would increase this similarity, experiments were made with anthranoylanthranilic acid with the result that this substance is found to resemble wool very closely in its behaviour towards dyes.

Other experiments, bearing on the constitution of wool, have been made with the object of determining the nature of the groups which impart to wool its capacity for fixing dyes. The results indicate that the dyeing of wool by basic dyes is conditioned by the presence of the carboxyl group in the wool. If the hydrogen of the carboxyl group is replaced by an alkyl radicle, basic dyes have no action on the resulting substance. On the other hand, both the amino- and the carbonyl groups of the wool appear to be concerned in the fixing of the acid dyes, and if one of these groups is rendered inactive, the result is simply a reduction in the colouring capacity of the acid dyes.

H. M. D.

**Action of Monochromatic Ultra-violet Rays on Amylase and Lipase from Pancreatic Juice.** CHAUCHARD and (Mme.) CHAUCHARD (*Compt. rend.*, 1914, **158**, 1575—1577. Compare A., 1913, ii, 653).—The amylase of pancreatic juice is attacked appre-

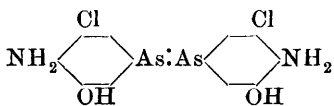
ciably only by rays where  $\lambda < 2800$ . The action increases very rapidly as the wave-length diminishes. The lipase is destroyed by the rays, where  $\lambda = 3300$ , these being without action on amylase. No relationship exists between the absorption of ultra-violet rays by pancreatic juice and the action on lipase or amylase, owing to the presence in the juice of different substances which absorb the ultra-violet rays unequally. W. G.

**Aromatic Arsenic Compounds. VI. Some Reactions of 3:5-Dichloro-4-diazophenylarsinic Acid.** P. KARRER (*Ber.*, 1914, 47, 1779—1783. Compare this vol., i, 342).—In order to compare polyhalogenated phenylarsinic acids with the mono-derivatives, the diazonium salt obtained by Witt's method (*A.*, 1909, i, 855) from 3:5-dichloroarsanilic acid (Bertheim, *A.*, 1910, i, 346) has been submitted to the usual decompositions. The diazo-compound was found to be highly reactive and only resisted the introduction of the hydroxyl group. When a solution of the salt is stirred with an acid-fixing salt, such as sodium acetate or sodium hydrogen carbonate, one chlorine atom is replaced by hydroxyl. The new diazonium salt now couples with "strong" azo-components, such as resorcinol and  $\beta$ -naphthol, whereas the original dichloro-derivative couples readily with *R*-salt. The azo-dye with  $\beta$ -naphthol has been reduced to a chlorinated *iso*-salvarsan.

The halogenated phenylarsinic acids have been examined biologically. The 3:5-dichloro-derivative is less toxic than *p*-iodophenylarsinic or 3:5-dichloro-4-iodophenylarsinic acid. The most remarkable effect of these preparations is that of causing extremely acute jaundice, the intensity of which rises with the number of halogen atoms.

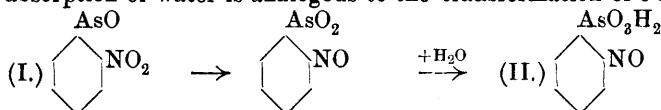
An intimate mixture of 3:5-dichloroarsanilic acid and potassium metadisulphite is added to ice-cold nitric acid (D 1.49) and then poured on ice. The diazo-compound soon crystallises from the clear solution. Such a solution, when mixed with alcohol, reacts with copper powder in the cold. The reaction is completed on the water-bath, when 3:5-dichlorophenylarsinic acid,  $C_6H_3Cl_2 \cdot AsO_3H_2$ , separates on cooling, in beautiful white leaflets. For the decomposition with potassium iodide or sodium azoimide, the crystalline diazo-compound is washed with ice-cold water, and dissolved in water. 3:5-Dichloro-4-iodophenylarsinic acid forms very sparingly soluble, slender, white needles, and 3:5-dichloro-4-triazophenylarsinic acid,  $N_3 \cdot C_6H_2Cl_2 \cdot AsO_3H_2$ , also separates in pure, white crystals.

A solution of the diazonium salt was also stirred with sodium acetate until it ceased to react with *R*-salt, when it was coupled with  $\beta$ -naphthol. The dye, which separated in coppery masses, was boiled with a large volume of water, filtered and acidified, when the free acid was precipitated in bright red flocks. This was dissolved in *N*-sodium hydroxide and *N*-sodium acetate, and warmed with sodium hyposulphite at 40—50°, until decolorised, when the solution was cooled, filtered from aminonaphthol and finally agitated with more of the reducing agent at 60°. Gradually, there separated 5:5'-dichloro-4:4'-diamino-3:3'-dihydroxyarsenobenzene (annexed formula) in yellow flocks.



J. C. W

**Aromatic Arsenic Compounds. VII. A Peculiar Light Reaction.** P. KARRER (*Ber.*, 1914, 47, 1783—1785).—When a moist ethereal solution of *o*-nitrophenylarsine dichloride, prepared by adding sufficient alcoholic hydrogen chloride to a suspension of the oxide, is exposed to sunlight for some weeks, yellowish-brown crystals are deposited which dissolve readily in sodium hydrogen carbonate, but are insoluble in all common solvents, and agree with the formula  $C_6H_6O_4NaAs$ . The compound is, therefore, an arsenic acid, but is not *o*-nitroarsinic acid, and must be regarded as *o*-nitrosoarsinic acid (II), although it gives none of the usual reactions of nitroso-compounds. The latter fact is not remarkable, for the compound is evidently highly polymerised, and *o*-nitrosobenzoic acid also fails to respond to the usual tests. The rearrangement of *o*-nitrophenylarsine oxide (I) with absorption of water is analogous to the transformation of *o*-nitro-



benzaldehyde into *o*-nitrosobenzoic acid under the influence of light (Ciamician and Silber, A., 1901, i, 547). J. C. W.

**Mercury Derivatives of cycloHexane.** GERHARD GRÜTTNER (*Ber.*, 1914, 47, 1651—1656).—By the action of mercuric haloids on magnesium *cyclohexyl* haloids (compare this vol., i, 261) the author has obtained *cyclohexyl* mercurihaloids. The preparation of mercury *dicyclohexyl*, however, was more difficult, but was effected by the action of mercuric bromide on a large excess of magnesium *cyclohexyl* bromide (compare Pfeiffer, A., 1904, i, 544). The compound is much less stable than mercury diphenyl (*ibid.*). The *cyclohexyl* derivatives in general are more soluble and less stable than the corresponding phenyl compounds. They readily reduce feebly acid or neutral solutions of silver or gold, but not ammoniacal silver oxide or Fehling's solution.

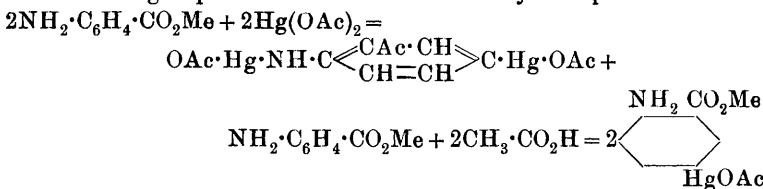
*cycloHexyl mercuribromide*,  $C_6H_{11}BrHg$ , forms brilliant, white leaflets, m. p.  $153^\circ$ , from benzene, 100 grams of which dissolve 3.33 grams at  $29^\circ$ . The *mercurichloride* has also a brilliant lustre, and melts at  $163$ — $164^\circ$ . Either of these salts may be converted into the iodide by warming a solution with potassium iodide. This, until now the only known mercury derivative of *cyclohexane*, was obtained by Kursanov by the action of sodium amalgam on *cyclohexyl* iodide (A., 1900, i, 89). A rapid current of hydrogen sulphide was passed into a pyridine solution of the bromide at  $-10^\circ$ , when the *sulphide*,  $(C_6H_{11}Hg)_2S$ , was partly precipitated as a pure white powder, which soon decomposed if left moist.

An ethereal solution of magnesium *cyclohexyl* bromide was treated with mercuric bromide (16.7% of the theory), and the dried ethereal extract was concentrated. The residue was filtered from a small quantity of *cyclohexyl* mercuribromide and the oil, which was a super-saturated solution of mercury *dicyclohexyl*, was shaken with alcohol, when it solidified. *Mercury dicyclohexyl* forms white, hard granules, m. p.  $78$ — $79^\circ$ , but decomposes into a black oil in a few hours, even

over phosphoric oxide in a dark vacuum desiccator. It combines directly with mercuric haloids or cyanide in any solvent. *cycloHexyl mecuricyanide* forms white, sparkling leaflets, m. p. 144°.

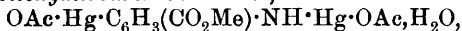
As all these compounds soon decompose in the molten condition, the melting points were found in a previously warmed bath. J. C. W.

**Mercuration of Anthranilic Ester and its Alkyl Derivatives.** Contribution to the Doctrine of Substitution. WALTER SCHOELLER and RICHARD HUETER [with E. FÖRSTER] (*Ber.*, 1914, **47**, 1930—1947).—According to Kekulé's views on the mechanism of substitution, recently supported by Fischer (*A.*, 1911, i, 418), an additive compound is first formed, this then either undergoing decomposition to give the substituted derivative, or yielding an intermediate product, re-arrangement of which gives rise to the substitution compound. In the study of the mercuration of aromatic carboxylic esters the authors have succeeded in obtaining, not a primary additive compound, but a true intermediate compound, which subsequently undergoes intermolecular change. The interaction of methyl anthranilate (1 mol.) and alcoholic mercuric acetate (1 mol.) yields a product containing 58% of mercury, which falls to 49% if the compound is left for a long time in the mother liquor. This product contains two acetoxymercuri-groups, one united firmly with the benzene nucleus, and the other, loosely held, displacing a hydrogen of the amino-group. The total substitution may be represented thus :



When, however, no excess of methyl anthranilate is present, gentle heating with alcoholic acetic acid results in the entry of the labile acetoxymercuri-group into the nucleus, with formation of methyl diacetoxymercurianthranilate (annexed formula). With mono- or di-alkylated anthranilic esters, such intermediate products are not observed, the mercuration then proceeding so rapidly that it is complete in a few minutes. The introduction of acid substituents into the amino-group causes a very considerable retardation of the mercuration, owing to the increased capacity for salt-formation of the imino-group and its consequent persistent retention of the substituent.

*Methyl diacetoxymercurianthranilate,*



forms an amorphous, white precipitate, and with moderately dilute hydrochloric acid gives up one of its acetoxymercuri-groups as mercuric chloride and forms methyl chloromercurianthranilate (see below). The isomeric *ester*,  $\text{OAc} \cdot \text{Hg} \cdot \text{C}_6\text{H}_2(\text{NH}_2)(\text{CO}_2\text{Me}) \cdot \text{Hg} \cdot \text{OAc}$ , has m. p. 221—222° (corr.) (decomp.).

*Methyl acetoxymercurianthranilate,*  $\text{OAc} \cdot \text{Hg} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CO}_2\text{Me}$ ,

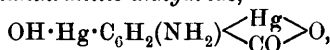
crystallises in spherical masses of pale yellow needles, m. p. 180—182° (corr.) (decomp.).

*Methyl chloromercurianthranilate*,  $\text{HgCl} \cdot \text{C}_6\text{H}_4 \begin{array}{c} \text{CO}_2\text{Me} \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array}$ , forms transparent prisms, m. p. 184° (corr.), the corresponding *bromo-derivative*,  $\text{C}_8\text{H}_8\text{O}_2\text{NBrHg}$ , stellar aggregates of slender white needles, m. p. 178° (decomp.), and the *iodo-compound*,  $\text{C}_8\text{H}_8\text{O}_2\text{NIHg}$ , spherical masses of needles, m. p. 173—174° (corr.) (decomp.).

*Hydroxymercurianthranilic anhydride*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{Hg} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$ , forms a white, flocculent precipitate decomposing at 212—214°. From this the *copper salt*,  $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Hg}_2\text{Cu}$ , of the acid was prepared.

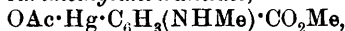
*Iodomercurianthranilic acid*,  $\text{HgI} \cdot \text{C}_6\text{H}_4(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , forms a white precipitate.

*Dihydroxymercurianthranilic anhydride*,



forms a pale yellowish-green, amorphous precipitate.

*Methyl acetoxymercurimethylanthranilate*,



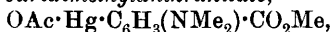
forms slender needles, m. p. 200° (corr.) (decomp.). The corresponding *chloride*,  $\text{C}_9\text{H}_{10}\text{O}_2\text{NClHg}$ , m. p. 210—212°, *bromide*, m. p. 215°, and *iodide*, m. p. 190—191° (decomp.), were prepared.

*Hydroxymercurimethylanthranilic anhydride*,  $\text{NHMe} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{Hg} \end{array} \text{O}$ , forms a greenish-yellow, amorphous precipitate, decomposing at 203°.

*Iodomercurimethylanthranilic acid*,  $\text{HgI} \cdot \text{C}_6\text{H}_3(\text{NHMe}) \cdot \text{CO}_2\text{H}$ , forms a precipitate.

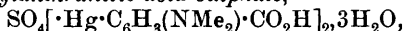
*Ethyl acetoxymercuriethylanthranilate*,  $\text{OAc} \cdot \text{Hg} \cdot \text{C}_6\text{H}_3(\text{NHEt}) \cdot \text{CO}_2\text{Et}$ , forms a felted mass of needles, m. p. 178° (corr.) (decomp.).

*Methyl acetoxymercuridimethylanthranilate*,



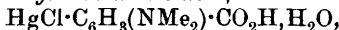
forms stout, prismatic crystals, m. p. 134° (corr.). The corresponding *chloride*,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{NClHg} \cdot \text{H}_2\text{O}$ , m. p. 162—163°, *bromide* (+  $\text{H}_2\text{O}$ ), m. p. 164°, and *iodide*, m. p. 159°, were prepared.

*Mercuridimethylanthranilic acid sulphate*,



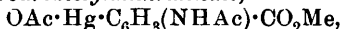
forms small, white needles, decomposing slowly at 180°.

*Chloromercuridimethylanthranilic acid*,



forms white, prismatic crystals, m. p. 175° (decomp.).

*Methyl acetoxymercuriacetylanthranilate*,



forms large, shining leaflets, m. p. 212° (corr.), and the corresponding *chloride*,  $\text{C}_{10}\text{H}_{10}\text{O}_3\text{NClHg}$ , slender needles, m. p. 245—246°. T. H. P.

## Physiological Chemistry.

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**The Influence of Adrenaline on Respiration.** L. B. NICE, JOHN L. ROCK, and R. O. COURTRIGHT (*Amer. J. Physiol.*, 1914, **34**, 326—331).—Doses of adrenaline which lower blood-pressure increase the depth of respiration; doses which elevate blood-pressure act similarly, but in both cases a preliminary stage of shallow breathing may occur. Excessive doses produce marked shallowness, as Oliver and Schäfer first stated. W. D. H.

**Factors Affecting the Coagulation-Time of Blood. V. The Effects of Hæmorrhage.** H. GRAY and L. K. LUNT (*Amer. J. Physiol.*, 1914, **34**, 332—351).—Hæmorrhage decreases the coagulation-time, unless the abdominal circulation is excluded. In the abdomen, exclusion of the adrenals alone, or of the intestines alone, does not abolish the effects of hæmorrhage on coagulation-time. The adrenals, intestine, and the liver together provide the necessary elements which hasten clotting after extensive bleeding. W. D. H.

**The Sugar of the Blood under Laboratory Conditions.** ERNEST LYMAN SCOTT (*Amer. J. Physiol.*, 1914, **34**, 271—312).—It is better to examine the blood than the urine; the latter only shows increase of sugar, and is not so closely related to the tissues as is the blood. The methods of estimation at present in use may give different results, and should be reduced to common terms. When blood is drawn, the concentration of sugar in the blood left within the animal falls; ether and chloroform increase the blood-sugar but to a variable extent. Cocaine lowers the percentage of sugar in the blood, and the amount of lowering is fairly constant. W. D. H.

**Certain New Principles Concerning the Mechanism of Hyperglycæmia and Glycosuria.** ALBERT A. EPSTEIN and GEORGE BAEHR (*J. Biol. Chem.*, 1914, **18**, 21—27).—In normal animals under constant conditions, the percentage of sugar in the blood may vary to such an extent that a simple estimation can warrant no positive conclusion. The authors also find that the increase in blood-sugar observable after hæmorrhage is more apparent than real; the percentage increases, but, if regard is had to the probable total volume of circulating blood before and after the experiment, it is found that the total amount of sugar present is practically unchanged. When the blood withdrawn was at once replaced by physiological salt solution, no alteration in the percentage of sugar could be observed, except in one case. These results indicate that the increase of sugar following hæmorrhage is not psychic, but is due to a compensatory effort on the part of the organism. R. V. S.

**Fibrin in its Relation to Problems of Biology and Colloidal Chemistry. The Problem of Blood Coagulation. II. Plasmas which Clot Spontaneously or under the Influence of Sera.** E. HEKMA (*Biochem. Zeitsch.*, 1914, 63, 184—203. Compare this vol., i, 754).—A detailed description of certain experiments is given, which show that citrate and fluoride plasmas will clot spontaneously. This is especially the case when the fluoride content in the former plasmas is more than 0.5—1% of sodium fluoride. The clot was examined microscopically by Weigert's method, and was seen to consist of a network of fibres. The part which clots first contains the formal elements of the blood in the mesh-work. If this is removed, fractions can be obtained of a fibrin preparation which is free both from calcium salts and formal elements. The clot forms very rapidly also on the addition of serum proteins, and spontaneous clotting can also be observed in transudates.

S. B. S.

**Fibrin in its Relation to Problems of Biology and Colloidal Chemistry. The Problem of Blood Coagulation. III. Reversibility of the Clots Formed in Plasmas as either Spontaneously or under the Influence of Sera.** E. HEKMA (*Biochem. Zeitsch.*, 1914, 63, 204—220).—The fibrin obtained by the spontaneous clotting of fluoride and citrate plasmas is in every respect similar to that obtained in other ways. It shows the phenomena of gel reversion on addition of acids to a solution in alkalis (see this vol., i, 754) and of alkalis to the solution in acid. Gel formation in solutions in alkalis of all preparations of fibrin can be produced by the following methods; by addition of: (a) acids and acid salts of potassium, sodium, and calcium to neutral point; (b) of hydrochloric, nitric, and phosphoric acids until the reaction is strongly acid; (c) of calcium chloride under certain conditions; (d) of saturated solutions of sodium chloride and fluoride and other salts; (e) of serum; (f) by warming to 56° with equal parts of 8% sodium chloride and 2% sodium fluoride solutions. The reactions (a) to (f) take place in alkaline solutions which have been previously heated. The alkaline solutions, when sufficiently concentrated, can also, under certain conditions, give rise to true gels.

S. B. S.

**The Fermentative Properties of Blood. III. Nucleases and Glucoside-splitting Ferments.** LUDWIG PINCUSOHN and CHARLOTTE KRAUSE (*Biochem. Zeitsch.*, 1914, 63, 269—275. Compare A., 1913, i, 788, 1404).—The degradation of nucleic acids by the serum was measured by the polarimeter. The serum was taken from patients with a variety of diseases. Yeast-nucleic acid is readily degraded by most sera, whereas thymus-nucleic acid appears to be degraded only by the sera of patients with exophthalmic goitre. The sera of dog, pigeon, and rabbit generally degrade both kinds of nucleic acid. In only a few cases was there any suspicion of a hydrolysis of arbutin by sera.

S. B. S.



**Can the Serum of Healthy Animals Decompose Protein or Peptones Prepared from It?** EMIL ABDERHALDEN and GOTTFRIED EWALD (*Zeitsch. physiol. Chem.*, 1914, **91**, 86—95).—The very numerous experiments of Abderhalden and his collaborators on this subject have shown that normal serum does not attack the proteins of the tissues, or the peptones prepared from them or from other proteins. In consequence of the contrary statement of Pincussohn (A., 1913, i, 788, 1404), the subject has been re-investigated, with the result that the observation is confirmed that normal serum does not decompose peptones prepared according to the method previously described by Abderhalden. A peptone is, however, attacked if the same peptone has been administered to the animal previously. In one thousand observations, the unexpected decomposition of the peptone derived from a particular organ occurred seventeen times, and in each case a lesion of the corresponding organ in the animal was subsequently discovered.

R. V. S.

**The Significance of the Concentration of Hydrogen Ions for Hæmolysis.** L. G. WALBUM (*Biochem. Zeitsch.*, 1914, **63**, 221—268).—It is shown by numerous experiments with different hæmolytics (cobra poison, sodium cholate, saponin, etc.), and with blood from various animals, that there are optimal and minimal conditions as regards hydrogen ion concentration for the production of hæmolysis. The suspension of blood corpuscles was treated with hydrochloric acid insufficient to produce hæmolysis, and in a series of samples the acid was more or less completely neutralised by sodium hydroxide. The amount of hæmolysis under definite conditions was then ascertained (colorimetrically). The same experiments were then carried out in the presence of hæmolytic substances, and the hæmolysis was again measured. By subtracting the amount of hæmolysis in the absence of hæmolytic substances from that produced under the same conditions in their presence, the change due to these substances was determined. In all cases, the hydrion concentration was directly measured electrometrically. The results are indicated in a series of graphs, in which the negative exponent of the hydrion concentration is plotted on the abscissæ, and the amount of hæmolysis (corrected) on the ordinates. There are too many factors involved to allow of any generalisations. It is pointed out that when hæmolysis experiments are carried out in the presence of serum, the latter can act as a buffer.

S. B. S.

**Direct Proof that Pathological Changes in the Percentage Concentration of Acid in the Pure Gastric Juice are not Produced by the Infusion of Salt or Magnesium Sulphate into the Stomach, as stated by O. Cohnheim.** SEÛCHIRO SATO (*Zeitsch. physiol. Chem.*, 1914, **91**, 1—14).—By direct titration of the pure gastric juice of the dog, the author finds that Cohnheim's statements that the injection into the stomach of magnesium sulphate causes hyperacidity, and that of sodium chloride hypo-

acidity (A., 1910, ii, 139), are incorrect. The secretion of juice is, however, increased in the first case and decreased in the second, as stated by that author.

R. V. S.

**The Ferments in the Contents of the Intestine (Meconium) and Stomach of the Human Fœtus and Newly-born Children.**

RUDOLF SCHMIDT (*Biochem. Zeitsch.*, 1914, 63, 287—303).—The following ferments were found in the meconium: lecithinase, monobutyrylase, esterase, glycerophosphatase, pepsin, rennin, a peptolytic ferment, and possibly a peroxidase and catalase. Oxydases were absent. The diastatic value varied between  $D_{35}^{24h} = 50$  and 100. The lecithinase, monobutyrylase, and esterase were weaker in the lower parts of the small intestine than in the upper parts. Trypsin is either entirely absent or present in very much smaller quantities in the upper part of the small intestine than it is in the lower part or colon. This fact is not due to the absence of an activator. The peptolytic ferment of the meconium is identical with trypsin. The peptic values (determined by the edestin method) are small in the intestine, and in the stomach they vary between 20 and 80 units. Pepsin and rennin exist in the stomach and intestine of the fœtus apparently in the form of a pro-ferment. The diastatic power of the fœtal stomach is apparently due to the saliva which has been swallowed, and varies between  $D_{35}^{24h} = 40$  and 66.

S. B. S.

**The Silk Peptone Method and Intracellular Proteases.**

GOTTWALT CHR. HIRSCH (*Zeitsch. physiol. Chem.*, 1914, 91, 78—80. Compare Abderhalden, A., 1911, ii, 1009).—Not only do the glands and tissues of the intestinal tract of marine snails give tyrosine crystals when investigated by Abderhalden's silk peptone method, but positive results are also obtained with any tissues from these or other animals (*Natica*, *Blenius*, *Martenia*, *Pleurobranchaea*, *Scyllium*, *Tapes*, *Macra*, *Leucina*, *Helix*). The production of tyrosine is somewhat less than is the case with glandular tissue, but is none the less evident. This indicates the presence of proteases in all cells; digestive glands merely produce an unusual amount of them.

R. V. S.

**Carbohydrate Metabolism. VI. Influence of Thyreoparathyroidectomy upon the Sugar Content of the Blood and the Glycogen Content of the Liver.**

FRANK P. UNDERHILL and NORMAN R. BLATHERWICK (*J. Biol. Chem.*, 1914, 18, 87—90).—After thyreoparathyroidectomy, glycogen entirely disappears from the liver, and the blood-sugar content is markedly lowered, or may even be reduced to zero. This action may be ascribed to the lack of parathyroid tissue, since the phenomena may be observed when all the parathyroids are removed and some thyroid tissue remains.

R. V. S.

**Protein Metabolism after Starvation and Subsequent Ingestion of Large Amounts of Proteins Derived both from the Same and Different Species of Animals.** CHARLES G. L. WOLF (*Biochem. Zeitsch.*, 1914, 63, 58—73).—The experiments were carried

out on dogs, with the object of submitting to a further test Michaud's conclusions as to the more economic nutritional value of the proteins derived from the same species of animal (compare A., 1909, ii, 498). After a period of starvation, the animal received a rich protein diet, which was followed by a subsequent period of starvation. In one experiment the protein consisted of the muscle of ox heart, and in a second of dog's flesh. The complete nitrogen, phosphorus, sulphur, calcium, and chlorine balances were determined during the various periods of feeding and starvation. The nitrogen retention during the period of feeding on dog's flesh was distinctly greater than during the period of feeding on the foreign protein, and in this respect the author's experiments appear to confirm Michaud's conclusions. S. B. S.

**Purine Metabolism in Man. III. Decomposition of Purine Substances in the Digestive Canal.** V. O. SIVÉN (*Pflüger's Archiv*, 1914, 157, 582—586. Compare A., 1912, ii, 575, 780).—Experiments with broth inoculated either with *B. coli* or with intestinal contents obtained at operation show that in both cases some of the purine substances originally present disappear, so that the loss of exogenous purine substances which occurs in man probably takes place chiefly as a result of bacterial action in the intestinal tract. R. V. S.

**The Metabolism of Endogenous and Exogenous Purines in the Monkey. III. The Purines of Monkey Urine.** ANDREW HUNTER (*J. Biol. Chem.*, 1914, 18, 107—114).—From a considerable quantity of the urine of *Cercopithecus*, the author has separated the purine substances, and identified in the mixture uric acid, xanthine and hypoxanthine. Guanine and most probably adenine were absent. R. V. S.

**Glycollaldehyde as an Assimilation Product.** WALTHER LÖB (*Biochem. Zeitsch.*, 1914, 63, 93—94).—In view of a recent communication of Fincke (this vol., i, 638), the author directs attention to the facts that glycollaldehyde has already been suggested as an assimilation product, and that it can be obtained from carbon monoxide and water under the influence of the silent electrical discharge. He further discusses the possible part played by the aldehyde in assimilation processes. S. B. S.

**Narcosis and Oxygen Consumption.** J. MOLDOVAN and FR. WEINFURTER (*Pflüger's Archiv*, 1914, 157, 571—581).—The authors' experiments were concerned with the injection into rabbits and guinea-pigs of solutions of dyes (alizarin-blue-S,  $\alpha$ -naphthol + dimethyl-*p*-phenylenediamine [oxidation to indophenol blue], methylene-blue). From the staining of various tissues found post mortem, conclusions are drawn as to the occurrence of oxidation or reduction in those situations. In this way it is found that in the normal brain cortex a large amount of oxygen is available, but in the same region methylene-blue is reduced. During deep narcosis (with chloroform), both oxidising and reducing power in the cortex is diminished, but oxidation is never entirely absent. The amount

of oxidation occurring elsewhere in the body (for example, in the blood) is also less during deep narcosis.

R. V. S.

**Chemical and Biochemical Investigations on the Nervous System under Normal and Pathological Conditions. VI. The Chemical Composition of the Brain in Progressive Paralysis. II.** GIACOMO PIGHINI (*Biochem. Zeitsch.*, 1914, 63, 304—335. Compare A., 1913, i, 128).—The brains taken from cases of progressive paralysis were submitted to analysis by six successive extractions with various solvents by Fränkel's method, and the results were compared with those obtained from normal brains. As compared with the latter, the former show an increase in the water and protein content, and an increased percentage of cholesterol, but a marked diminution in the amount of unsaturated phosphatides (leucopoliin and cephalin fractions) and of saturated phosphatides and cerebrosides. In spite, however, of the diminution of phosphatides, the histological examination of the diseased brain, when stained by various methods (Aschoff, L. Smith, Fischler, and Ciaccio), shows an increase in the amount of lipoids. A similar histological appearance is exhibited by normal brains after autolysis. Attention is called to the similarity of the behaviour of lipoids in other tissues under pathological conditions. It is assumed that in normal brains the lipoids are in some form of combination in which their histochemical detection is masked. The first stage of degeneration consists in the breakdown of this combination. Lipoids other than cholesterol are removed into the circulation by phagocytic processes. The cholesterol is not so removed, but it is remarked that the blood in cases of syphilis and other diseases contains abnormally large amounts of this substance, which serves, furthermore, as a protection against the action of certain toxins, and is subject to somewhat different laws to the other lipoids found in the brain.

S. B. S.

**Chemical and Biochemical Investigations on the Nervous System under Normal and Pathological Conditions. VII. The Autolysis of Nervous Tissue. I.** GIACOMO PIGHINI and CARLO FONTANESI (*Biochem. Zeitsch.*, 1914, 63, 336—352).—An account is given of the histological changes which take place when the spinal column of a dog is submitted to aseptic autolysis. Nile-blue sulphate, Sudan III, Scarlet R, and chromium and copper hæmatoxylin methods (methods of Smith, Fischler, Daddi, Herxheimer, Ciaccio, etc.) were employed. The main change observed in the autolysed as compared with the fresh tissue was the formation of coloured granules, presumably due to phosphatides. During autolysis, the lipoids appear to be set free from some form of combination (compare preceding abstract).

S. B. S.

**A Simplification of Bang's Micro-Kjeldahl Method and the Nitrogen Content of the Vitreous Humour of the Eye of Rabbit and Dog.** M. KOCHMANN (*Biochem. Zeitsch.*, 1914, 63, 479—482).—The author substitutes a long, hard, glass delivery tube

for the glass-wool filter used in the distillation by Bang (A., 1913, ii, 740), and titrates the excess of acid with  $N/100$ -sodium hydroxide solution, employing tincture of cochineal as an indicator instead of using the iodometric method. The nitrogen content of the vitreous humour of the rabbit's eye was found to be 50.6 mg. per 100 gram. The corresponding number for a dog was about 44.

S. B. S.

### Formation of Lactic Acid and Sugar in the Isolated Liver.

**I. Degradation of *d*-Sorbitol. II. Fate of *d*-Sorbitol and Some other Hexitols.** GUSTAV EMBDEN and WALTER GRIESBACH (*Zeitsch. physiol. Chem.*, 1914, **91**, 251—286. Compare Embden, Schmitz and Wittenberg, A., 1913, i, 1411).—In perfusion experiments with the liver of the dog (freed from glycogen by phloridzin poisoning), in one case *d*-lactic acid was formed from *d*-sorbitol, in another case it was not produced. In similar circumstances, *d*-sorbitol is converted into dextrose, from which, presumably, the lactic acid was produced.

*d*-Sorbitol is converted into *d*-lactic acid on perfusion through the liver of a hungry dog, and in the phloridzin liver into a mixture of *d*-lævulose and dextrose; in this case, *d*-lævulose is probably first formed. *d*-Mannitol, dulcitol and inositol do not form sugar or lactic acid in the isolated liver.

R. V. S.

**Specific Action of Cell Ferments. III.** EMIL ABDERHALDEN, GOTTFRIED EWALD, ISHIGURO and R. WATANABE (*Zeitsch. physiol. Chem.*, 1914, **91**, 96—106. Compare Abderhalden and Fodor, A., 1913, i, 1118; Abderhalden and Schiff, A., 1913, i, 1118).—Further experiments on this subject here recorded show that liver extract obtained by maceration decomposes peptone prepared from liver, whilst peptone from lung, brain, kidney, pancreas, silk-fibroin and gelatin is never affected. These results were obtained by both the optical and the dialysing methods. The liver extract generally attacks a peptone prepared from muscle, which certainly contains simple decomposition products of muscle protein. A similar lung extract decomposes peptone prepared from lung, but not peptone from muscle, liver, or kidney. As previously stated, kidney extract decomposes all kinds of peptones; of those investigated, only gelatin peptone remained unattacked. The results, in general, do not indicate ferments peculiar to individual animal species.

Reference is made to the considerable difficulties attending the preparation of the extracts and peptones if confusing results are to be avoided. Casual errors were eliminated in the experiments here described by using portions of the same sample of extract to act on the various peptones, and by having the experiments repeated by different observers.

R. V. S.

**Parathyroid Deficiency and Sympathetic Irritability.** R. G. HOSKINS and HOMER WHEELON (*Amer. J. Physiol.*, 1914, **34**, 263—271).—Destruction of the parathyroid in dogs increases the vasomotor irritability towards nicotine, adrenaline, and pituitrin;

all components (sympathetic cells, myoneural junction), and the muscle fibres, are affected, but to a varying degree in different cases. The evidence that calcium injections neutralise the effect is inconclusive.

W. D. H.

**The Swelling Capacity of Different Kinds of Muscle in Acid Solutions.** RUDOLF ARNOLD (*Koll. Chem. Beihefte*, 1914, 5, 411—426).—Observations have been made on the swelling which takes place when different kinds of human muscle are immersed in acid solutions. The experiments were made with material obtained within twenty-four hours of death.

The curves obtained by plotting the swelling of the fibre against time are of two types. The one type is characterised by great rapidity of swelling and little tendency to reversal, whilst the other type of curve shows a much more gradual rise, and also a considerable reduction of the swelling when the immersion of the fibre in the acid solution is prolonged.

Hydrochloric acid is more active in promoting swelling than lactic acid, and from experiments with hydrochloric acid solutions of varying concentration, it has been found that a 0.025% solution gives the optimum effect.

H. M. D.

**Influence of Various Substances on the Gaseous Interchange of Surviving Frog's Muscle. XII. Action of Cyanogen Compounds, especially Potassium Ferricyanide.** TORSTEN THUNBERG (*Chem. Zentr.*, 1914, i, 905; from *Skand. Arch. Physiol.* 1913, 30, 332—336).—Both the oxygen uptake and the carbon dioxide evolution of frog's muscle are considerably lessened by very minute quantities of potassium cyanide, whereas the exchange is not influenced by the thiocyanate or ferrocyanide. Sodium nitroprusside is very poisonous. Potassium ferricyanide, however, has a quite specific action in that the carbon dioxide output is scarcely diminished, although the oxygen uptake is completely stopped.

J. C. W.

**Comparative Chemistry of Muscle. Betaine from the Scallop, Periwinkle and Lamprey. Creatine from the Lamprey.** D. WRIGHT WILSON (*J. Biol. Chem.*, 1914, 18, 17—20).—Betaine has been isolated from the extracts of muscles from the scallop, periwinkle and lamprey, creatine from the muscles of the lamprey.

R. V. S.

**Urea. Its Distribution in and Elimination from the Body.** E. K. MARSHALL, jun., and DAVID M. DAVIS (*J. Biol. Chem.*, 1914, 18, 53—80).—Applying the method for the estimation of urea previously described (compare Marshall, A., 1913, ii, 640, 991), the authors find that this substance is present in all the organs and tissues of normal animals. The amount present in all organs and tissues is approximately equal to that of the blood, both in normal conditions and when an abnormal amount is present. Fat, however, contains little urea, whilst the amount

in the urinary tract is high. When a solution of urea is injected intravenously, it diffuses to all parts of the body very rapidly. Urea is very rapidly eliminated by the kidneys. The rate of excretion may rise to 16 grams per kilo. of body-weight per day, or much higher. The rate of excretion is directly proportional to the concentration of the substance in the blood; it may be retarded, however, by dehydration of the organism. When excretion is prevented, the entire amount formed is stored in the body, except for small amounts secreted in the bile, sweat, etc., and there is no evidence that it is converted into other substances.

R. V. S.

**The Effect of Calcium and Protein on the Offspring of Swine.** J. M. EVVARD, ARTHUR W. DOX, and S. C. GUERNSEY (*Amer. J. Physiol.*, 1914, **34**, 312—325).—Maize is deficient in calcium and poor in protein; the addition of calcium to a diet of maize and sodium chloride given to pregnant swine increases the size and general nutritive condition of the offspring. The addition of much protein has a similar, but better, effect. Calcium carbonate produces a better effect than the chloride.

W. D. H.

**Action of Ultra-violet Monochromatic Rays on the Tissues. Measurement of the Energy of Radiation Corresponding with Sunstroke.** VICTOR HENRI and VENCESLAS MOYCHO (*Compt. rend.*, 1914, **158**, 1509—1511. Compare A., 1913, i, 424, 678).—A study of the effect of monochromatic ultra-violet rays, from  $\lambda$  2300 to  $\lambda$  3300, on the ear of the rabbit, the time of exposure for production of a redness, after twelve to twenty-four hours, being measured. The extreme ultra-violet rays  $\lambda$  2300—2500 have no sensible action on the tissues of the ear. The most active region in the ultra-violet is at  $\lambda$  2800, the energy necessary to produce an irritation of the tissues being  $0.057 \times 10^7$  ergs. For  $\lambda$  3300, no visible effect could be obtained. At the sea-level the solar spectrum stops at about  $\lambda$  3000, and the amount of energy which reaches the earth from this region of the spectrum is such as would produce sunstroke in one hundred minutes. At levels higher than this, the time of exposure would get less as the height increased.

W. G.

**Occurrence of Trimethylamine Oxide in Cephalopods.** M. HENZE (*Zeitsch. physiol. Chem.*, 1914, **91**, 230—232).—From the muscles of mussels the author has isolated trimethylamine oxide, identifying it by the preparation and analysis of various salts.

R. V. S.

**Dependence of the Composition of Cow's Milk on the Degree of Dispersity of the Separate Constituents.** GEORG WIEGNER (*Zeitsch. Nahr. Genussm.*, 1914, **27**, 425—438).—From an examination of the data obtained in the analysis of a large number of samples of cow's milk, it has been found that the variability in the percentage content of the constituents decreases as the

degree of dispersity of the constituents increases. The fat, which occurs in the form of coarse particles varying very considerably in size, varies to the largest extent. The more highly disperse colloidal particles of casein and albumin show smaller variation in the size of the particles, and the proportion of these varies also to a less extent than the fat content. The variability of the amount of milk sugar and ash, which are molecular disperse in character, is considerably less than that of the protein constituents.

The above relation between the composition and the degree of dispersity of the constituents holds, not only for the mixed milk obtained from different breeds of cows, but also for the changes which occur in the milk of a single cow during the period of lactation, and for the changes which are brought about by variations in the food supply.

H. M. D.

**Colloid-chemistry of Sugar Diuresis.** MARTIN H. FISCHER and ANNE SYKES (*Kolloid. Zeitsch.*, 1914, 14, 223—229).—The diuretic action of sucrose, dextrose, and lævulose has been investigated by experiments on healthy rabbits. Whilst dextrose and lævulose are of approximately equal activity, sucrose is much more effective at the same molar concentration. The authors suppose that the kidneys are not directly concerned in the effects which have been observed, and attribute the action to the dehydrating influence of the sugars on the whole of the body tissues. The greater activity of sucrose is quite in accordance with the results obtained in experiments on the swelling of gelatin and fibrin (compare this vol., ii, 542).

H. M. D.

**Gluconeogenesis. VIII. Velocity of Formation and Elimination of Dextrose by Diabetic Animals.** A. I. RINGER and E. M. FRANKEL (*J. Biol. Chem.*, 1914, 18, 81—86).—Dextrose is very rapidly excreted by the kidneys after it has entered the blood-stream. After administration of dextrose, the curve of its elimination reaches in less than two hours a point which, after administration of propionic acid (as sodium propionate), is only reached in four or five hours. The difference must be attributed to the time required for the synthesis of dextrose from propionic acid.

R. V. S.

**Extent of the Formation of Hippuric Acid in the Organism of the Pig.** EMIL ABDERHALDEN and HERMANN STRAUSS (*Zeitsch. physiol. Chem.*, 1914, 91, 81—85. Compare Abderhalden and Hirsch, A., 1912, ii, 579).—The animal used excreted 1·15 grams of hippuric acid under normal conditions. When benzoic acid was administered, the daily excretion of hippuric acid increased to 2·5—3·0 grams, whilst administration of benzoic acid and glycine raised the daily excretion to 4·5 grams. Alanine did not cause a similar increase. Ammonium carbonate brought about a decrease in the daily excretion (2·2 grams). The experiments show that the pig has available much more glycine than it absorbs in the proteins of its food.

R. V. S.



**Resorption of Guaiacolhexamethylenetetramine ("Hexamecol") by the Skin, also a New Method for the Detection of Guaiacol in Urine.** O. SAMMET (*Zeitsch. physiol. Chem.*, 1914, 91, 233—240).—When "hexamecol" is rubbed into the moist skin, guaiacol and hexamethylenetetramine subsequently appear in the urine.

Guaiacol can best be detected in urine by acidifying with 5% sulphuric acid and distilling the guaiacol, along with the phenols thus liberated, with steam. The distillate is extracted with ether, and the residue, after removal of the ether, is boiled for some time with hydriodic acid. After adding water, the catechol now present is extracted with ether and identified by one of the usual tests. The method does not appear suitable for quantitative work.

R. V. S.

**Behaviour of Propylene Glycol, Paracetaldehyde, and Urethane in Phloridzin Diabetes.** FRITZ HERING (*Chem. Zentr.*, 1914, i, 805; from *Beitr. Phys.* [Cremer], 1914, 1, 1—22).—The author administered propylene glycol, paracetaldehyde, and urethane to dogs under constant phloridzin diabetes, and found that the dextrose to nitrogen ratio was considerably exalted thereby, especially in the case of urethane. There seemed, therefore, to be a "washing out" of sugar.

J. C. W.

**[Physiological] Effects of Sodium Bromate.** C. G. SANTESSON and GÖSTA WICKBERG (*Chem. Zentr.*, 1914, i, 904; from *Skand. Arch. Physiol.*, 1913, 30, 337—374. Compare A., 1910, ii, 431).—A further account of the action of bromates, the important features of which have already been described.

J. C. W.

**The Distribution and Fate of Colloidal Silver in the Mammalian Body. II. What can be Ascertained by Quantitative Analysis as to the Distribution?** J. VOIGT (*Biochem. Zeitsch.*, 1914, 63, 409—424. Compare this vol., ii, 462).—Analyses were made of various organs of animals which have received injections of colloidal silver preparations under different conditions (large doses at once, or repeated smaller doses at intervals). The greater part of the silver found in the body was in the liver, but the metal was also found in the lungs, bone-marrow, and spleen. Its distribution is discussed by the author at some length.

S. B. S.

**Pharmacodynamic Investigation of Cupric Iodide.** A. FONTES (*Chem. Zentr.*, 1914, i, 1099; from *Mem. Inst. Oswaldo Cruz.* [*Rio de Janeiro*], 5, 239—251).—The cupric iodide was obtained as a sol, and could be given in accurate dosage. Iodine is set free by 0.01 mg. hydrogen peroxide. Apart from the action of the water, cupric iodide has no hæmolytic action. Hæmoglobin is reduced, white blood corpuscles are fixed, and red corpuscles agglutinated by it. It does not destroy the fibrin ferment or catalase of the blood, and the serum proteins remain unprecipitated (*in vitro*). Intravenous injection does not injure animals, whereas the intra-

peritoneal injection into rabbits and guinea-pigs produced death within twenty-four hours. Subcutaneous injection into guinea-pigs and rats produced a harmful effect. The hydrosol was useless in the treatment of sporotrichosis and tuberculosis produced experimentally.

S. B. S.

**Quantitative Researches on Acetylation Processes in the Animal Organism. I. Formation of *p*-Acetylaminobenzoic Acid from *p*-Aminobenzaldehyde and *p*-Aminobenzoic Acid.** ALEXANDER ELLINGER and MARIE HENSEL (*Zeitsch. physiol. Chem.*, 1914, 91, 21—44).—When *p*-aminobenzaldehyde is administered to rabbits, *p*-acetylaminobenzoic acid appears in the urine, and the yield may equal the amount of *p*-aminobenzaldehyde taken. *p*-Aminobenzoic acid is also acetylated in the organism of the rabbit, as much as 30% being found in the urine as *p*-acetylaminobenzoic acid. The authors' experiments with *m*- and *p*-nitrobenzaldehyde confirm the results of Cohn (A., 1893, ii, 514), with slight differences.

R. V. S.

**Changes in the Mobile Oxygen of the Blood during the Application of Antipyrine, Phenacetin, and Antifebrin.** GUIDO M. PICCININI (*Chem. Zentr.*, 1914, i, 902—903; from *Arch. Farmacol. sperim.*, 1913, 16, 484—512).—The author estimated the mobile oxygen of the blood, that is, the oxygen which may be removed by a mild reducing agent, such as sodium hyposulphite, after the oral administration of antipyrine, phenacetin, and acetanilide to dogs. The results show that the action of these antipyretics falls into two periods. During the first, the pharmaco-therapeutic period, the outer respiration, that is, the fixation of oxygen by the hæmoglobin, and also the tissue respiration, are diminished. This period is followed by a toxic period, which is accompanied by methæmoglobinæmia, in which the fixation of oxygen is diminished to a greater extent than the tissue respiration. Whereas phenacetin and acetanilide scarcely differed in their action, antipyrine exhibited considerable deviations, for small doses caused an increase in the mobile oxygen, and large doses a much smaller and less enduring diminution.

J. C. W.

**Decomposition of Aromatic Amino-acids in the Animal Organism according to Experiments on the Normal and Alcaptonuric Individual.** KONRAD FROMHERZ and LEO HERMANN (*Zeitsch. physiol. Chem.*, 1914, 91, 194—229. Compare this vol., i, 358).—Both *m*- and *p*-tolylalanines are completely decomposed in the alcaptonuric organism without formation of a quinol derivative. The same is true of *m*-methyltyrosine, both in the normal and in the alcaptonuric organism. The alcaptonuric individual can also decompose *p*-hydroxyphenylpyruvic acid. When simple quinols (*m*-dimethylquinol, toluquinol) are administered, neither the normal nor the alcaptonuric organism can oxidise them, and no formation of quinol is observed. Experiments with 3:4-dihydroxyphenylalanine show that it can be oxidised in the

organism to the same extent as the 4-hydroxy-compounds of natural origin.

4-Methoxy-*m*-tolualdehyde condenses with hippuric acid in presence of sodium acetate and acetic anhydride, and the azlactone formed dissolves in alkali, yielding (after acidification) *α*-benzoylamino-4-methoxy-3-methylcinnamic acid,  $C_{18}H_{17}O_4N$ , which forms needles, m. p.  $246^\circ$ . This, on reduction with sodium amalgam, yields the corresponding *α*-benzoylamino-4-methoxy-3-methylphenylpropionic acid,  $C_{18}H_{19}O_4N$ , which crystallises in leaflets, m. p.  $148-149^\circ$ . On boiling with hydriodic acid, *m*-methyltyrosine,  $C_{10}H_{13}O_3N$ , crystallising in tufts of prisms, m. p.  $277^\circ$ , is obtained.

Vanillin condenses with hippuric acid, forming *α*-benzoylamino-4-hydroxy-3-methoxycinnamic acid,  $C_{17}H_{15}O_5N$ , which crystallises in prisms, m. p.  $211^\circ$ . The corresponding saturated acid,  $C_{17}H_{17}O_5N$ , crystallises in leaflets, m. p.  $164^\circ$ . From this, by the action of hydriodic acid, inactive *α*-amino-*β*-3:4-dihydroxyphenylpropionic acid (dihydroxyphenylalanine; compare Guggenheim, this vol., i, 49) can be prepared; it has m. p.  $285^\circ$  (rapid heating).

R. V. S.

**The Newer Therapeutic Treatments of Leucæmia.** A. PAPPENHEIM (*Chem. Zentr.*, 1914, i, 1011; from *Zeitsch. exp. Path. Ther.*, 15, 39—85).—Attempts were made to ascertain the principles of the action of benzene and light petroleum on the hæmopoetic apparatus and other tissues, and to compare the results with those obtained by treatment with Röntgen and thorium rays. The action of benzene and of thorium causes atrophy of the bone-marrow, and produces a diminution in the number of leucocytes in the peripheral circulation. In other respects, however, there is marked difference in the action of the drugs. The action of light petroleum is similar to that of benzene, but the former is better tolerated, and larger doses can be administered. The general conclusion drawn is that the two organic substances cannot be regarded as rivals to replace the thorium treatment, but that in certain cases they can supplement it.

S. B. S.

**Formation of Amino- and Hydroxy-acids from Glyoxals in the Animal Organism.** H. D. DAKIN and H. W. DUDLEY (*J. Biol. Chem.*, 1914, 18, 29—51).—The authors' attempt to effect the synthesis of amino-acids directly from glyoxals by acting on them or on their acetals with ammonia or derivatives of it were uniformly unsuccessful. In perfusion experiments, however, they have obtained evidence indicating the synthesis of optically active leucine, *α*-aminophenylacetic acid and, possibly, phenylalanine from *isobutyl*, *phenyl*- and *benzyl*-glyoxals respectively. Unimolecular glyoxal (prepared by distilling ordinary glyoxal with phosphoric oxide, and collecting the distillate in water) used in similar experiments gave indications of the formation of glycine, isolated as the *β*-naphthalenesulphonate. The formation of alanine from methylglyoxal could not be observed. The experiments were conducted by perfusing dogs' livers with defibrinated dog's blood

containing the glyoxal together with ammonium hydrogen carbonate. In addition to the amino-acids formed from glyoxals on perfusion, the corresponding hydroxy-acids, glycollic, lactic, leucic, mandelic and phenyl-lactic acids, are produced. These are due to the action of glyoxalase on the glyoxals, and can be effected also in each case *in vitro*.

When benzylglyoxal is given to a rabbit, phenaceturic acid cannot be detected in the urine, showing that the first stage in the decomposition of benzylglyoxal does not consist in the removal of the aldehyde-group by oxidation.

Glyoxals are best prepared by a new method to be published shortly, but those used in these experiments were obtained by the method of Wohl and Lange. *isoButylglyoxalacetal* (from magnesium *isobutyl* bromide and diethoxyacetopiperidide) is a colourless liquid; on hydrolysis, *isobutylglyoxal* is obtained as a yellowish-green liquid, b. p. 45—46°/12 mm. The *semicarbazone*,  $C_{17}H_{18}O_2N_3$ , forms colourless prisms, m. p. 249—250°. The *bis-p-nitrophenylhydrazone*,  $C_{18}H_{20}O_4N_6$ , forms scarlet needles, m. p. 288—290° (with evolution of gas).

From perfusion experiments with *isobutylglyoxal*, pure *d*-leucic acid was prepared. Its properties are identical with those of the *l*-acid already known, except in the sign of its rotation.

*Benzylglyoxal*,  $C_9H_8O_2$ , crystallises in colourless needles, which soften at about 115° and melt at 120—122°. The *bis-p-nitrophenylhydrazone*,  $C_{21}H_{18}O_4N_6$ , forms scarlet needles, m. p. 275—278°.

*l*-Phenylalanine is converted into *l*-phenyl-lactic acid on treatment with nitrous acid.

Inactive  $\alpha$ -carbamidophenylacetic acid has m. p. 196—196·5° (with effervescence); Pinner (A., 1888, 1102) gave 178°. Inactive phenylhydantoin has m. p. 184—185° (Pinner, *loc. cit.*, gives 178°).

R. V. S.

**Formation of *l-p*-Hydroxyphenyl-lactic Acid from *p*-Hydroxyphenylpyruvic Acid in the Animal Organism.** YASHIRŌ KOTAKE and ZENJI MATSUOKA (*Zeitsch. physiol. Chem.*, 1914, 89, 475—481).—In the organism of the dog *p*-hydroxyphenylpyruvic acid is converted, at any rate to a small extent, into *l-p*-hydroxyphenyl-lactic acid, so that the latter substance may arise in pathological cases from tyrosine by way of *p*-hydroxyphenylpyruvic acid.

R. V. S.

**The Influence of Lecithin on the Action of Drugs. IV.** D. M. LAVROV (*Biochem. Zeitsch.*, 1914, 63, 425—435).—A large number of experiments are cited which were carried out with the object of ascertaining the effect of lecithin on the toxic action of mercuric chloride when administered to frogs. In some series the toxic effect was increased, and in others diminished. The results, which are not very regular, depend, according to the author, on the magnitude of the doses, the condition of the animals, and the method of administration.

S. B. S.

**Relationships of the Physiological Actions of Pituitary Extract, Adrenaline, the Substances Derived from Ergot, and 4- $\beta$ -Aminoethylglyoxaline.** PETRE NICULESCU and H. BORUTTAU (*Chem. Zentr.*, 1914, i, 1004; from *Zeitsch. exp. Path. Ther.*, 1914, 15, 1—12).—The influence on one another of the above drugs as regards their action on the blood-pressure in rabbits, and on the surviving uterus of guinea-pigs, was investigated. Pituitary extract was found to activate the adrenaline as regards its effect on blood-pressure, in that a minimal dose of adrenaline was found to exert a marked action when administered after an injection of pituitary extract. Secacornin does not act in a similar way. If 4- $\beta$ -aminoethylglyoxaline and adrenaline are given together the fall of blood-pressure which usually follows the rise caused by the former drug alone does not take place.

Secacornin causes an increase in the number and strength of the rhythmical movements of the uterus, whereas aminoethylglyoxaline and infundibular extract cause an intensive and rapid increase of tone. Adrenaline paralyses the uterus, and this action can be employed for titrating the action of medicaments which increase the tone. Thus, 1/1000 infundibular extract and 1/400,000 adrenaline neutralise one another, although the tone-increasing effect finally predominates. Aminoethylglyoxaline, 1/200,000, has a stronger action than adrenaline, 1/200,000.

S. B. S.

**Action of Pituitrin on the Quantity of Blood Flowing through the Aorta.** CARL TIGERSTEDT and YRJÖ AIRILA (*Chem. Zentr.*, 1914, i, 904—905; from *Skand. Arch. Physiol.*, 1913, 30, 302—308).—A measurement of the blood flowing through the aorta of a rabbit, after injection of pituitrin into the blood stream, shows that the main effect is vaso-constriction. Unlike adrenaline, however, the flow never returns to its original volume, from which it appears that pituitrin contracts and damages the coronary vessels.

J. C. W.

**The Value of the "Biological Reaction" in Picrotoxin Poisoning.** PIO MARFORI and ALFREDO CHISTONI (*Chem. Zentr.*, 1914, i, 906; from *Arch. Farmacol. speriment.*, 1913, 16, 529—538).—After leaving picrotoxin with decaying blood or urine for some time, the characteristic convulsive action on the frog fails, although chemical tests still give positive results. The decomposition of picrotoxinin is even more marked, for, in a few days, both kinds of tests fail.

J. C. W.

**Action of Poisons on the Coronary Vessels of the Heart.** N. P. KRAVKOV (*Pflüger's Archiv*, 1914, 157, 501—530).—The vaso-motor action of a number of substances on the coronary vessels of the heart has been investigated by a special method, which is described, the heart being entirely inactive during the experiment. Adrenaline does not constrict the coronary vessels, and in most cases even causes dilation. Caffeine and theobromine dilate the

vessels. Histamine, tyramine, nicotine, pilocarpine and barium chloride constrict the vessels. The constricting effect usually appears much more weakly in the heart vessels than in the peripheral vessels, whilst the dilatation is more pronounced than in the latter. It is probable that the sympathetic nervous system of the coronary vessels contains chiefly dilatatory fibres, the vasoconstricting fibres belonging to the vagus.

R. V. S.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Changes in the Hydrogen-ion Concentration during Fermentation.** LÜERS (*Chem. Zentr.*, 1914, i, 1101; from *Zeitsch. ges. Brauwesen*, 1914, 37, 79—82).—The hydrogen-ion concentration was measured electrometrically in a fermentation mixture of sugar 10° Balling, containing in a litre 0.25 gram of magnesium sulphate, 5 grams of ammonium sulphate, and 5 grams of phosphoric acid. Fermentations were carried out at 8° and 25°. The following results were obtained at 8°:  $p_H$  at commencement 5.47, after 160 hours, 2.73. Amount of sugar fermented, 67.3%. The following results were obtained at 25°:  $p_H$  at commencement, 5.47, after sixty-five hours, 2.71. Amount of sugar fermented, 60.7%. If the mixture starts with the concentration  $p_H$  2.71, the change during fermentation is very small. The substance to which the alteration of  $p_H$  is due, is derived from the sugar, as similar changes were observed in the fermentation of pure sugar solutions.

S. B. S.

**The Relationship between the Protein Substances of Yeast and Invertase.** PIERRE THOMAS (*Compt. rend.*, 1914, 158, 1597—1600).—Finely powdered cerevisin, isolated from yeast (compare A., 1913, i, 942, 1026) after contact with water, has a hydrolysing influence on sucrose, its power increasing with the fineness of the powder and the temperature at which maceration with water takes place. This phenomenon is not exhibited by the protein obtained in the coagulated state from yeast; thus precluding the possibility of any diastase having been carried down during the precipitation process. The invertase must, therefore, apparently be formed at the expense of the molecule of cerevisin under the influence of water. The hydrolysing power of the cerevisin is greater in the case of autolysed than of fresh yeast, this point being of interest in connexion with Bertrand and Rosenblatt's recent work on the thermo-regeneration of invertase (compare following abstract).

W. G.

**The Thermo-regeneration of Invertase.** GABRIEL BERTRAND and M. ROSENBLATT (*Compt. rend.*, 1914, 158, 1455—1458).—A study of the hydrolysing powers of invertase, obtained from yeast

by different processes, after exposure to varying temperatures. A maceration of dried yeast heated at 70° or 80° for one minute loses all its hydrolysing power, whereas if heated at 90° or 100° for one minute it regains the greater part of its hydrolysing power. A sample of fresh baker's yeast, ground with sand and water, does not show this regeneration of hydrolysing power at the higher temperature. Successive treatment of this yeast with alcohol and ether yields a powder, which shows no sign of regeneration, whereas two successive treatments with acetone, followed by rapid filtration and dehydration, gives an invertase which exhibits the above phenomenon of thermo-regeneration. A sample of the yeast which has undergone autolysis for from one to two days or even four days, when putrefaction has set in, yields, by subsequent maceration with water, a solution of invertase which shows very marked regeneration when heated to 90° or 100° for one minute, whilst being almost inactive after heating to 70° or 80° for the same time.

W. G.

**The Production of Pyruvic Acid by Yeast.** A. FERNBACH and M. SCHOEN (*Compt. rend.*, 1914, 158, 1719—1722. Compare this vol., i, 237).—The authors have isolated from the products of the action of yeast on a solution of invert-sugar, in a mineral medium containing calcium carbonate, both pyruvic acid and a product of its condensation, namely,  $\alpha$ -ketovalerolactonecarboxylic acid (compare Wolff, A., 1901, i, 499), which gives a *p*-nitrophenylhydrazone, m. p. 218—219°. The pyruvic acid was identified through its *p*-nitrophenylhydrazone, m. p. 219—220°, and its *brucine* salt was also prepared. The actual pyruvic acid obtained corresponded with 1.23% of the sugar used, whilst an estimation of the pyruvic acid formed during fermentation, by determining the acetic acid formed by oxidation of the crude intermediate calcium salts with chromic acid, showed that the pyruvic acid represented 8.04% of the sugar used. Following the course of the fermentation by conversion of the pyruvic acid and its salts into iodoform, it was seen that the quantity of pyruvic acid formed increased proportionately with the amount of sugar consumed up to a maximum corresponding with the moment of disappearance of the sugar, after which it decreased.

W. G.

**Formation of Benzoylcarbinol and Other Substances from Phenylglyoxal by the Action of Fermenting Yeast.** H. D. DAKIN (*J. Biol. Chem.*, 1914, 18, 91—93).—The main products of the action of fermenting yeast on phenylglyoxal are benzoylcarbinol and *l*-mandelic acid. Smaller amounts of benzyl alcohol, benzaldehyde and phenylpyruvic acid were detected.

R. V. S.

**The Asymmetric and Symmetric Action of Yeast on the Racemic Forms of Amino-acids which Occur in Nature.** FELIX EHRLICH [and, in part, L. ZAMKOV] (*Biochem. Zeitsch.*, 1914, 63, 379—401).—By fermentation by yeast in the presence of sugar, it has been found possible to prepare *l*-glutamic acid, *d*-histidine,



and *l*-isoleucine from the corresponding racemic forms. Also, an active preparation of the dipeptide alanyl-glycine was isolated from the racemic form, but in this case a pure optical isomeride was not obtainable. On the other hand, neither from aspartic acid, tyrosine, nor proline could an asymmetric degradation be produced, and by using a large excess of yeast and sugar, it was found to be possible to destroy the whole of the aspartic acid; in no experiment was an asymmetric residue left. The author discusses the question as to whether both optical forms of these three amino-acids occur in natural products. It is shown that *l*-aspartic acid and proline, when treated with hydrochloric acid under the conditions employed for protein hydrolysis, do not undergo racemisation, and it is possible, therefore, that racemic forms exist in the protein molecule. S. B. S.

**Synthetic Processes Taking Place During the Autolysis of Yeast.** NICOLAUS IVANOV (*Biochem. Zeitsch.*, 1914, 63, 359—368).—In these investigations, the proteins were precipitated by cupric hydroxide, the proteoses by lead acetate and the diamino-acids by phosphotungstic acid, and the nitrogen in the various fractions was estimated during the progress of autolysis. It was found that the addition of dipotassium hydrogen phosphate to the mixture caused an increase in the protein fraction, at the expense of the fraction precipitated by lead acetate, a fact which indicated a synthesis of proteins. This synthesis can, however, only be demonstrated when the protein degradation has reached a certain limit.

S. B. S.

**The Biological Decomposition of Arsenic Compounds.** HARALD HUSS (*Chem. Zentr.*, 1914, i, 801—802; from *Zeitsch. Hyg. Infekt.-Krank.*, 1914, 76, 361—406).—Many moulds have the power of decomposing any of the arsenic compounds provided that air, moisture, and a suitable substrate are present. The arsenic-containing gases evolved do not appear to be very toxic. These "arsenic-moulds" have been met with in all manner of places, but in small number compared with the other micro-organisms which accompany them. *Penicillium brevicaulis* is one of the most active, but has not been found in living rooms, whereas *Actinomyces* *sp.*, which is quite as active, frequently occurs in isolated groups on moist walls.

J. C. W.

**Presence of Inorganic Iron Compounds in the Chloroplasts of the Green Cells of Plants, considered in Relationship to Natural Photo-synthesis and Origin of Life.** BENJAMIN MOORE (*Proc. Roy. Soc.*, 1914, B, 87, 556—570).—The colourless part of the chloroplast of green plant cells in many plants contains inorganic iron. Whilst the green colouring matter itself is free from iron, it cannot develop in the leaf unless iron is present. In presence of sunlight, the iron-containing substance of the chloroplast develops the colouring matter, which is, therefore, a product of photo-synthesis induced by the substance containing iron.

N. H. J. M.

**The Mobility of Potash in Plant Tissues.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1914, 158, 1400—1404).—The authors have submitted the leaves and stems of a number of plants and trees to electrolytic action by inserting the end of the stem in distilled water in one vessel and the leaf in distilled water in a second vessel. Through the water in the latter vessel air was bubbled continuously, and in each vessel a platinum electrode was inserted. A current was passed for two to four days at a tension of 40—100 volts, and an intensity of 2—3 milliamperes/cm.<sup>2</sup> of stem. At the end of the time the cathode liquid was evaporated to dryness, the residue weighed, and the potassium estimated in it. In almost every case four-fifths of the total residue consisted of potassium carbonate, the remainder consisting of calcium carbonate or magnesium carbonate. In two cases only the anode liquid was examined and found to contain a small amount of phosphoric acid, a trace of sulphuric acid, and still less of hydrochloric acid, in addition to undetermined organic matter.

W. G.

**Behaviour of Hydrocyanic Acid when Injected into Plants.** S. DEZANI (*Chem. Zentr.*, 1914, i, 899; from *Arch. Pharmacol. experim.*, 1913, 16, 539—546).—Hydrocyanic acid is decomposed by cell-sap, one of the products being ammonia. Maize and *Canape nostrana* were killed by injection of a solution corresponding with 0.01 gram of hydrocyanic acid, some of the poison being secreted by the leaf axils. Successive doses of 0.0002, 0.0005, and 0.0013 grams were absorbed without harm, and a day after the last injection no hydrocyanic acid could be detected in the plants. None had escaped through the leaves or roots.

J. C. W.

**The Sterins in the Milky Sap of *Alstonia scholaris*.** R. BR. A. J. ULTÉE (*Chem. Weekblad*, 1914, 11, 456—458).—The latex of *Alstonia scholaris* contains  $\alpha$ -amyrin (m. p. 185°), lupeol, and a small proportion of  $\beta$ -amyrin.

A. J. W.

**Some Basic Extractive Substances of *Amanita muscaria*.** ALBERT KÜNG (*Zeitsch. physiol. Chem.*, 1914, 91, 241—250).—From extracts of this fungus choline, putrescine, herzynine (histidine-betaine) and betaine can be isolated.

R. V. S.

**Action of Individual Nitrates in the Period of Germination of *Avena sativa*.** IV. F. PLATE (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 506—512. Compare this vol., i, 367, 638).—The action of chromium nitrate is similar to that of manganese. Uranyl nitrate killed all the seedlings. Manganous nitrate is not fatal in concentrations less than  $N/200$ . Solutions of the nitrates of iron, nickel and cobalt gave negative results.

A summary is given of the results of the whole investigation.

R. V. S.

**Manganese in *Folia Digitalis*.** HANS FREUND (*Pharm. Zentr.-h.*, 1914, 55, 481—485).—Results of estimations of manganese in ten

samples of *Folia Digitalis* showed that the dry matter contained from 0.0969 to 0.4347% of manganese, whilst the ash contained from 0.8195 to 3.8387%. The analytical method employed is described.

N. H. J. M.

**New Glucosamine Compound and the Constitution of Chitin. II. Formation of Lycoperdin from Lycoperdon bovista and Geaster granulatus on Hydrolysis.** YASHIRŌ KOTAKE and YOSHITA SERA (*Zeitsch. physiol. Chem.*, 1914, 89, 482—484. Compare A., 1913, i, 1212).— $\alpha$ - and  $\beta$ -Lycoperdin can be obtained also from these two fungi.

R. V. S.

**Chemistry of Heterotrophic Phanerogams.** JULIUS ZELLNER (*Monatsh.*, 1914, 35, 333—374).—Analyses of *Neottia nidus avis*, *Monotropa hypopitys*, *Cuscuta europaea*, *Lathraea squamaria*, and *Orobancha gracilis*, including nitrogen in different forms, and various organic compounds. The results show that the composition of heterotrophic phanerogams is not analogous to that of fungi, and does not differ essentially from that of ordinary plants.

Parasitic plants require for their nourishment only a few compounds of simple constitution. It is suggested that the inability of parasites to grow on host plants other than those on which they usually occur, is not due to any deficiency in the food materials supplied by the host plant, but, in some cases, to the presence of substances injurious to the parasite.

The presence of some chlorophyll in the plants examined indicates that they are derived from normally assimilating forms which have more or less lost their chlorophyll by becoming accommodated to heterotrophic conditions.

N. H. J. M.

**The Composition of the Scilla: the Toxic Principle.** W. KOPACZEWSKI (*Compt. rend.*, 1914, 158, 1520—1522).—The author has isolated three substances from *Scilla maritima*, differing from those previously found (compare Wehmer, *Pflanzenstoffe*, 1911), of which one is a bitter, extremely toxic substance, the second a sour-tasting, feebly toxic substance, which is a diuretic, and the third is a polysaccharide. Only the toxic substance is described. It is a pale yellow, very light powder, not hygroscopic, but having a very bitter taste. All attempts to obtain it in a crystalline form failed. It is very soluble in saturated, aliphatic alcohols, acetone or acetic acid, and moderately so in water. It has m. p. 152—154°, and molecular weight,  $335 \pm 24$ . It does not reduce Fehling's or Böttcher's solution or ammoniacal silver nitrate, and is not precipitated by basic lead acetate. On hydrolysis with dilute acids or alkalis it gives highly coloured, resinous substances, together with dextrose, as identified by its osazone. Analysis shows it to be a non-nitrogenous glucoside, having the composition  $C_{17}H_{25}O_6$ , for which the name *scillitin* is proposed.

W. G.

**Presence of a Glucoside in the Sunflower.** AUGUSTO ZANOTTI (*Boll. chim. farm.*, 1914, 53, 4—5).—The leaves of the sunflower

contain a *glucoside* of the probable formula  $C_{11}H_{19}O_4N_2$ . The substance has not yet been completely purified. R. V. S.

**Forms of Sulphur in Plant Materials and their Variation with the Soil Supply.** W. H. PETERSON (*J. Amer. Chem. Soc.*, 1914, **36**, 1290—1300).—The work described in this paper was undertaken in view of the importance of sulphur in relation to crops and soils. The volatile sulphur, sulphates, soluble non-oxidised sulphur, and insoluble non-oxidised sulphur have been estimated in samples of rutabagas, cabbage, sugar beet, lucerne, rape, radishes, clover, June grass, milk, oats, and wheat.

A new method is described for estimating the volatile sulphur in plants. The material is dried at 95—100° in a tube through which purified air is drawn, and the gases are led over heated copper oxide and afterwards into an absorption bottle containing glass beads and a concentrated solution of potassium hydroxide. At the close of the experiment, the copper oxide is boiled with water in order to dissolve the copper sulphate formed. The solution in the absorption bottle is combined with the washings from the copper oxide, and the mixture is concentrated on the water-bath, cooled, and carefully neutralised with hydrochloric acid. The neutral solution is poured slowly into bromine water, heated to oxidise any sulphites, and the resulting sulphates are precipitated with barium chloride. When only small quantities of sulphur are present in the material, the whole is fixed as copper sulphate.

The addition of large quantities of sulphates to the soil causes an increase of sulphur in the plant tissue. When sulphates are not added to the soil, 50—65% of the total sulphur in normally grown plants is found to be present as non-oxidised sulphur, probably in the form of proteins. E. G.

**Germination of Tobacco Seeds.** R. SPALLINO (*Ann. Chim. Applicata*, 1914, **1**, 414—435).—The author has investigated the effect of preliminary immersion of tobacco seeds in various solutions on the subsequent germination. Within limits, the action of the solutions increases with their concentration and with the duration of steeping. Inorganic acids, oxalic, citric, malic, and acetic acids, and ammonium, manganese, and uranyl nitrates accelerate germination considerably. Germination is also favoured to some extent by not more than an hour's immersion of the seeds in sodium nitrate solution not exceeding 0.5% in concentration. Sodium chloride and manganese sulphate slightly hasten the development of the seeds, whilst sulphuric and hydrochloric acids and ammonium chloride retard it, and potassium hydroxide and sodium vanadate prevent it. In general, those compounds which favour enzymic actions accelerate germination of the seeds. The vigour of the plants obtained in the different cases has not yet been investigated. T. H. P.

**Survival of Amylase in Dried Fodders.** RAY E. NEIDIG (*J. Amer. Chem. Soc.*, 1914, **36**, 1312—1314).—A study has been made of the quantity of amylase in four dried fodders, namely,

lucerne hay, clover hay, timothy hay, and maize stover. The method of examination was based on that described by Sherman (A., 1910, ii, 1012). The results showed that, in each case, the fodder retained some degree of amylolytic activity and that this was roughly proportional to the number of living cells in the plant at the time of cutting.

E. G.

**The Ripening of Cheese. I. The Presence of *p*-Hydroxyphenylethylamine in Normal Cheese and its Formation by Lactic Acid Bacteria.** FELIX EHRLICH and FRITZ LANGE (*Biochem. Zeitsch.*, 1914, 63, 156—169).—Tyrosol and *p*-hydroxyphenyl-lactic acid, normal degradation products of tyrosine, could not be detected in cheese. On the other hand, *p*-hydroxyphenylethylamine could be isolated from the aqueous extract in a yield of 0.06% from Gruyère cheese (or 0.092% as calculated on the dried substance). The authors have succeeded also in obtaining a pure culture of bacteria, similar in properties to the *B. casei* described by E. von Freudenreich, which does not belong to the group of *B. coli*, and when grown in a culture medium containing tyrosine, lactose, and inorganic salts produces *p*-hydroxyphenylethylamine and *d*-lactic acid.

S. B. S.

**Do the Ferments of the Flora of the Rind of Hard Cheeses Play any Part in the Scission of the Casein and Fats of the Interior?** O. GRATZ and ST. SZANYI (*Biochem. Zeitsch.*, 1914, 63, 436—478).—The work, which is mainly of technological interest, is concerned chiefly with the examination of horizontal layers of the cheese during various intervals of the ripening process. The water-soluble nitrogen, the nitrogen of decomposition, and ammonia nitrogen were estimated, also the acidity. Some of the cheeses were coated on the outside when fresh with paraffin, in others a flora was allowed to develop. The general conclusion is drawn that the outside flora plays no part in the chemical changes in the interior of the cheese, and that there is no diffusion of enzymes from without.

S. B. S.

**The Adsorption Capacity of Soils.** PAUL ROHLAND (*Biochem. Zeitsch.*, 1914, 63, 87—92).—The author regards the capacity of adsorbing dyes as a trustworthy criterion as to the amount of colloidal matter in a soil. He recapitulates some of the chief properties of such colloids.

S. B. S.

**Nature of Red Soils.** E. BLANCK and J. M. DOBRESCU (*Landw. Versuchs-Stat.*, 1914, 84, 427—445).—The results of analyses of a typical red soil ("Roterde") from Lussin in the Adriatic, and a red soil ("rote Erde") derived from augite-porphry, from Bozen, showed that the latter contains far more constituents soluble in hydrochloric acid than the former; and that the silica and alumina of the augite-porphry soil are very much more soluble in alkali and hydrochloric acid, respectively, than in the case of the "Roterde." The alumina of the Bozen soil is practically all soluble in hydrochloric acid.

The conclusion is drawn that the chief distinction between

"Roterde" and "rote Erde" is that the former is mainly colloidal, whilst in the latter non-colloids predominate. N. H. J. M.

**Presence of Benzene Derivatives in Soils.** EDMUND C. SHOREY (*J. Agric. Research*, 1914, 1, 357—363).—Benzoic acid was found in only one soil, a subsoil, the corresponding surface soil failing to give any indication of its presence.

*m*-Hydroxytoluic acid was found in several soils, but only in any quantity in subsoils.

Vanillin, which has already been detected in soils by its odour, and by some of its reactions, has now been isolated from some Florida soils. N. H. J. M.

**Vegetation Experiments with ["Brown Ammonium Sulphate"] containing Thiocyanate.** A. STUTZER and S. GOY (*J. Landw.*, 1914, 62, 149—158).—The results of water-culture experiments with maize, and of pot experiments with mustard, rye and oats grown in a loam, showed that small amounts of thiocyanate are not injurious, and that ammonium sulphate which does not contain more than 1% of thiocyanate may be employed in the usual amounts without injury.

In pot experiments in which mustard was manured with pure ammonium thiocyanate, it was found that a small amount of the salt (CNS=2.5 kilos. per hectare) was distinctly beneficial, whilst eight times that amount (0.08 gram per 400 square centimetres, or 20 kilos. per hectare) diminished the yield. N. H. J. M.

**Chemical Composition of Rain in the Union of South Africa.** CHARLES FREDERICK JURITZ (*South African J. Sci.*, 1914, 10, 170—193).—Monthly analyses of rain-water, collected at (1) Grahamstown, (2) Kokstad, (3) Bloemfontein, (4) Durban, and (5) Cedara, Natal, 1910—1912; and for shorter periods at Retreat, Douglas, Cradock, Johannesburg, Potchefstroom, Modderpoort, and Weenen.

The yearly averages for the five first-mentioned places are as follows:

	Rainfall, inches.	N per million		N per acre			Chlorine	
		as am- monia.	as nitrates.	as am- monia. lb.	as nitrates. lb.	Total. lb.	per million.	per acre. lb.
1. 1911-12	24.37	0.171	0.132	0.944	0.731	1.675	4.26	23.5
2. 1912	26.54	0.186	0.112	1.118	0.670	1.788	—	—
3. 1910-11	27.82	0.582	0.258	3.658	1.620	5.278	1.06	6.7
1911-12	15.49	1.389	0.388	4.870	1.363	6.233	0.66	2.3
4. 1911	42.34	0.381	0.129	3.651	1.234	4.885	6.39	61.2
1912	31.07	0.556	0.178	3.906	1.249	5.155	10.01	70.4
5. 1912	26.68	0.780	0.143	4.710	0.865	5.575	2.68	16.2

Comparing summer and winter rain, it is shown that the former brings down more nitrogen in both forms than the latter.

Sulphates were estimated in a few samples of rain at Bloemfontein ( $\text{SO}_3=2.10-6.19$ ), and at Durban ( $\text{SO}_3=0.50-5.80$  per million). At the latter place the sulphates brought down during the eight months in which most of the rain fell amounted to 18.9 lb. per acre (as  $\text{SO}_3$ ). N. H. J. M.

## Organic Chemistry.

**Synthetic Preparation of Coal-gas.** LÉO VIGNON (*Bull. Soc. chim.*, 1914, [iv], 15, 601—604).—A gas similar to coal-gas can be prepared from water-gas by heating with lime and steam at  $400^{\circ}$ ; from a mixture of coke and lime in the presence of steam at  $600$ — $1000^{\circ}$ , in accordance with the equation:  $4C + 6H_2O = 3CO_2 + 4H_2 + CH_4$ ; and from coal and lime at  $900$ — $950^{\circ}$ . The method of preparation from coal yields 8 to 10 times the volume of gas obtainable by distillation, and converts most of the nitrogen of the coal into ammonia. The gas can also be prepared free from carbon monoxide, and non-toxic.

A. J. W.

**Preparation of Hexatriacontane.** A. OSKERKO (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 416—417).—*Hexatriacontane*,  $C_{36}H_{74}$ , was obtained as a secondary product in the synthesis of nonadecic acid from octadecyl bromide and magnesium (compare this vol., i, 921):  $2C_{18}H_{37}Br + Mg = C_{36}H_{74} + MgBr_2$ . It forms large, white scales with a satiny lustre, m. p.  $76.5^{\circ}$ ,  $D_4^{20}$  0.764, cannot be distilled without decomposing, and has the normal molecular weight in boiling ethyl acetate.

T. H. P.

**Manufacture of Unsaturated Hydrocarbons.** WILLIAM HENRY PERKIN, FRANCIS EDWARD MATTHEWS, EDWARD HALFORD STRANGE, and HENRY JAMES WHEELER BLISS (Brit. Patent, 29988).—Doubly unsaturated hydrocarbons may be obtained by heating amino-alcohols with or passing them over catalysts such as phosphoric acid; for example,  $NH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot OH = CH_2 : CH \cdot CH : CH_2 + NH_3 + H_2O$ . The admixture of a diluent, such as steam, with the vapour of the amino-alcohol or the conduction of the process in a vacuum hinders secondary decomposition of the product, and the action of a substance like hydrogen chloride on the amino-alcohol may be employed as an intermediate step.

T. H. P.

**Preparation of Trimethylethylene [ $\beta$ -Methyl- $\Delta^{\beta}$ -butylene] and of *iso*Amyl Alcohols from  $\beta$ -Methylbutane.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (Austrian Patent, 63819).—The mixture of four *iso*amyl chlorides, b. p.  $85$ — $105^{\circ}$ , obtained by chlorinating  $\beta$ -methylbutane, is treated with agents such as potassium acetate or alkali hydroxides which remove hydrogen chloride, and the resulting  $\beta$ -methyl- $\Delta^{\beta}$ -butylene distilled. The products of this reaction may be separated by distillation into a fraction boiling at a low temperature and containing the  $\beta$ -methyl- $\Delta^{\beta}$ -butylene, and one boiling at a higher temperature and containing the *iso*amyl alcohols or their esters.

T. H. P.

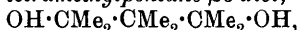
**The Physical Constants of Isoprene.** C. HARRIES (*Ber.*, 1914, 47, 1999—2003).—As there appears to be slight discrepancies between the recorded physical constants of isoprene (compare Steimmig, this

vol., i, 560 ; Harries A., 1911, i, 798), the author has submitted samples of isoprene from two different sources to careful fractionation with the exclusion of air, and from his examination of the products arrives at the values b. p. 33·75—34·0°/762 mm,  $D_4^{16.5}$  0·6867,  $n_D^{16.5}$  1·42617 as the most probable for this substance. D. F. T.

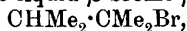
**Action of Metal-Ammoniums on the Halogen Derivatives of Methane Hydrocarbons.** Application to the Estimation of the Halogens in Organic Compounds. E. CHABLAY (*Ann. Chim.*, 1914, [ix], 1, 469—519).—A résumé of work already published (compare A., 1905, i, 502 ; 1906, i, 130, 722 ; 1907, i, 53, ii, 195 ; 1911, i, 939 ; 1912, i, 3, 244, 528 ; 1913, i, 241, 438). W. G.

**Investigation of the Grignard-Valeur Reaction for the Preparation of Glycols from Completely Substituted Ethyl Malonate and Organo-magnesium Iodides.** A. KALISCHEV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 427—453).—In spite of the statements of Valeur (A., 1901, i, 317 ; 1903, i, 416) and Dilthey and Last (A., 1904, i, 667), the author finds that not all esters of dibasic acids react completely with organo-magnesium compounds.

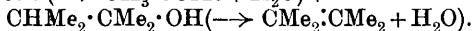
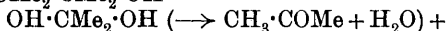
The interaction of ethyl dimethylmalonate and magnesium methyl iodide and subsequent decomposition by means of water of the product obtained yield (1) principally ethyl  $\beta$ -hydroxy- $\alpha\alpha$ - $\beta$ -trimethylbutyrate,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , which decomposes into ethyl isobutyrate and acetone, and (2)  $\beta\gamma\delta$ -tetramethylpentane- $\beta\delta$ -diol,



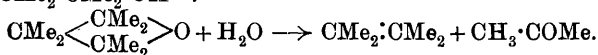
which forms feathery crystals, m. p. 75—76°, b. p. 233·5—234·5°/755 mm., and has the normal molecular weight in boiling ether. When heated with dilute sulphuric acid (1 : 10) or crystalline oxalic acid, the glycol yields  $\beta\gamma$ -dimethyl- $\Delta^2$ -butylene (tetramethylethylene), acetone, and water ; a similar decomposition takes place initially when the glycol is treated (1) with red phosphorus and bromine, which give  $\beta\gamma$ -dibromo- $\beta\gamma$ -dimethylbutane,  $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br}$ , m. p. 169·5—170·5°, or (2) with hydrobromic acid saturated at 0°, which gives  $\beta\gamma$ -dibromo- $\beta\gamma$ -dimethylbutane and the liquid  $\beta$ -bromo- $\beta\gamma$ -dimethylbutane,



treatment of the latter with cold water giving dimethylisopropylcarbinol. According to Slavjanov (A., 1907, i, 578), the decomposition of the glycol would be represented by the scheme :



Since, however, no trace of the intermediate monohydric alcohol could be detected among the products of the action of either dilute sulphuric acid (1 : 10) or 5% acetic acid on the glycol, the author regards the course of the decomposition as :

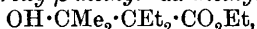


In order to determine the influence of different radicles in com-



pletely substituted malonic esters on the reactivity of the two carbethoxy-groups, the following attempts to synthesise glycols have been carried out.

Ethyl diethylmalonate and magnesium methyl iodide yield no glycol, but only *ethyl β-hydroxy-β-methyl-αα-diethylbutyrate*,



b. p. 102—104°/8 mm.,  $D^{21}_D$  0.9696,  $n^{21}_D$  1.4450, and its decomposition products, acetone and ethyl α-ethylbutyrate, which, together with traces of β-hydroxy-β-methyl-αα-diethylbutyric acid, are obtained on treating the hydroxy-ester with 10% barium hydroxide solution at the ordinary temperature. Thus, in this case only one of the two carbethoxy-groups reacts with the magnesium methyl iodide.

Similarly, ethyl dipropylmalonate and magnesium methyl iodide yield no glycol, the product being ethyl β-hydroxy-β-methyl-αα-dipropylbutyrate, which gives acetone and ethyl α-propylvalerate on hydrolysis.

Ethyl dimethylmalonate and magnesium ethyl iodide yield ethyl β-hydroxy-αα-dimethyl-β-ethylvalerate, which decomposes on distillation under reduced pressure, and gives diethyl ketone and ethyl isobutyrate on hydrolysis.

Ethyl dimethylmalonate and magnesium propyl iodide give ethyl β-hydroxy-αα-dimethyl-β-propylhexoate, which decomposes into dipropyl ketone and ethyl isobutyrate. The corresponding *acid*,  $\text{OH} \cdot \text{CPr}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , decomposes without melting at 175°.

Ethyl dimethylmalonate and magnesium phenyl iodide yield ethyl β-hydroxy-ββ-diphenyl-αα-dimethylpropionate, which decomposes into benzophenone and ethyl isobutyrate, and diphenyl, the latter resulting from the action of magnesium on iodobenzene.

In order to ascertain how the second carbethoxy-group of a completely substituted ethyl malonate behaves towards magnesium alkyl haloid after the first carbethoxy-group has been already substituted, a mixture of dipropyl ketone and ethyl α-bromoisobutyrate was treated with zinc. The resultant compound,  $\text{ZnBr} \cdot \text{O} \cdot \text{CPr}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$ , was found to be unacted on by magnesium ethyl iodide, decomposition by means of water giving ethyl β-hydroxy-αα-dimethyl-β-propylhexoate, which yields dipropyl ketone and ethyl isobutyrate on hydrolysis.

The following general conclusions are drawn. The reaction,  $\text{CR}^1\text{R}^2(\text{CO}_2\text{Et})_2 + 4\text{MgR}^3\text{I}$ , proceeds completely only when  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  represent methyl groups. When one of these three methyl groups is replaced by another radicle, the second carbethoxy-group of the malonic ester loses its power to react with the magnesium alkyl haloid, so that the resulting compound is the ester of a hydroxy-acid. When one of the three radicles is hydrogen, the hydroxy-acid retains its tendency to rearrangement and rupture of the carbon skeleton; the smaller the radicles, the more stable is this skeleton. The reactions considered above afford a good method for obtaining symmetrical ketones.

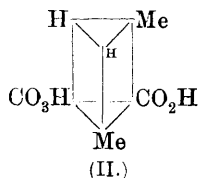
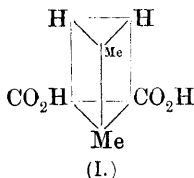
T. H. P.

**Preparation of Ethyl Sulphate.** LEON LILIENFELD (Austrian Patent, 63526).—Ethyl sulphate may be obtained in 83—90% yield by distilling sodium ethyl sulphate in a vacuum.

T. H. P.

**Preparation of Aluminium Acetate Compounds Soluble in Water even after Evaporation.** KALLE & Co. AKTIEN-GESELLSCHAFT (D.R.-P. 272516).—When aluminium acetate solutions are treated with hexamethylenetetramine, with or without addition of a compound such as glycerol, mannitol, citric, lactic or tartaric acid, which increases the solubility of the aluminium acetate in water, evaporation of the liquids under diminished pressure results in the deposition of double compounds of hexamethylenetetramine and aluminium acetate. These double compounds are of more pleasant and less pronounced taste than aluminium acetate itself, and exhibit the therapeutic activity of the latter, together with the antiseptic action of the hexamethylenetetramine. T. H. P.

**Asymmetric Synthesis of *l*- and *d*- $\alpha$ -Methylbutyric Acids by means of Asymmetric Induction.** EMIL ERLÉNMEYER [with F. LANDSBERGER] (*Biochem. Zeitsch.*, 1914, **64**, 366—381).—The author develops his conceptions as to relative asymmetry in the case of methylethylmalonic acid. Marckwald has shown that an optically active  $\alpha$ -methylbutyric acid can be obtained by decomposing the acid brucine salt of this dibasic acid. It is supposed by the author that the symmetric form (I) can be converted into the asymmetric form (II).



The two forms on heating will decompose at different rates; and the formation of optically active  $\alpha$ -methylbutyric acid is not due in Marckwald's experiments merely to the fact that the crystalline salt employed contained more of the one antipode of the acid brucine salt than of the other, as, according to the theory, two acid brucine salts of the acid should exist. Experiments lead to the conclusion that the formation of the active  $\alpha$ -methylbutyric acid is due to asymmetric induction. In the first place an active  $\alpha$ -methylbutyric acid was obtained from the acid brucine salt by adding the brucine (in theoretical quantity) to an alcoholic solution of methylethylmalonic acid, and evaporating off the solvent entirely. Under such conditions, no separation of fractions of a brucine salt could take place. In the second place it was shown that *l*- $\alpha$ -methylbutyric acid could be obtained by heating methylethylmalonic acid with one equivalent of *d*-tartaric acid, and *d*- $\alpha$ -methylbutyric acid could be obtained in a corresponding manner when *l*-tartaric acid was employed. S. B. S.

**Preparation of Hexamethylenetetramine Salts of Palmitic and Stearic Acids.** PHILIPP RÖDER-BRUNO RAABE AKTIENGESELLSCHAFT and ARTHUR WÖBER (Austrian Patent, 63822).—These salts are prepared by heating the molten acid (1 mol.) with the base (1 mol.), either solid or dissolved in water or aqueous alcohol. Both are readily soluble in hot water, giving neutral solutions.

*Hexamethylenetetramine stearate*,  $C_6H_{12}N_4 \cdot C_{17}H_{35} \cdot CO_2H$ , forms a stable, microcrystalline powder, decomposing at about  $140^\circ$  with liberation of formaldehyde and ammonia.

*Hexamethylenetetramine palmitate*,  $C_6H_{12}N_4 \cdot C_{15}H_{31} \cdot CO_2H$ , forms a stable, crystalline powder, decomposing at  $130$ — $140^\circ$ , with liberation of formaldehyde and ammonia. T. H. P.

**Preparation of  $\Delta^9$ -Nonadecenoic Acid.** A. OSKERKO (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 411—416).—Ethyl stearate was reduced by means of sodium to octadecyl alcohol, which was converted by heating with hydrobromic acid into octadecyl bromide, the latter being treated with magnesium and carbon dioxide to obtain nonadecic acid, and this heated with bromine and red phosphorus to transform it into  $\alpha$ -bromononadecic acid. Removal of hydrogen bromide under the influence of diethylaniline resulted in the formation of  $\Delta^9$ -nonadecenoic acid.

*Octadecyl bromide*,  $CH_3 \cdot [CH_2]_{16} \cdot CH_2Br$ , crystallises from absolute alcohol in silvery-white scales, m. p.  $28.5^\circ$ .

*$\alpha$ -Bromononadecic acid*,  $CH_3 \cdot [CH_2]_{16} \cdot CHBr \cdot CO_2H$ , crystallises from light petroleum in yellowish, and from alcohol in snow-white, plates, m. p.  $59$ — $60^\circ$ .

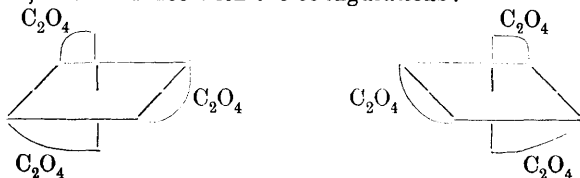
*$\Delta^9$ -Nonadecenoic acid*,  $CH_3 \cdot [CH_2]_{15} \cdot CH:CH \cdot CO_2H$ , separates from alcohol or light petroleum in drusy masses of small, white crystals, m. p.  $51.5^\circ$ . It decolorises alkaline permanganate solution, and in chloroform solution rapidly combines with bromine in the cold, thus differing from  $\Delta^9$ -oleic acid (compare Le Sueur, T., 1904, 85, 1708; Ponzio, A., 1904, i, 548).

*$\alpha$ -Hydroxynonadecic acid*,  $CH_3 \cdot [CH_2]_{16} \cdot CH(OH) \cdot CO_2H$ , forms white leaflets, m. p.  $83$ — $84^\circ$ . T. H. P.

**Naphthenic Acids of High Molecular Weight from Baku Petroleum** EWALD PYHÄLÄ (*Zeitsch. angew. Chem.*, 1914, 27, 407).—By treatment of the alkaline machine oil residues from Baku petroleum with sulphuric acid, and subsequent purification of the precipitated oil by extraction with alcoholic potassium hydroxide and by distillation, a colourless, viscid oil, consisting of a mixture of naphthenic acids, was obtained. It possessed the following physical constants:  $D_{15}^{20}$  0.9470, acid value 168.7, iodine value 2.54. By fractional distillation 13% was obtained boiling at  $310$ — $320^\circ$ , and 63% at about  $340^\circ$ . The lower fraction had an acid number 180.4, corresponding with a molecular weight of 310, and is therefore regarded as an *eicosenoic acid*,  $C_{19}H_{37} \cdot CO_2H$ , an assumption in accord with the composition of the *silver salt*. The higher fraction,  $D_{15}^{21}$  0.9400, had a acid number 147.6, corresponding with a molecular weight of 380. The analysis of the *silver* and *barium* salts showed it to be *eicosipentacosenoic acid*  $C_{24}H_{47} \cdot CO_2H$ . G. F. M.

**Mirror Image Isomerism with Rhodium Compounds. II.** A. WERNER [with J. POUPARDIN] (*Ber.*, 1914, 47, 1954—1960).—

The rhodium oxalates of the formula  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{M}_3$  should give optical isomerides, in accordance with the configurations:



The resolution of the potassium salt,  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , was readily accomplished by means of strychnine nitrate. Fractional crystallisation gave the *d*-strychnine salt as the least soluble fraction, the *l*-salt being much more readily soluble. From the strychnine salts the potassium, sodium, rubidium, and barium salts were obtained by double decomposition with the respective iodides.

The rotatory power of the rhodium oxalates is less than that of the corresponding chromium oxalates, but whereas the latter undergo racemisation very readily in aqueous solution, the former are quite stable; their aqueous solutions can be warmed on the water-bath without appreciable change. The rotation-dispersion of the rhodium salts is very marked, the direction of rotation undergoing a change at the *D*-line, as shown by the following figures for the potassium salt,

$$[\alpha]_{\text{C}} - 26.4^\circ, [\alpha]_{\text{D}} 0^\circ, [\alpha]_{\text{E}} + 114.4^\circ.$$

It is noteworthy that all the metal oxalates which have been obtained as optically active isomerides, namely, those of chromium, rhodium and cobalt, show abnormal dispersion.

The active rhodium salts crystallise in well-developed, garnet-red crystals, which are more readily soluble than the racemic salts. The potassium salts can crystallise out together from the solution of the racemate and the isomerides be separated mechanically; the crystals show hemihedral faces and belong to the triclinic system. This is the first case of the resolution of inorganic compounds by spontaneous crystallisation.

*Strychnine d-rhodium oxalate*,  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{H}_3\text{Str}_3 \cdot 2\text{H}_2\text{O}$ , in a 0.1% solution has  $[\alpha]_{\text{C}}^{18} - 30^\circ$ ,  $[\text{M}]_{\text{C}}^{18} - 421.74^\circ$ ,  $[\alpha]_{\text{G}}^{18} - 25^\circ$ ,  $[\text{M}]_{\text{G}}^{18} - 351.45^\circ$ ,  $[\alpha]_{\text{F}}^{18} + 14.5^\circ$ ,  $[\text{M}]_{\text{F}}^{18} + 203.8^\circ$ ,  $[\alpha]_{\text{E}}^{18} + 102.3^\circ$ ,  $[\text{M}]_{\text{E}}^{18} + 1438.1^\circ$ . The corresponding *l*-salt,  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{H}_3\text{Str}_3 \cdot 9\text{H}_2\text{O}$ , has  $[\alpha]_{\text{C}}^{18} - 40^\circ$ ,  $[\text{M}]_{\text{C}}^{18} - 346.4^\circ$ ,  $[\alpha]_{\text{G}}^{18} - 165^\circ$ ,  $[\text{M}]_{\text{G}}^{18} - 1429^\circ$ ,  $[\alpha]_{\text{F}}^{18} - 75^\circ$ ,  $[\text{M}]_{\text{F}}^{18} - 649.5^\circ$ .

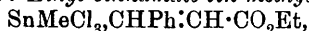
The *d*- and *l*-potassium rhodium oxalate,  $\text{K}_3\text{Y} \cdot \text{H}_2\text{O}$ , where  $\text{Y} = \text{Rh}(\text{C}_2\text{O}_4)_3$ , give well-developed, red, prismatic crystals. The former has  $[\alpha]_{\text{C}}^{18} - 26.4^\circ$ ,  $[\text{M}]_{\text{C}}^{18} - 132.53^\circ$ ,  $[\alpha]_{\text{E}}^{18} + 114.4^\circ$ ,  $[\text{M}]_{\text{E}}^{18} + 574.28^\circ$ , and the latter,  $[\alpha]_{\text{C}}^{18} + 30^\circ$ ,  $[\text{M}]_{\text{C}}^{18} + 150^\circ$ ,  $[\alpha]_{\text{E}}^{18} - 124^\circ$ ,  $[\text{M}]_{\text{E}}^{18} - 622^\circ$ , both in 0.5% solution. The *d*- and *l*-sodium rhodium oxalates,  $\text{Na}_3\text{Y} \cdot 4\text{H}_2\text{O}$ , have  $[\alpha]_{\text{C}}^{18} - 30^\circ$ ,  $[\text{M}]_{\text{C}}^{18} - 152^\circ$ , and  $[\alpha]_{\text{C}}^{18} + 28^\circ$ ,  $[\text{M}]_{\text{C}}^{18} + 142^\circ$ , both in 0.5% solution; they form orange-red, hygroscopic crystals. The *d*- and *l*-rubidium rhodium oxalates,  $\text{Rb}_3\text{Y} \cdot \text{H}_2\text{O}$ , form garnet-red, tetrahedral crystals, having respectively  $[\alpha]_{\text{C}}^{23} \mp 30^\circ$ ,  $[\text{M}]_{\text{C}}^{23} \mp 192^\circ$ , in 0.5% solution. The *d*- and *l*-barium salts,  $\text{Ba}_3\text{Y} \cdot 3$  or  $2\text{H}_2\text{O}$ , crystallise in efflorescent, red needles, and have  $[\alpha]_{\text{C}}^{18} \mp 24^\circ$ ,  $[\text{M}]_{\text{C}}^{18} \mp 275^\circ$ , in 0.5% solution. One gram of the anhydrous salt is soluble in 246 c.c. of water at  $18^\circ$ . T. S. P.

**The Variable Affinity of the Subsidiary Valencies of Tin.** P. PFEIFFER and O. HALPERIN (*Zeitsch. anorg. Chem.*, 1914, 87, 335—352).—Stannic chloride has the greatest power of forming additive compounds of all the tin haloids as it combines with esters of carboxylic acids, in addition to ethers and similar compounds. The derivatives of stannic bromide are less stable, and it does not form solid compounds with all the esters examined. Stannic iodide and tin alkyl haloids have much less power of forming additive compounds, phenyl having a still greater effect than alkyl. The derivatives of dicarboxylic esters must be formulated as cyclic compounds.

*Di-ethyl carbonate tin tetrachloride*,  $\text{SnCl}_4 \cdot 2\text{CO}(\text{OEt})_2$ , forms highly hygroscopic, colourless leaflets, decomposed by water. The *ethyl malonate* compound,  $\text{SnCl}_4 \cdot \text{CH}_2(\text{CO}_2\text{Et})_2$ , has m. p. 115—117°, and a compound with 2 mols. of the ester has not been obtained. The compounds with *methyl succinate*,  $\text{SnCl}_4 \cdot \text{C}_2\text{H}_4(\text{CO}_2\text{Me})_2$ , and *ethyl succinate*,  $\text{SnCl}_4 \cdot \text{C}_2\text{H}_4(\text{CO}_2\text{Et})_2$ , melt at 138° and 95° respectively. *Ethyl glutarate* forms a compound  $\text{SnCl}_4 \cdot \text{CH}_2(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$ , and *ethyl phthalate* a compound,  $\text{SnCl}_4 \cdot \text{C}_6\text{H}_4(\text{CO}_2\text{Et})_2$ .

*Di-ethyl cinnamate tin tetrabromide*,  $\text{SnBr}_4 \cdot 2\text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , has m. p. 70—72; the compounds with ethyl carbonate, ethyl malonate (m. p. 63—65°), and ethyl succinate contain 2 mols. of the ester, and are very unstable. *Acetonitrile tin tetrabromide*,  $\text{SnBr}_4 \cdot 2\text{MeCN}$ , decomposes readily at the ordinary temperature. Ether and many dicarboxylic esters fail to form compounds. Tin tetraiodide crystallises unchanged from the esters, and also from ether and acetonitrile.

The alkyl derivatives combine in very few cases. The only compound obtained is: *Ethyl cinnamate tin methyl chloride*,

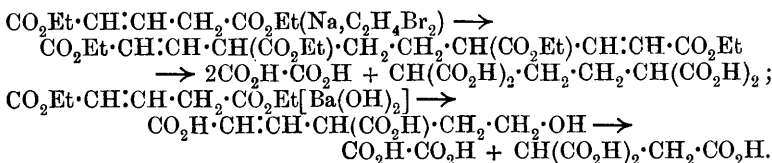


m. p. 50—55°.

C. H. D.

**Trimethyleneglutaric [ $\alpha\alpha$ -Ethyleneglutaric Acid].** B. K. MERESHKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 517—526).—The author has repeated the work of Fecht (A., 1907, i, 906), who regarded (1) the acid, described as  $\alpha\alpha$ -ethyleneglutaric acid, obtained by hydrolysis of the nitrile formed from the dibromide of vinyltrimethylene as identical with (2) that prepared from ethyl glutaconate, ethylene dibromide and sodium ethoxide in alcoholic solution and drew the conclusion that vinyltrimethylene is actually *spiropentane*. Fecht, however, miscalculated the results of his analyses, his weighings showing that acid (1) contains 55.57% C and 6.63% H and not 53.05% C and 6.56% H, and acid (2) 52.78% C and 6.29% H and not 52.98% C and 6.26% H.

Further, an acid of the structure  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$  should give, when oxidised with alkaline permanganate, oxalic and cyclopropane-1 : 1-dicarboxylic acids, whereas the author obtains oxalic, formic, ethanetricarboxylic (carboxysuccinic), and hexanedicarboxylic acids, together with a number of other products, but no cyclopropanedicarboxylic acid. A more probable scheme for the condensation of ethyl sodioglutaconate and ethylene bromide and for subsequent hydrolysis and oxidation of the resultant product is as follows:



In the preparation of the ester of dicarboxysodioglutaconic acid from ethyl sodiomalonate and chloroform according to the equation:  $4\text{CHNa}(\text{CO}_2\text{Et})_2 + \text{CHCl}_3 = \text{C}(\text{CO}_2\text{Et})_2\cdot\text{CNa}\cdot\text{CH}(\text{CO}_2\text{Et})_2 + 3\text{NaCl} + 2\text{CH}_2(\text{CO}_2\text{Et})_2$ , yields of 86, 152, and 176 grams were obtained instead of the theoretical quantities, 70.4, 131 and 141.6 grams, whereas the ethyl malonate also formed amounted to only 20% instead of 50% of the original quantity. It seems probable that further condensation occurs between the tetracarboxylic ester and the malonic esters.

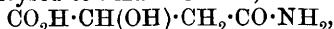
The conclusion is drawn that the acid examined by Fecht was not  $\alpha\alpha$ -ethyleneglutaric acid, but a complex mixture of condensation products.

T. H. P.

**Preparation of an Acid Calcium Lactate.** CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 271643).—A calcium hydrogen lactate containing three lactic acid residues per atom of calcium may be obtained (1) by treating the ordinary acid salt composed of 1 mol. of calcium lactate and 1 mol. of lactic acid with a solvent, such as cold alcohol, for lactic acid, or (2) by evaporating calcium oxide, hydroxide, carbonate or lactate with sufficient or more than sufficient lactic acid to give 3 mols. of the acid per atom of calcium, any excess of acid being subsequently removed by means of a solvent. The salt is readily soluble in water, and its free lactic acid is more stably held than the second molecule of acid in the ordinary acid lactate.

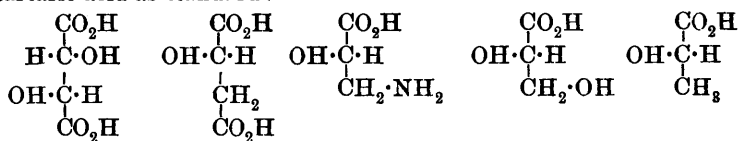
T. H. P.

**The Configuration of the Glyceric and Lactic Acids.** KARL FREUDENBERG (*Ber.*, 1914, 47, 2027—2037).—The configuration of *d*-tartaric acid as derived from that of dextrose (Fischer, A., 1896, i, 525) should also decide that of the malic acids, for the reduction of *d*-tartaric acid gives *d*-malic acid, although in poor yield. On treatment with barium hydroxide solution at 60°, the amide of *l*-malic acid is hydrolysed to *l*-malamic acid,



which is smoothly converted by barium hydroxide solution and bromine into *l*-isoserine,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$ . This substance, under the action of nitrous acid, gives *d*-glyceric acid (compare Fischer and Jacobs, A., 1907, i, 393), the yield being 22% of the theoretical. When treated in hydrobromic acid solution with nitric acid and bromine, *l*-isoserine undergoes conversion into *d*- $\beta$ -bromolactic acid, m. p. 80°,  $[\alpha]_D^{18} + 2.01^\circ$  (in aqueous solution), which can also be obtained by resolution of the synthetic racemic acid with morphine. Reduction with sodium amalgam and dilute sulphuric acid at 15—20° converts *d*-bromolactic acid into *d*-lactic acid (zinc salt,  $[\alpha]_D^{17} - 7.44^\circ$  in water).

From these results the following structures are deduced, taking *d*-tartaric acid as standard :



*d*-Tartaric acid. *l*-Malic acid. *l*-isoSerine. *d*-Glyceric acid. *d*-Lactic acid.

These configurations agree with those indicated by the action of *Penicillium glaucum* on the various racemic acids (Mackenzie and Harden, T., 1903, 83, 424; compare, however, Neuberg and Silbermann, A., 1907, i, 408). D. F. T.

**Behaviour of Crotonic Acid in Ultra-violet Light. I.** R. STÖRMER and H. STOCKMANN (*Ber.*, 1914, 47, 1786—1793).—The only exceptions which Störmmer has yet encountered, to the rule that the simple ethylenic acids are transformed into labile varieties under the influence of ultra-violet light, are crotonic and mesaconic acids. The former acid has again been examined but with no better result, which is remarkable, since the amide is transformed into *isocrotonamide* to an unusually great extent. When crotonic acid is illuminated in other than indifferent solvents, however, addition of the medium takes place, according to the common rule that the active hydrogen atom enters the  $\alpha$ -position, and the remaining radicle, the  $\beta$ -position.

One of the difficulties in deciding whether crotonic acid is transformed into *isocrotonic* acid at all, is to separate a trace of the labile acid from the unchanged material. The few methods which have been proposed have been tried and found to be unsatisfactory. In one case, the product, after illuminating 100 grams of crotonic acid in benzene solution before a Uviol lamp for five weeks, was converted into the sodium salt, only 1.2 grams of which dissolved readily in absolute alcohol. The dry salt was suspended in ether, treated with thionyl chloride, and then with aniline, but it was impossible to isolate an anilide with the m. p. of pure *isocrotonanilide*.

The amides have now been prepared in a pure state, and these differ sufficiently in solubility. An ethereal solution of crotonyl chloride, prepared as above, was strongly cooled and slowly added to liquid ammonia, and the dry residue left on evaporation was recrystallised from acetone. *Crotonamide*,  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ , forms glistening, white needles, m. p. 159.5—160°, which are more soluble in water than in organic media. The amide was dissolved in acetone, and exposed to the Uviol lamp for three weeks, when the residue was extracted with hot benzene. The unchanged amide crystallised at once and was filtered, when *isocrotonamide* separated in slender leaflets, m. p. 102°, the transformation having taken place to the extent of 41.6%.

An aqueous solution of sodium crotonate was illuminated for six weeks, when the dried salt was extracted with alcohol. A yield of 24% of sodium  $\beta$ -hydroxybutyrate was obtained from the extract. Free crotonic acid does not so readily combine with water, the yield of

$\beta$ -hydroxybutyric acid being only 10%. The insolubility of sodium crotonate was also made use of in separating the products obtained in methyl or ethyl alcohol. Slightly less than a 10% yield of  $\beta$ -methoxybutyric acid, b. p.  $117-118^\circ/20$  mm.,  $212-214^\circ/\text{atm.}$ , was obtained in the one case, and a 6.8% yield of  $\beta$ -ethoxybutyric acid, b. p.  $113^\circ/14$  mm., in the other. J. C. W.

**Does Osmium Dioxide Act as a Catalyst in Hardening Fats?** W. NORMANN and F. SCHICK (*Arch. Pharm.*, 1914, 252, 208-210).—When osmium tetroxide (which is a non-conductor) is heated with oleic acid, the undissolved residue, after being freed from the blackened oil and washed with petroleum, is a good conductor of electricity. The tetroxide under these conditions, therefore, is not converted into osmium dioxide, as Lehmann states (*A.*, 1913, ii, 331), but is reduced to the metal. In this case, therefore, as also in those of the oxides of copper and nickel (Meigen and Bartels, this vol., i, 482), the catalyst in the hydrogenation of fats is the metal, not the oxide. C. S.

**Determination of the Constitution of Enols.** JOHANNES SCHEIBER and PAUL HEROLD (*Annalen*, 1914, 405, 295-346).—According to Claisen's rule a substance containing the group  $R\cdot CO\cdot\dot{C}H\cdot COR'$  enolises to  $OH\cdot CR\cdot\dot{C}\cdot COR'$  if  $-COR$  is the more negative acyl group, for example, benzoylacetone enolises to  $OH\cdot CMe\cdot CHBz$ .

His titration method leads Meyer to the opposite opinion, the enol having the formula  $CHAc\cdot CPh\cdot OH$ , since the enolisation tendency of the benzoyl group is greater than that of the acetyl (*A.*, 1912, i, 940). The authors have made a comprehensive survey of the numerous physical and chemical methods which have been employed to determine the constitution of enols, and are of opinion that a generally applicable process has not yet been brought forward. They have applied the ozonide method to the solution of the problem (*A.*, 1913, i, 490) and claim for it the following advantages. Enols rapidly unite additively with ozone at  $-20^\circ$ , therefore under conditions which prevent or render improbable any transformation of the primarily existent complex into a more reactive form. Desmotropic ketonic modifications do not react with ozone, whilst the corresponding enols do. Keto-enolic transformations are not catalytically influenced by ozone, because partly enolised substances are only partly converted into ozonides.

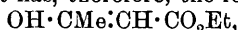
The method of working is as follows. A solution of 1-2 grams of the substance in dry chloroform or carbon tetrachloride is cooled to  $-20^\circ$  with careful exclusion of moisture, and is then treated with 6-8% unwashed ozone until a persistent odour of the latter is observed. The time required may be only a few moments, but usually two to three hours is sufficient. The solvent is removed by a current of dry air at  $0^\circ$ , and the residue is treated with water at the ordinary temperature. The decomposition of the ozonide proceeds vigorously, but not explosively. The fission products are always kept in contact with the water overnight before being examined.

Ethyl malonate is quite stable to ozone, and does not yield a trace



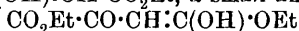
of carbon dioxide or of ethyl glyoxalate; its formula, therefore, is  $\text{CH}_3(\text{CO}_2\text{Et})_2$ , a result in agreement with that of Meyer's volumetric process.

Even after many hours' treatment, ethyl acetoacetate yields only a small quantity of an ozonide, the decomposition products of which contain acetic acid and ethyl glyoxylate (*loc. cit.*), but not carbon dioxide, methylglyoxal, or alcohol. The enol present in ethyl acetoacetate in small amount has, therefore, the formula



not  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{OEt}$  (compare Bielecki and Henri, this vol., ii, 318).

Ethyl oxalacetate is easily and completely converted into an ozonide, the decomposition products of which contain oxalic acid, ethyl glyoxylate (identified as the phenylhydrazone, m. p. 128°), and a small quantity of carbon dioxide. The predominating enol, therefore, has the formula  $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , a small amount of



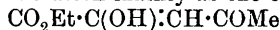
also being present (compare Meyer, *loc. cit.*).

Ethyl benzoylacetate is only partly converted into an ozonide the decomposition of which yields benzoic acid and ethyl glyoxylate, but not carbon dioxide. The enol, therefore, is  $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ .

Acetylacetone is incompletely but easily ozonised. The decomposition products contain methylglyoxal (osazone, m. p. 146°) and carbon dioxide. The enolised portion of the diketone is, therefore, partly the enol,  $\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{COMe}$ , and partly the dienol,  $\text{CMe}(\text{OH})\cdot\text{C}\cdot\text{CMe}\cdot\text{OH}$  (see below).

The results previously recorded in connexion with benzoylacetone (*loc. cit.*) require correction. The ozonide is obtained quantitatively, and gives by its decomposition an almost quantitative yield of benzoic acid, methylglyoxal (the directly precipitated osazone has m. p. 135—140°, instead of 146°, and therefore contains an impurity, probably phenylglyoxalosazone), and carbon dioxide. Benzoylacetone exists in solution, therefore, mainly as the enol  $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COMe}$ ; the other enol,  $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COPh}$ , and the dienol,  $\text{OH}\cdot\text{CPh}\cdot\text{C}\cdot\text{CMe}\cdot\text{OH}$ , are also present in small amount.

Oxalacetone exists in solution mainly as the enol



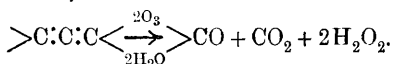
and to a small extent as the enol  $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  (*loc. cit.*); in addition, a considerable amount of the dienol must be present because the decomposition of the ozonide yields a considerable quantity of carbon dioxide, and, moreover, Meyer's volumetric process gives results indicating far more than 100% of enol.

Oxalacetophenone exhibits remarkable behaviour. It is only slightly attacked by ozone even although Meyer's method shows the presence of at least 100% of enol. The decomposition products of the ozonide are benzoic and oxalic acids, phenylglyoxal and ethyl glyoxylformate (both identified as the osazones), and carbon dioxide. The first four of these products are those which would be expected from the decomposition of the two enols  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}\cdot\text{CPh}\cdot\text{OH}$  and  $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{COPh}$ . Oxalacetophenone, however, cannot consist of these two enols because there is no reason why they should not

form ozonides. The production of carbon dioxide during the decomposition of the ozonide indicates that a dienol is present, but a satisfactory explanation of the behaviour of oxaloacetophenone cannot yet be given. Dibenzoylmethane is another substance which is scarcely attacked by ozone at 0°, although the volumetric method indicates the presence of about 100% of enol.

The ketonic modification, m. p. 108—110°, of dibenzoylacetylmethane is unattacked by ozone, but the enol, m. p. 80—85°, yields a yellow ozonide by the decomposition of which are produced benzoic acid and the hydrate, m. p. 55—60°, of phenyl methyl triketone (identified as the semicarbazone, m. p. 190°, and phenylhydrazone, m. p. 165°). The formation of these two substances indicates that the enol of dibenzoylacetylmethane is mainly  $\text{OH}\cdot\text{CPh}\cdot\text{C}(\text{COMe})\cdot\text{COPh}$ , but the presence of a small amount of the other enol,  $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{COPh})_2$ , is possible even although acetic acid and diphenyl triketone could not be detected among the products of decomposition of the ozonide.

The presence of carbon dioxide amongst the decomposition products of the ozonides of diacetylmethanes indicates the presence of accumulated double linkings, that is, of dienols:



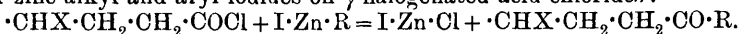
The estimation of carbon dioxide produced by the decomposition of an ozonide is not easy, but a gravimetric apparatus is described which gives quite satisfactory results, the absorption vessel gaining only about 2 mg. in weight when the ozonide of a substance which cannot contain accumulated double linkings is decomposed. The following generalisations are deduced from the amounts of carbon dioxide produced during the decomposition of the ozonides of the substances mentioned above. The groups  $\cdot\text{CO}_2\text{Et}$ ,  $\cdot\text{COMe}$ ,  $\cdot\text{COPh}$ , and  $\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  tend to enolise in the order given; the carbethoxy has little or no tendency, whilst  $\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  has a very great tendency. A group which has little tendency to enolise may be induced to do so by the presence of a pronouncedly enolisible group; thus, ethyl acetoacetate does not form any dienol, whereas ethyl oxalacetate does to a slight extent, the carbethoxy-group enolising in the presence of the  $\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  group.

The  $\alpha$ -,  $\beta$ -, and  $\gamma$ -modifications of ethyl formylphenylacetate (Wislicenus, A., 1912, i, 623) each form an ozonide by the decomposition of which are produced formic acid and ethyl phenylglyoxylate (identified as the phenylhydrazone), together with a little carbon dioxide, formed, probably, by the ozonisation of performic acid (d'Ans and Frey, A., 1912, i, 601). The enol in the  $\alpha$ -ester and the  $\gamma$ -ester, therefore, are stereoisomeric oxymethylenes, not structural isomerides as Wislicenus is inclined to believe (*loc. cit.*; compare also Meyer, A., 1912, i, 861).

The authors have also examined the enolic modifications of ethyl diacetylsuccinate (Knorr, A., 1899, i, 673). The  $\alpha_3$ -ester, m. p. 31—32°, does not form an ozonide. The  $\alpha_1$ -ester yields an ozonide the decomposition products of which are oxalic acid, ethyl diketobutyrate, and probably formaldehyde. The  $\alpha_4$ -ester (prepared from the di-sodio-

derivative) forms an ozonide which yields oxalic and acetic acids, formaldehyde, and ethyl diketobutyrate, but not ethyl diketosuccinate. The authors interpret these results to denote that (i) the  $\alpha_3$ -ester is ketonic, not enolic; they show that it does not react with alcoholic bromine; (ii) the  $\alpha_1$ -ester is a mixture of an enolic and a ketonic (probably  $\alpha_3$ ) modification. Meyer's volumetric method indicates that there is also present an enol which does not react with bromine, but does form an ozonide; (iii) the  $\alpha_4$ -ester is also a mixture of an enolic and a ketonic modification. C. S.

**Syntheses by means of Mixed Organo-metallic Derivatives of Zinc.  $\gamma$ -Chloroketones and Corresponding Products of Hydrolysis.** HENRI WOHLGEMUTH (*Compt. rend.*, 1914, 159, 80—82).— $\gamma$ -Halogenated ketones can be readily prepared by the action of zinc alkyl and aryl iodides on  $\gamma$ -halogenated acid chlorides:



A number of such ketones have been prepared from  $\gamma$ -chlorobutyryl chloride,  $\gamma$ -chloro-*n*-valeryl chloride and  $\gamma$ -bromo-*n*-valeryl chloride. The condensation of these acid chlorides with zinc ethyl iodide at 0° only gives a small yield of the required ketone, the main products being tarry, resulting from a more advanced condensation, amongst which esters of tertiary  $\gamma$ -chloro-alcohols have been isolated. The author has prepared  $\delta$ -chloro- $\alpha\alpha$ -diethylbutyl  $\gamma$ -chlorobutyrate,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{Et})_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , b. p. 172—174°/17 mm. Good yields of the required ketones are, however, obtained by effecting the condensation at -15° to -20°, and the following compounds are described: *ethyl  $\gamma$ -chloro-*n*-butyl ketone*, b. p. 79°/13 mm., giving a *semicarbazone*, m. p. 129—129·5°; *ethyl  $\gamma$ -chloropropyl ketone*, b. p. 80—80·5°/17 mm., giving a *semicarbazone*, m. p. 118°, and a *p*-nitrophenylhydrazone, m. p. 106—107°; *ethyl  $\gamma$ -bromo-*n*-butyl ketone*, b. p. 88—89°/11 mm., giving a *semicarbazone*, m. p. 142° (decomp.); *phenyl  $\gamma$ -chloro-*n*-butyl ketone*, b. p. 155—156°/15 mm., giving a *semicarbazone*, m. p. 123°; and *p*-tolyl  $\gamma$ -chloropropyl ketone, white leaflets, m. p. 33·5°, giving a *semicarbazone*, m. p. 186°.

These  $\gamma$ -chloro-acyclic ketones are easily hydrolysed by boiling with water, giving the corresponding  $\gamma$ -hydroxyketones which readily undergo dehydration, giving  $\alpha$ - and  $\beta$ -dihydrofuran derivatives, these latter being obtained by distilling the  $\gamma$ -hydroxyketones under atmospheric pressure. Thus *ethyl  $\gamma$ -hydroxy-*n*-butyl ketone*, a colourless, oily liquid, b. p. 86·5°/11 mm., gives an *anhydride*, b. p. 122—123°, a *semicarbazone*, m. p. 91°, and a *phenylurethane*, m. p. 79°.

*Ethyl  $\gamma$ -hydroxypropyl ketone*, b. p. 115—116°/21 mm., gives an *anhydride*, b. p. 109—110°, and a *phenylurethane*, m. p. 84°.

On reduction with sodium amalgam the  $\gamma$ -hydroxyketones readily yield the corresponding  $\gamma$ -glycols, colourless oils, which, on boiling with 33% aqueous sulphuric acid, yield quantitatively alkyltetrahydrofurans. Thus *hexane- $\alpha\delta$ -diol*, b. p. 134—135°/18·5 mm., yields a *diacetate*, a mobile liquid, b. p. 122°/14 mm., a *diphenylurethane*, m. p. 82°, and 2-ethyltetrahydrofuran, b. p. 107—108°/770 mm.

*Heptane- $\beta\epsilon$ -diol*, b. p. 132°/18·4 mm., yields a *diphenylurethane*, m. p. 147°, and 2-methyl-5-ethyltetrahydrofuran, b. p. 117—118°.

Methyl  $\gamma$ -hydroxypropyl ketone reacts in the cold in alcohol with phenylhydrazine to give a cyclic compound (compare Lipp, A., 1889, 843), and its oxime at 100° loses water and gives a cyclic compound (compare Marshall and Perkin, T., 1891, 59, 880).

Ethyl  $\gamma$ -hydroxy-*n*-butyl ketone, on the other hand, yields a normal *phenylhydrazone*, an oil, and an *oxime*, a colourless oil, b. p. 149—150°/13 mm., without change. The  $\gamma$ -chloro-ketones, however, readily yield cyclic compounds. W. G.

**Plant Colloids. IV. Displacement of the Phosphorus Content by Changes of Condition and the Diastatic Decomposition of Starch.** MAX SAMEC (*Koll. Chem. Beihefte*, 1914, 6, 23—54. Compare A., 1913, i, 17, 1155).—By the action of 0.125*N*-potassium hydroxide on a starch suspension, it has been found possible to separate the starch into two fractions, one of which contains phosphoric acid, whilst the other is practically free. The products were purified by prolonged dialysis, and as a result, 38 grams of phosphorus-free amylose and 49 grams of amylopectin were obtained. The aqueous solutions of amylose are non-conducting, and their viscosity is not affected by the addition of acid or alkali. The readiness with which the amylose is coagulated by alcohol is, however, as in the case of the original starch, increased by acids and diminished by alkalis. These observations show clearly that the physico-chemical properties of starch solutions are to a considerable extent determined by the phosphorus content.

Since it is probable that the high viscosity of starch solutions is determined by the amylopectin, and since this is decomposed by the action of diastase, it was to be expected that diastatic decomposition of starch would lead to the liberation of the inorganic substance. The experiments which have been made in this connexion confirm this view, for it has been found that dextrans containing phosphorus are formed in the action of diastase on starch and that these compounds exhibit the properties of electronegative colloids. By the action of boiling water, phosphoric acid is set free from the products of the diastatic action. H. M. D.

**The Action of Ultra-violet Rays on Lævulose. The Formation of Formaldehyde and Carbon Monoxide.** ALBERT RANG (*Biochem. Zeitsch.*, 1914, 64, 257—287; *Bull. Soc. chim. Biol.*, 1914, 1, 26—36).—Under the action of ultra-violet rays, lævulose in solution undergoes scission with the formation of formaldehyde, carbon monoxide, carbon dioxide, methyl alcohol, and substances of aldehydic and acid character, which have not been further identified. It is claimed that the degradation of this sugar has been produced for the first time without the agency of either chemicals or ferments.

S. B. S.

**Inversion of Sucrose Solution by Aspartic Acid.** LEOPOLD RADLBERGER and WILHELM SIEGMUND (*Chem. Zentr.*, 1914, i, 1556—1557; from *Österr.-ung. Zeitsch. Zucker-Ind. Landw.*, 43, 29—43).—Experiments on the inversion of sucrose by inactive

aspartic acid have been carried out at temperatures from 30° to 80° with an interval of 5°. The periods were 0, 5, 10, 15, 30, 60, 120, 180, and 240 minutes. At the end of each experiment, the solution was immediately rendered alkaline with sodium hydroxide, cooled to 20°, and the invert-sugar estimated by Herzfeld's method. The results are given in a series of tables and curves. The increase in the formation of invert-sugar during equal intervals with increasing temperature, and also with increasing periods, can be represented by fairly regular curves which rise more rapidly at higher than at lower temperatures.

H. W.

**Lactal and Hydrolactal.** EMIL FISCHER and GEORGE O. CURME, jun. (*Ber.*, 1914, 47, 2047—2057).—In a recent paper on the reduction of acetobromoglucose to triacetylglucal and the hydrolysis of the latter to glucal, it was briefly stated that acetobromolactose behaved similarly (this vol., i, 253). A complete account of "acetolactal," or more strictly speaking, hexa-acetyl-lactal and of lactal and hydrolactal is now given. The relationship between these compounds and lactose is demonstrated by the production of mucic acid on oxidation. The formation of hydroglucal, by the action of emulsin on hydrolactal, also shows that it is the dextrose part of the lactose molecule which is affected by the above reduction.

Acetobromolactose, prepared by the action of hydrogen bromide and glacial acetic acid on octa-acetyl-lactose, was shaken with zinc dust and 50% acetic acid at 0°, until the sugar completely dissolved. The filtrate was then neutralised with sodium hydrogen carbonate and extracted with ether. *Hexa-acetyl-lactal* ("acetolactal"),  $C_{22}H_{32}O_{15}$ , has m. p. 113—114° (corr.), and the optically pure specimens obtained after six recrystallisations from alcohol have  $[\alpha]_D^{20} - 12.27^\circ$ ,  $-12.14^\circ$ , in *s*-tetrachloroethane. It absorbs bromine, forming a *dibromide*, which separates in microscopic, thin prisms, m. p. 207° (corr., decomp.),  $[\alpha]_D^{18} + 135.5^\circ$ ,  $[\alpha]_D^{16} + 135.7^\circ$ , in *s*-tetrachloroethane. When left with barium hydroxide solution at 37°, it is hydrolysed to *lactal*,  $C_{12}H_{20}O_9$ , which crystallises with  $1H_2O$ , in slender, white prisms, m. p. 184—186° (corr.), whilst the anhydrous compound, obtained in a high vacuum, is pale yellow and has m. p. 165—170° (decomp.). For the hydrate, the values  $[\alpha]_D^{19} + 26.92^\circ$  and  $+26.77^\circ$  were obtained, and for the anhydride,  $[\alpha]_D^{22} + 28.53^\circ$ , or, calculated for the hydrate,  $+26.95^\circ$ . The agreement in rotation is strange, seeing that the compounds differ so widely in m. p.'s. Lactal is faintly sweet, does not give the pine-splinter test, and is practically indifferent towards Fehling's solution or phenylhydrazine, but it resembles glucal in that its solutions restore the colour to Schiff's reagent, decolorise bromine water, and become dark on warming with hydrochloric acid.

Hexa-acetyl-lactal is quickly reduced in presence of spongy platinum to *hexa-acetylhydrolactal*,  $C_{24}H_{34}O_{15}$ , a colourless powder which softens at 50—60°, and is readily hydrolysed by baryta water at 37°. *Hydrolactal*,  $C_{12}H_{22}O_9$ , is also most readily obtained by the reduction of lactal. It crystallises from 80% alcohol in slender prisms, with  $1H_2O$ ,  $[\alpha]_D^{20} + 26.82^\circ$ ,  $[\alpha]_D^{19} + 26.79^\circ$ ,  $26.58^\circ$ , in water, and this hydrate, like the anhydride, has m. p. 204—205° (corr.). It has none

of the aldehydic and reducing properties of lactal, but is hydrolysed by dilute acids, the production of galactose being proved by the isolation of mucic acid on evaporation with dilute nitric acid. It was found to be extremely difficult actually to separate the products of hydrolysis, but, after destroying the galactose produced by the action of emulsin, by yeast fermentation, a good yield of hydroglucal could be isolated from the residue.

J. C. W.

**Cellobial and Hydrocellobial.** EMIL FISCHER and KÁLMÁN VON FODOR (*Ber.*, 1914, 47, 2057—2063).—Acetobromocellobiose has been reduced and submitted to the further treatment which was described in the cases of dextrose (A., 1913, i, 445; this vol., i, 252) and lactose (preceding abstract). The relation of hydrocellobial to hydrolactal and hydroglucal is demonstrated by the formation of a reducing sugar and of hydroglucal by the action of emulsin.

Analytically pure acetobromocellobiose should be used in the reduction, since the presence of unchanged octa-acetylcellobiose hinders the purification of the new products.

*Hexa-acetylcellobial*,  $C_{12}H_{14}O_9Ac_6$ , separates from chloroform and petroleum in small, rhombic leaflets, m. p. 134—135° (corr.),  $[\alpha]_D^{17} - 19.8^\circ$ ,  $-19.6^\circ$ , in *s*-tetrachloroethane, and forms a *dibromide*, in very pale yellow, microscopic prisms, m. p. 165—166° (corr.),  $[\alpha]_D^{20} + 57.9^\circ$ ,  $+57.4^\circ$ . When left with baryta water, it is hydrolysed to *cellobial*,  $C_{12}H_{20}O_9$ , which forms colourless prisms, m. p. 175—176° (corr.),  $[\alpha]_D^{20} + 1.0^\circ$ , in water, and reacts like lactal.

*Hexa-acetylhydrocellobial*,  $C_{12}H_{16}O_9Ac_6$ , is obtained, by catalytic reduction, in colourless, microscopic prisms or tablets, m. p. 133—134°,  $[\alpha]_D^{19} + 11.2^\circ$ ,  $[\alpha]_D^{18} + 11.1^\circ$ , in *s*-tetrachloroethane, and *hydrocellobial*,  $C_{12}H_{22}O_9$ , crystallises in colourless prisms, m. p. 222° (corr.),  $[\alpha]_D^{18} + 4.3^\circ$ ,  $[\alpha]_D^{21} + 4.1^\circ$ , in water. After hydrolysis by emulsin, followed by destruction of the dextrose by yeast, hydroglucal was isolated in good yield.

J. C. W.

**Action of Concentrated Sulphuric Acid on Cellulose.** S. TSCHUMANOV (*Kolloid. Zeitsch.*, 1914, 14, 321—322).—In reference to the preparation of colloidal carbon by the action of sulphuric acid on sucrose (Sabbatani, this vol., ii, 198), the author communicates observations relative to the action of the concentrated acid on cellulose. Strips of filter paper were left for some days in contact with the acid, and the resulting dark-coloured liquid then treated with a large volume of water. The precipitate, washed until free from sulphuric acid, and dried at 100—112° until the weight became constant, was found to contain C 62.1%, H 5.0%, and O 32.9%, corresponding with the formula  $(C_2H_2O)_n$ .

At the end of two and a-half years it was found that the liquid obtained from 2.59 grams of cellulose and 100 c.c. of acid had solidified to a gelatinous mass.

H. M. D.

**Action of Ammoniacal Copper Hydroxide on Cellulose.** EDM. CONNERADE (*Bull. Soc. chim. Belg.*, 1914, 28, 176—186).—Experiments have been made on the solubility of cellulose in ammoniacal copper hydroxide, and on the relationships existing between the concentrations

of ammonia, copper and the quantity of cellulose dissolved. It is shown that a solution of ammoniacal cuprous hydroxide, prepared at low temperatures, contains, in comparison with cupric hydroxide, a large excess of colloidal ammoniacal cuprous hydroxide. The cupric hydroxide only plays a secondary part in the solution of the cellulose. The solubility of cellulose is proportional to the concentration of the colloidal ammoniacal cuprous hydroxide. The solution of cellulose is brought about by the combination of quantities of colloidal ammoniacal cuprous hydroxide and water in amounts which increase to a point at which an equilibrium exists between the liquid and solid phases. The strongly hydrated colloidal complex combines with ammonia in proportion to its concentration, and this tends to render the complex more stable. The coagulation of the colloidal complex can be effected reversibly in solution.

J. F. S.

The Asymmetric Cobalt Atom. X. A. WERNER [with H. KUH and P. WÜST] (*Ber.*, 1914, **47**, 1961—1979).—The tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte salts have the constitutional formula  $\left[ \text{en}_2 \overset{\text{III}}{\text{Co}} \begin{array}{c} \text{NH}_2 \\ \text{O}_2 \end{array} \overset{\text{IV}}{\text{Co}} \text{en}_2 \right] \text{X}_4$  (compare A., 1910, ii, 857). Calling the two radicles  $\left( \text{en}_2 \overset{\text{III}}{\text{Co}} \right)$  and  $\left( \text{en}_2 \overset{\text{IV}}{\text{Co}} \right)$ , A and B, four optically active series of isomerides should exist, namely: + A + B, - A - B, + A - B, and - A + B. Hitherto only the first two series and the corresponding racemates have been isolated. The resolution was accomplished by treating the aqueous solution of the bromide with *d*- or *l*-bromocamphorsulphonate. The filtrate from the precipitate was fractionally crystallised, and the precipitate, which contained the tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte bromosulphonates besides silver bromide, was fractionally extracted with hot water and the extracts fractionally crystallised. The final yield was very small, but the pure *d*- and *l*-bromocamphorsulphonates of the isomeric dicobalt salts were obtained, either in dark green leaflets or in olive-green needles, the former being the more readily soluble. The specific rotatory powers were:

	From <i>d</i> -acid.	From <i>l</i> -acid.
Leaflets . . . .	+ 520°	- 520°
Needles . . . .	- 280°	+ 280°

The bromides prepared from these had  $[\alpha] \pm 840^\circ$ ,  $[M] \pm 6855^\circ$ , which is the greatest rotatory power hitherto observed. This high activity is connected with the presence of quadrivalent cobalt in the molecule, since when it is reduced to the trivalent condition the activity diminishes considerably.

The active tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte salts are fairly stable in aqueous solution, but after keeping the solution for some weeks the activity completely disappears. This loss of activity is accompanied by decomposition, the olive-green solutions changing to a brownish-yellow colour.

By the action of ammonia the active tetraethylenediamine- $\mu$ -imino-

peroxocobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{O}_2 \end{array} \text{Co en}_2 \right] \text{X}_3$ , are obtained from the aminoperoxocobaltic salts. A change of rotation occurs, the *d*- and *l*-aminoperoxo-salts giving respectively the *l*- and *d*-iminoperoxo-salts. At the same time the rotation diminishes considerably, the iodides having  $[\alpha] \pm 160^\circ$ ,  $[\text{M}] \pm 1372^\circ$ . Also the active aminoperoxo-salts could be converted into the valency isomeric, red tetraethylenediamine- $\mu$ -ammoniumperoxo-salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{O}_2 \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{Co en}_2 \right] \text{X}_3$  ;

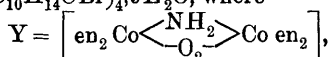
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again, there is a change in the sign of, and a diminution in, the rotation, the dithionates having  $[\alpha] \pm 192^\circ$ ,  $[\text{M}] \pm 1625^\circ$ . Comparing the bromides of the green aminoperoxo- and the red ammoniumperoxo-series, the change in molecular rotation is from  $-6854^\circ$  to  $+1510^\circ$ , a total change of  $8364^\circ$ , thus showing the astonishingly great effect which a change from principal to subsidiary valency has on the optical rotation.

From the active  $\mu$ -aminoperoxo-salts were also prepared the active  $\mu$ -amino-ol-dicobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array} \text{Co en}_2 \right] \text{X}_4$ , the active  $\mu$ -aminonitrodicobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NO}_2 \end{array} \text{Co en}_2 \right] \text{X}_4$ , and the active  $\mu$ -amino-sulphatodicobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{SO}_4 \end{array} \text{Co en}_2 \right] \text{X}_3$ . In each case there is a change in the sign of, and a considerable diminution in, the rotation.

The relation between the rotatory powers in the various series has still to be studied with homogeneous light, since the rotation dispersion is great in all cases. For example, in the  $\mu$ -aminoperoxo-series the values  $[\alpha]_D^{19} + 814.4^\circ$  and  $[\alpha]_E^{19} + 1200^\circ$ , were observed.

*d*-Tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte-*d*-bromocamphorsulphonate,  $\text{Y} (\text{SO}_3 \cdot \text{C}_{10}\text{H}_{14}\text{OBr})_4 \cdot 9\text{H}_2\text{O}$ , where



forms dark green leaflets;  $[\alpha]^{20} + 520^\circ$ ,  $[\text{M}]^{20} + 9734.4^\circ$ . The corresponding *ld*-salt,  $\text{Y}(\text{SO}_3 \cdot \text{C}_{10}\text{H}_{14}\text{OBr})_4 \cdot 8\text{H}_2\text{O}$ , crystallises in olive-green needles, and has  $[\alpha]^{20} - 280^\circ$ ,  $[\text{M}]^{20} - 5191.2^\circ$ . The *d*- and *l*-bromides,  $\text{YBr}_4 \cdot 5\text{H}_2\text{O}$ , prepared from the bromocamphorsulphonates by double decomposition with sodium bromide, form greenish-black, glistening prisms,  $[\alpha]^{17} \pm 840^\circ$ ,  $[\text{M}]^{17} \pm 6854.4^\circ$ . The *d*- and *l*-dithionates,  $\text{Y}(\text{S}_2\text{O}_6)_2 \cdot 5\text{H}_2\text{O}$ , gives greenish-black, glistening crystals, and have respectively  $[\alpha]^{17} + 848^\circ$ ,  $[\text{M}]^{17} + 6919.6^\circ$ , and  $[\alpha]^{22} - 840^\circ$ ,  $[\text{M}]^{22} - 6854.4^\circ$ . The *d*- and *l*-nitrates,  $\text{Y}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ , consist of crystalline, light olive-green powders, and have  $[\alpha]^{17} \pm 920^\circ$ ,  $[\text{M}]^{17} \pm 6348^\circ$ .

Further investigation of the racemic tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte bromide (compare *loc. cit.*) shows that it possesses six molecules of water of crystallisation and not five as previously stated. The *r*-chloride,  $\text{YCl}_4 \cdot 6\text{H}_2\text{O}$ , obtained from the bromide and silver chloride, forms dark green, regular, cube-shaped crystals. The *r*-dithionate,  $\text{Y}(\text{S}_2\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$ , gives dark-green crystals, and the *r*-platini-



chloride,  $Y(PtCl_6)_2 \cdot 3H_2O$ , glistening, slender leaflets, with a greenish shimmer.

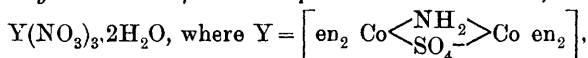
d- and l-Tetraethylenediamine- $\mu$ -iminoperoxocobalticobalte iodides,  $\left[en_2 Co \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ O_2 \end{array} Co en_2\right] I_3 \cdot 4H_2O$ , are obtained by dissolving respectively the l- and d- $\mu$ -aminoperoxo-bromides in concentrated ammonia and precipitating the filtered solution with ammonium iodide. They form dark brown needles,  $[\alpha]^{17} \pm 160^\circ$ ,  $[M]^{17} \pm 1372.8^\circ$ .

d- and l-Tetraethylenediamine- $\mu$ -ammoniumperoxocobalticobalte bromides,  $\left[en_2 Co \begin{array}{c} O_2 \\ \diagup \quad \diagdown \\ \text{NH} \\ | \\ HBr \end{array} Co en_2\right] Br_3 \cdot 5H_2O$ , were obtained in an impure

condition by dissolving the respective l- and d- $\mu$ -aminoperoxo-bromides in concentrated ammonia, and then treating the cooled solution with concentrated hydrobromic acid until the reddish-brown colour of the solution changed to red. On trituration, the reddish-brown, impure bromide crystallised out. The pure d-bromide was obtained by transforming the impure salt into the dithionate and then converting the latter back into the bromide. It is a bright red, crystalline powder,  $[\alpha]^{19} + 208^\circ$ ,  $[M]^{19} + 1510^\circ$ . The pure l-bromide was not obtained, owing to insufficient material. The d- and l-dithionates,

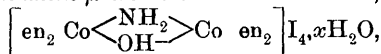
$\left[en_2 Co \begin{array}{c} O_2 \\ \diagup \quad \diagdown \\ \text{NH} \\ | \\ H \end{array} Co en_2\right] S_2O_6 \cdot 7H_2O$ , crystallise in salmon-coloured, slender needles,  $[\alpha]^{18} \pm 192^\circ$ ,  $[M]^{18} \pm 1625.8^\circ$ .

r-Tetraethylenediamine- $\mu$ -aminosulphato-dicobaltic nitrate,



is obtained from the  $\mu$ -aminoperoxo-nitrate by dissolving the latter in a concentrated solution of sulphur dioxide. Solution takes place with development of heat, and, on cooling, reddish-brown crystals separate. Further treatment with sulphur dioxide gives a red salt, from the aqueous solution of which, concentrated nitric acid precipitates the required nitrate as light-red needles. The bromide was obtained from the nitrate by double decomposition with ammonium bromide, and from the bromide, the d-bromocamphorsulphonate,  $Y(SO_3 \cdot C_{10}H_{14}OBr)_3 \cdot 4H_2O$ , was prepared; it forms light-red needles, and is not resolved into the active isomerides by fractional recrystallisation. The active d-nitrate,  $Y(NO_3)_3 \cdot 2H_2O$ , was, however, obtained from l-tetraethylenediamine- $\mu$ -aminoperoxo-cobalticobalte nitrate by treatment with sulphur dioxide, as for the racemic nitrate. It crystallises in well developed, red prisms;  $[\alpha] + 200^\circ$ ,  $[M] + 1384^\circ$ .

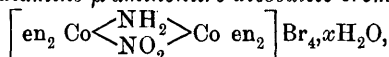
d-Tetraethylenediamine- $\mu$ -amino-ol-dicobaltic iodide,



is obtained as follows: the l- $\mu$ -aminoperoxo-nitrate is dissolved in water containing acetic acid and the black periodide obtained by treatment with sodium iodide. Sodium thiosulphate is then added until the solution and salt become red, after which the solution is saturated with

sodium iodide. On recrystallisation from water, the iodide forms bluish-red leaflets, and has  $[\alpha]^{20} + 110^\circ$ ,  $[M]^{20} + 990^\circ$ . The salts are being further investigated.

*d-Tetraethylenediamine- $\mu$ -aminonitro-dicobaltic bromide,*



is obtained from an aqueous solution of the *l*- $\mu$ -aminoperoxo-bromide by treatment with sodium nitrite, followed by concentrated hydrobromic acid. It forms dark-red cubes, and has  $[\alpha]^{19} + 158^\circ$ ,  $[M]^{19} 1311.4^\circ$ .

In the resolution of the salts of the tetraethylenediamine- $\mu$ -aminoperoxo-series, brownish-green and brown needles were obtained as an impurity. They were purified by a complicated process and shown not to be isomeric with the green salts, but their constitution has not yet been elucidated.

T. S. P.

**The Asymmetric Cobalt Atom. XI. Oxalatodiethylenediaminecobaltic Salts, and a New Method for Resolving Racemic Inorganic Compounds.** A. WERNER [with J. BOSSHART] (*Ber.*, 1914, 47, 2171—2182).—The study of the active oxalatodiethylenediaminecobaltic salts (Werner and McCutcheon, A., 1913, i, 19) has again been undertaken in order to investigate the separation of the active compounds from the racemates by crystallisation methods. The bromide was found to give the best results, 100 grams of water at  $17^\circ$  dissolving 1.05 grams of the *d*-bromide and 1.85 grams of the *r*-bromide respectively. The pure active bromide was readily obtained from the impure salt by fractional crystallisation and served for the preparation of other salts (see later).

The great difference in solubility of the active and racemic bromides led the authors to investigate the preparation of the active bromide by precipitation of the aqueous solution with alcohol, or with a mixture of alcohol and ether. If the solution contains the racemate and an excess of the *d*-salt, the latter is readily precipitated, but the mother liquor, instead of being inactive, is found to be laevorotatory, and further precipitation with alcohol and ether gives the *l*-salt, which is obtained pure by one more precipitation. The same thing holds good if a mixture of the *l*-salt and the racemate is fractionally precipitated, the *l*-salt being first obtained and then the *d*-salt. Thus by simple precipitation of a mixture of an active salt and the racemate, resolution of the racemate takes place. Similar results are obtained with dinitrodiethylenediaminecobaltic chloride, and as a general result it may be stated that resolution takes place in this manner when the active salt is less soluble than the racemate. If the racemate is the more soluble salt, no resolution takes place.

It is not necessary for the active salt to belong to the same series of salts as the racemate for resolution of the latter to take place. For example, if a mixture of *d*-oxalatodiethylenediaminecobaltic chloride with *r*-dinitrodiethylenediaminecobaltic chloride is fractionally precipitated with alcohol, the first precipitate consists of a mixture of *d*-oxalato-chloride and *d*-dinitro-chloride, which are readily separated, owing to their differing solubilities; from the mother liquor the *l*-dinitro-chloride is obtained.

In a similar manner the active salt of one metal can be used to resolve the racemate of another metal. In this way *r*-oxalatodiethylenediaminechromium bromide has been resolved by the addition of one-tenth of its weight of *d*-oxalatodiethylenediaminecobaltic bromide. The *d*-cobalt salt is less soluble than the *d*-chromium salt, which latter is therefore readily obtained pure. By the addition of active chromium salts thus obtained to further quantities of the racemate, the latter can readily be resolved.

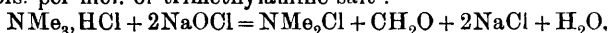
The above methods of resolving racemates must be further studied before a theoretical interpretation of the results can be given; in some respects they are similar to the results obtained with other compounds by Ostromisslenski (A., 1908, ii, 913).

Werner and McCutcheon (*loc. cit.*) investigated the rotatory power of the active oxalatodiethylenediaminecobaltic salts towards white light. Using monochromatic light the dispersion is found to be very marked, as the following results show.

*d*-Oxalatodiethylenediaminecobaltic chloride,  $[\text{C}_2\text{O}_4 \text{ Co en}_2]\text{Cl}$ , has  $[\alpha]_{\text{D}} + 848^\circ$ ,  $[\text{M}]_{\text{D}} + 2561^\circ$ ,  $[\alpha]_{\text{C}} + 308^\circ$ ,  $[\text{M}]_{\text{C}} + 930^\circ$ ; the corresponding *l*-chloride has  $[\alpha]_{\text{D}} - 840^\circ$ ,  $[\text{M}]_{\text{D}} - 2536^\circ$ ,  $[\alpha]_{\text{C}} - 304^\circ$ ,  $[\text{M}]_{\text{C}} - 918^\circ$ . Equimolecular quantities of the active salts, when mixed, give prisms of the inactive racemate. The *d*-bromide,  $[\text{C}_2\text{O}_4 \text{ Co en}_2]\text{Br}$ , which was obtained from the chloride by treatment with concentrated hydrobromic acid, has  $[\alpha]_{\text{D}} + 736^\circ$ ,  $[\text{M}]_{\text{D}} + 2546^\circ$ ,  $[\alpha]_{\text{C}} + 268^\circ$ ,  $[\text{M}]_{\text{C}} + 927^\circ$ ; the corresponding *l*-bromide has  $[\alpha]_{\text{D}} - 728^\circ$ ,  $[\text{M}]_{\text{D}} - 2518^\circ$ ,  $[\alpha]_{\text{C}} - 269^\circ$ ,  $[\text{M}]_{\text{C}} - 899^\circ$ . From the *d*- and *l*-bromides the following salts were prepared by double decomposition with the alkali metal salts of the appropriate acids. *d*-Oxalatodiethylenediaminecobaltic perchlorate,  $\text{YClO}_4 \cdot \text{H}_2\text{O}$ , where  $\text{Y} = [\text{C}_2\text{O}_4 \text{ Co en}_2]$ , forms long needles, and has  $[\alpha]_{\text{D}} + 688^\circ$ ,  $[\text{M}]_{\text{D}} + 2518^\circ$ ,  $[\alpha]_{\text{C}} + 240^\circ$ ,  $[\text{M}]_{\text{C}} + 878^\circ$ ; the *l*-perchlorate has  $[\alpha]_{\text{D}} - 696^\circ$ ,  $[\text{M}]_{\text{C}} - 2547^\circ$ ,  $[\alpha]_{\text{C}} - 248^\circ$ ,  $[\text{M}]_{\text{C}} - 907^\circ$ . The *d*- and *l*-thiocyanates,  $\text{YSCN}$ , crystallise in leaflets and have  $[\alpha]_{\text{D}} \pm 784^\circ$ ,  $[\text{M}]_{\text{D}} \pm 2548^\circ$ ,  $[\alpha]_{\text{C}} + 280^\circ$  and  $-284^\circ$ ,  $[\text{M}]_{\text{C}} + 910^\circ$  and  $-923^\circ$ . The *d*- and *l*-dithionates,  $\text{Y}_2\text{S}_2\text{O}_6$ , form short, glistening needles, and have  $[\alpha]_{\text{D}} + 600^\circ$  and  $596^\circ$ ,  $[\text{M}]_{\text{D}} + 2562^\circ$  and  $-2544^\circ$ ,  $[\alpha]_{\text{C}} + 216^\circ$  and  $-212^\circ$ ,  $[\text{M}]_{\text{C}} + 922^\circ$  and  $-905^\circ$ . The *d*- and *l*-iodides,  $\text{YI}$ , form a dull, crystalline powder, and have  $[\alpha]_{\text{D}} + 640^\circ$  and  $-644^\circ$ ,  $[\text{M}]_{\text{D}} + 2521^\circ$  and  $-2537^\circ$ ,  $[\alpha]_{\text{C}} \pm 232^\circ$ ,  $[\text{M}]_{\text{C}} \pm 914^\circ$ . The *d*- and *l*-nitrates,  $\text{YNO}_3 \cdot x\text{H}_2\text{O}$ , crystallise in long, dark-red needles, and have  $[\alpha]_{\text{D}} \pm 724^\circ$ ,  $[\text{M}]_{\text{D}} \pm 2512^\circ$ ,  $[\alpha]_{\text{C}} \pm 264^\circ$ ,  $[\text{M}]_{\text{C}} \pm 916^\circ$ .

*d*- and *l*-Oxalatodiethylenediaminechromic bromides,  $[\text{C}_2\text{O}_4 \text{ Cr en}_2]\text{Br}$ , form orange-red powders, and have  $[\alpha]_{\text{D}} + 332^\circ$  and  $-316^\circ$ ,  $[\text{M}]_{\text{D}} + 1129^\circ$  and  $-1075^\circ$ ,  $[\alpha]_{\text{C}} + 164^\circ$  and  $-156^\circ$ ,  $[\text{M}]_{\text{C}} + 557^\circ$  and  $-530^\circ$ . Their aqueous solution rapidly undergoes racemisation. T. S. P.

**Preparation of Dimethylamine and Dimethylaminomethyl Alcohol.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 269430. Compare this vol., i, 150).—The yield of dimethylaminomethyl alcohol may be raised from about 30% to almost its theoretical value by increasing the amount of hypochlorite or hypobromite used to 2 mols. per mol. of trimethylamine salt:



The halogenated dimethylamine may be separated and reduced by means of a sulphite or hydrogen sulphite or zinc dust to dimethylamine, or the liquid may be treated directly with the reducing agent and then rendered alkaline, in order to obtain dimethylaminomethyl alcohol.

T. H. P.

**Preparation of Betaine Salts.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 269338).—When treated with a methyl haloid in presence or absence of an indifferent organic solvent, methyl dimethylaminoacetate is readily converted into the methyl ester of the corresponding halogen salt of betaine. This ester is hydrolysed by heating its aqueous solution, preferably acidified with a mineral acid, the betaine salt being thus obtained in almost quantitative yield.

T. H. P.

**The Esters of Choline.** E. FOURNEAU and HAROLD J. PAGE (*Bull. Soc. chim.*, 1914, [iv], 15, 544—553).—The authors have prepared a number of esters of choline with the view of studying their hæmolytic properties as compared with those of lysocithin (compare this vol., i, 781). A number of these esters have been previously studied from the point of view of their effect on blood pressure, but have apparently never been isolated except in the form of their platinichlorides or aurichlorides, and these not characterised. The chlorides, bromides, and iodides of a number of choline esters have been prepared by the action of trimethylamine on the chloro- or iodo-ethyl esters of the higher fatty acids, the latter having been first prepared by the condensation of  $\beta$ -chloro- or iodo-ethyl alcohol with the acid chlorides. The following halogen-ethyl esters were prepared:  $\beta$ -chloroethyl stearate,  $C_{17}H_{35}CO_2 \cdot C_2H_4Cl$ , voluminous plates, m. p.  $49.5^\circ$ ;  $\beta$ -chloroethyl palmitate, nacreous plates, m. p.  $41.5^\circ$  (compare Krafft, A., 1904, i, 136);  $\beta$ -chloroethyl dodecoate, a liquid, b. p.  $165^\circ/19$  mm., m. p.  $17^\circ$  (Krafft, *loc. cit.*);  $\beta$ -chloroethyl octoate, a liquid, b. p.  $135^\circ/18$  mm.;  $\beta$ -iodoethyl stearate, nacreous plates, m. p.  $59.5^\circ$ ;  $\beta$ -iodoethyl palmitate, m. p.  $54^\circ$ ;  $\beta$ -iodoethyl tetradecoate, m. p.  $45.5^\circ$ ;  $\beta$ -iodoethyl dodecoate, m. p.  $35^\circ$ ;  $\beta$ -iodoethyl nonoate, b. p.  $169^\circ/15$  mm.;  $\beta$ -iodoethyl octoate, b. p.  $170^\circ/26$  mm.;  $\beta$ -iodoethyl butyrate, b. p.  $100^\circ/16$  mm.;  $\beta$ -iodoethyl oleate, a very viscous liquid, crystallising at  $6^\circ$ , but which could not be purified.

All the iodoethyl esters readily react with trimethylamine on heating in benzene solution in sealed tubes at  $100^\circ$ , giving the corresponding alkyloxycholine iodides; but of the chloroethyl esters, only those which are esters of the  $C_8$  or lower acids give this reaction. The choline chlorides can, however, be prepared from the corresponding iodides by shaking their solutions in methyl alcohol with excess of silver chloride. All the iodides prepared were hygroscopic, but not deliquescent, whilst the chlorides below the term in  $C_{12}$  were deliquescent and difficult to purify. All the salts were soluble in water, giving solutions, soapy to the touch and frothing on shaking. The chlorides of the higher members melt to very viscous, transparent, highly-refractive liquids at a relatively low temperature, fairly well-defined, and on heating to about  $200^\circ$  the liquids become mobile,

much gas is evolved, and the residues solidify. Concentrated aqueous solutions of the chlorides or iodides do not give a precipitate with silver nitrate, the silver haloid being kept in colloidal solution until alcohol is added.

The following substituted choline salts and their derivatives have been prepared :

*Stearylcholine iodide*, nacreous plates, yielding with silver chloride the *chloride*, long prisms, first m. p.,  $73^{\circ}$ , second m. p.,  $193^{\circ}$ , which gives an *aurichloride*, rhombohedra, m. p.  $109-110^{\circ}$ , a *platinichloride*, hexagonal plates, m. p.  $218^{\circ}$ , and a *picrate*, m. p.  $102^{\circ}$ .

*Palmitylcholine iodide*, nacreous plates, giving the *chloride*, prismatic needles, first m. p.,  $66^{\circ}$ , second m. p.,  $194.5^{\circ}$ , giving an *aurichloride*, large plates, m. p.  $110^{\circ}$ , a *platinichloride*, slender needles, m. p.  $218^{\circ}$ , and a *picrate*, m. p.  $101.5^{\circ}$ .

*Dodecylcholine iodide* and the *chloride*, long plates, first m. p.,  $54^{\circ}$ , second m. p.,  $196^{\circ}$ , giving an *aurichloride*, rectangular plates, m. p.,  $106^{\circ}$ , a *platinichloride*, slender needles, m. p.  $117^{\circ}$ , and a *picrate*, rhombic plates, m. p.  $97.5^{\circ}$ .

*Octylcholine iodide* and the *chloride*, first m. p.,  $35^{\circ}$ , second m. p.,  $198^{\circ}$ , giving an *aurichloride*, lenticular, rhombic plates, m. p.  $87-88^{\circ}$ , a *platinichloride*, long, prismatic needles, m. p.  $203-204^{\circ}$ , and a *picrate*, rhombic plates, m. p.  $94^{\circ}$ .

*Butyrylcholine iodide* and the *chloride*, large, very deliquescent, prismatic needles, giving an *aurichloride*, rhombic plates, m. p.  $93-94^{\circ}$ , a *platinichloride*, long, rectangular prisms, m. p.  $209^{\circ}$ , and a *picrate*, rectangular plates.

*Oleylcholine iodide*, crystallising in stout plates, and the *chloride*, which yields a *platinichloride*, short prisms, m. p.  $104-105^{\circ}$ , and a *picrate*, rectangular plates, m. p.  $88-89^{\circ}$ .

*Acetylcholine bromide*, crystallising in deliquescent, rectangular prisms.

*Tetradecylcholine chloride*, plates, first m. p.,  $58^{\circ}$ , second m. p.,  $195^{\circ}$ , giving an *aurichloride*, thin plates, m. p.  $108-109^{\circ}$ , a *platinichloride*, long needles, m. p.  $217.5^{\circ}$ , and a *picrate*, rhombic plates, m. p.  $98.5^{\circ}$ .

*Acetylcholine chloride* was prepared by the interaction of trimethylamine and chloroethylacetate, but could not be purified on account of the readiness with which it hydrolysed.

*Benzoylcholine chloride*, long, transparent prisms, m. p.  $200^{\circ}$  (decomp.), gives an *aurichloride*, silky needles, m. p.  $182^{\circ}$ , a *platinichloride*, small rhombohedra, m. p.  $224^{\circ}$ , and a *picrate*, rectangular plates.

The hæmolytic properties of these choline derivatives is being studied, and at present it can only be stated that the hæmolyzing powers of the palmityl and stearyl derivatives are but little inferior to those of lysocithin (compare *loc. cit.*).

W. G.

**Preparation of  $\alpha$ -Dichloroisopropyl Carbamate.** BRUNO BECKMANN, CHEMISCHE FABRIK (D.R.-P. 271737).—The compound,  $\text{NH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ , m. p.  $82-83^{\circ}$ , obtained from chloroformamide and  $\alpha$ -dichloropropan- $\beta$ -ol, differs from Otto's dichloroisopropyl carbamate (A., 1891, 1373), in its melting point, its solubility, and its bitter taste.

T. H. P.

**Creatine and Creatinine Metabolism. I. The Preparation of Creatine and Creatinine from Urine.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1914, 18, 183—190).—New methods for the preparation of creatine and creatinine from urine are described in detail. The zinc chloride compound is first formed, and from this, creatine is obtained by boiling with calcium hydroxide, and creatinine, in 60—80% yield, by dissolving in concentrated ammonia and allowing to cool in ice. The creatinine which crystallises out is usually quite pure, but may be recrystallised from warm concentrated ammonia.

H. W. B.

**Effect of Formaldehyde on Sheep's Wool and Constitution of the Latter.** ALBERT KANN (*Chem. Zentr.*, 1914, i, 1193; from *Färber-Zeit.*, 25, 73—75).—Small quantities of formaldehyde (up to 0.1% commercial formaldehyde by weight) render sheep's wool less sensitive to alkali, etc., without influencing its behaviour towards dyes, and this property is not affected by a preliminary treatment of the wool with nitrous acid. Wool treated with formaldehyde gives the same yellow colour with nitrous acid as the untreated product. The author is led to the conclusion that nitrous acid behaves as a nitrosating and not as a diazotising agent, and that formaldehyde causes an aldol condensation. The wool molecule therefore contains imino- and carboxy-, not amino- and keto-groups. Acetaldehyde behaves similarly but more weakly, whilst acraldehyde has a more powerful action than formaldehyde. The greatest resistance to alkali is developed in wool which has been previously treated with weak formaldehyde and is subsequently subjected to the action of the aldehyde in the alkaline bath.

H. W.

**Synthesis of Polypeptides by the Action of Glycerol on Glycine.** L. C. MAILLARD (*Ann. Chim.*, 1914, [ix], 1, 519—578).—A fuller account of work already published (compare A., 1912, i, 13).

W. G.

**Preparation and New Reactions of the Esters of Hydrazinocarboxylic Acids.** OTTO DIELS (*Ber.*, 1914, 47, 2183—2195).—Although at higher temperatures the alkyl carbonates and hydrazine give rise exclusively to carbohydrazide, at the ordinary temperature or at 0°, excellent yields of alkyl hydrazinocarboxylates are obtainable. These compounds, of which the ethyl member has already been described (Diels, A., 1903, i, 324; Gutmann, *Diss.*, Heidelberg, 1903), are colourless, crystalline solids.

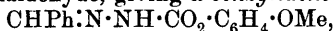
When ethyl carbonate is shaken with hydrazine hydrate and the mixture kept at the ordinary temperature for about seven hours, the resultant clear liquid on distillation yields ethyl hydrazinocarboxylate,  $\text{NH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , m. p. 45°, b. p. 93°/9 mm., 108—109°/22 mm., in almost theoretical quantity. On distillation under ordinary pressure, the ester undergoes partial decomposition with formation of ethyl

hydrazinodicarboxylate, m. p. 132°, and urazine,  $\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{NH}\cdot\text{NH}_2$  (Busch, A., 1907, i, 564), m. p. 270°.

Methyl carbonate and hydrazine hydrate when shaken together give a homogeneous mixture in a very short time, subsequent distillation under reduced pressure leaving a residue of *methyl hydrazinodicarboxylate*,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ , m. p. 73°, in 90—95% yield. At 150° the hydrochlorides of the ethyl and methyl esters undergo decomposition, in which the corresponding alkylhydrazine is formed, the yield of pure methylhydrazine from 52 grams of the hydrochloride of the methyl ester being 3—4 grams.

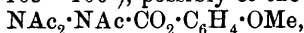
*o*-Methoxyphenyl hydrazinodicarboxylate,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , obtained by the interaction of hydrazine hydrate and guaiacyl carbonate in the presence of alcohol at 0°, forms lustrous prisms, m. p. 99—100°; it decomposes near 160°, giving a distillate of guaiacol, the residue being a brittle, amorphous *substance* of the composition  $\text{OMe}\cdot\text{C}_6\text{H}_4(\text{OH})(\text{CH}_2\text{ON}_2)_{10}$ , the brown solution of which in solutions of an alkali on the addition of a little Fehling's solution changes to a deep olive-brown, the colour passing into a violet where the wall of the test glass is wet with a film of the liquid. The amorphous substance appears to dissolve unchanged in cold water, but, on warming, decomposition ensues with formation of guaiacol and a sparingly soluble *substance* of the composition  $(\text{CH}_2\text{ON}_2)_x$ ; this is a heavy, crystalline powder, and gives the same effect as the amorphous compound with alkali and Fehling's solution.

In hot alcoholic solution *o*-methoxyphenyl hydrazinodicarboxylate condenses with benzaldehyde, giving a *benzylidene* derivative,



a colourless, crystalline solid, m. p. 176°, to a yellow fluid, with previous sintering at 168°. When heated under a pressure of 14 mm. at 185°, decomposition ensues, giving an almost quantitative yield of guaiacol and a very sparingly soluble *substance*,  $\text{C}_8\text{H}_6\text{ON}_2$ , prisms or needles, m. p. 268—269° (decomp.), whilst a small amount of benzaldazine is also produced.

If *o*-methoxyphenyl hydrazinodicarboxylate is heated with acetic anhydride and the resulting liquid is distilled under reduced pressure, the *acetyl* compound present undergoes decomposition between 125° and 220° giving guaiacol, guaiacyl acetate, a *substance*,  $\text{C}_{14}\text{H}_{16}\text{O}_6\text{N}_2$  (well formed crystals, m. p. 105—106°), possibly of the structure



and another *substance*,  $\text{C}_5\text{H}_6\text{O}_3\text{N}_2$  (possibly diacetyl-hydrazicarbonyl,

$\begin{smallmatrix} \text{NAc} \\ | \\ \text{NAc} \end{smallmatrix} > \text{CO}$ ), fine needles, m. p. 79—80°. The *o*-methoxyphenyl ester

similarly gives a *formyl* derivative,  $\text{CHO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , quadratic tablets, m. p. 114—115° with previous sintering at 110°, which when heated at 160—220°/14 mm. decomposes with the formation of guaiacol and a *substance*,  $\text{C}_2\text{H}_2\text{O}_2\text{N}_2$  (possibly formylhydrazicarbonyl,

$\begin{smallmatrix} \text{CO} \\ | \\ \text{NH} \end{smallmatrix} > \text{N}\cdot\text{CHO}$ ), stout, colourless, prismatic crystals, m. p. 120°, some-

what resembling alum in taste.

D. F. T,

**Transformation of *d*-isopropylmalonamic Acid into its Optical Antipodes by Interchanging the Carboxyl and Amido-groups.** EMIL FISCHER and FRITZ BRAUNS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 714—727).—An attempt was recently made to interchange the amido- and carboxyl groups in an active amic acid, in order to determine whether inversion would thereby result, in accordance with the theory of the asymmetric carbon atom (this vol., i, 247). This has now been accomplished in the case of *d*-isopropylmalonamic acid by the following series of reactions. The acid was converted into the methyl ester, the amido-group was replaced by carboxyl, and then, instead of treating the ester with ammonia, wherein lay the failure at the previous attempt, it was mixed with hydrazine and the hydrazide was converted into the azoimide. This reacted readily with ammonia, with the formation of the optical isomeride of the original acid. The reactions were first investigated in the racemic series, and then carried through with the *d*-acid in much the same way.

Ethyl  $\alpha$ -cyanoisovalerate (A., 1909, i, 628) was heated with concentrated sulphuric acid on the water-bath for twenty hours, and then poured on ice, when *isopropylmalonamic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$ , crystallised from the solution. The acid separated from water in envelope-shaped crystals, m. p.  $158^\circ$  (corr., decomp.), and, by treatment with diazomethane in methyl acetate suspension, yielded the *methyl ester*, slender needles, m. p.  $121^\circ$  (corr.). This was suspended in cold ether and treated with nitrous fumes until a clear solution resulted, whereby it was transformed into *methyl hydrogen isopropylmalonate*,  $\text{CO}_2\text{Me}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$ , b. p.  $95\text{--}100^\circ$  (bath)/0.3 mm.,  $D_4^{20} 1.1055$ . This was mixed with anhydrous hydrazine at  $0^\circ$ , and left for a day, when the excess of the base was removed in a vacuum. The solid hydrazide which remained was dissolved in water and precipitated with lead acetate, when the lead salt separated in sparkling leaflets. The free *isopropylmalonhydrazidic acid*,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$ , which formed glistening leaflets, m. p.  $172^\circ$  (corr.), was suspended in water, shaken with sodium nitrite until dissolved, and then acidified. The oily azoimide was immediately extracted with ether, and ammonia was passed into the cold extract. The crystalline mass which remained on evaporation was dissolved in water and acidified, when azoimide was evolved and the original *isopropylmalonamic acid* separated.

An aqueous solution of the racemic acid and quinine was left in ice, when the salt of the *d*-acid separated as a granular mass. The filtrate contained the salt of the *l*-acid, but, owing to the racemisation, it deposited a further quantity of the salt of the *d*-acid after some weeks, or after it had been warmed. The yield of *d*-acid was therefore much more than 50%. The salt was suspended in chloroform and water, cooled to  $0^\circ$ , and shaken with 0.5*N*-sodium hydroxide. After removing the chloroform extract, the aqueous solution was washed with ether and quickly treated with *N*-hydrochloric acid. It was necessary to carry out these operations with dispatch, since the acid is quickly racemised in alkaline solution. The *d*-isopropylmalonamic acid crystallised from water in prisms. The following values for  $[\alpha]_D^{25}$  were observed; in 4.31% alcoholic solution,  $+49.81^\circ$ , 4.09%,  $+49.40^\circ$ , 2.02%,  $+46.52^\circ$ ; in the equivalent quantity of *N*-sodium hydroxide,  $+12.63^\circ$ .



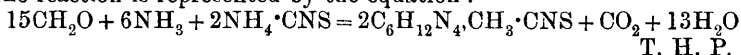
The course of the racemisation in alkaline solution was studied, and the acid was also converted into isopropylmalonic acid by the action of nitrous fumes. The *d*-methyl ester had m. p.  $141^{\circ}$  (corr.) and  $[\alpha]_D^{18}$  in 8.843% alcoholic solution,  $+55.41^{\circ}$ , 9.26%,  $+55.29^{\circ}$ . Change of sign occurred on removing the amido-group. The active amic ester was suspended in ether, mixed with amyl nitrite and a few drops of water, and treated with nitrous fumes. Methyl hydrogen l-isopropylmalonate, once distilled, had  $[\alpha]_D^{18} - 0.87^{\circ}$ , or, in the equivalent quantity of *N*-sodium hydroxide,  $[\alpha]_D^{18} + 38.4^{\circ}$ . The undistilled ester was converted, as above, into l-isopropylmalonhydrazidic acid which was not obtained optically pure, the highest value being  $[\alpha]_D^{20} - 28.7^{\circ}$ .

In order to reach the desired end, these reactions were carried through quickly, sacrificing the yields with the view of avoiding racemisation. Four grams of methyl *d*-isopropylmalonamate were brought to the above stage, and the crude hydrazide was converted into the azoimide, which was treated with ammonia. The l-isopropylmalonamic acid which separated was almost pure, a 4.52% solution in alcohol having  $[\alpha]_D^{18} - 44.40^{\circ}$ .

J. C. W.

**Preparation of Hexamethylenetetramine Camphorates.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (Austrian Patent, 63529 & D.R.-P. 270180).—Mono- and di-camphorates of hexamethylenetetramine may be obtained by crystallising a solution of the calculated proportions of the acid and base in an indifferent solvent. They have not the unpleasant effects of hexamethylenetetramine itself, whilst they increase diuresis and render alkaline urine acid. T. H. P.

**Preparation of Hexamethylenetetramine Methyl Thiocyanate.** KARL HEINRICH SCHMITZ (D.R.-P. 270486).—The original process (this vol., i, 20, 503) is altered as follows. Either methylamine salts or ammonium salts or inorganic or organic acids are allowed to act on a mixture of formaldehyde and ammonia or on hexamethylenetetramine; or hexamethylenetetramine salt is heated with or without formaldehyde and the hexamethylenetetramine methyl thiocyanate separated by addition of readily soluble thiocyanates; or methylamine thiocyanate or ammonium thiocyanate or thiocyanic acid is heated either with solutions of formaldehyde and ammonia or with hexamethylenetetramine thiocyanate, in the presence or absence of formaldehyde. The latter may be replaced by its polymerides in all cases. The reaction is represented by the equation:



T. H. P.

**Preparation of a Compound Containing Silicon.** HERMANN WEILAND (D.R.-P. 272338).—When heated in presence of light petroleum in a platinum autoclave for six hours at  $170$ – $180^{\circ}$ , carbamide and silicon tetrachloride interact to form a compound which contains silicon and exhibits the properties of a feeble acid. With sodium hydroxide it gives a soluble sodium salt, which yields the original compound when treated with carbon dioxide. Boiling of the compound with hydrochloric acid results in the separation of gelatinous silicic acid.

T. H. P.

**Preparation of  $\alpha$ -Bromo- $\alpha$ -ethylbutyrylcarbamide.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 271682).— $\alpha$ -Bromo- $\alpha$ -ethylbutyrylcarbamide, m. p.  $115^\circ$  (compare A., 1911, i, 118), may be prepared by treating  $\alpha$ -bromo- $\alpha$ -ethylbutyryl bromide, in presence of an indifferent solvent, with mercurous cyanate, and subjecting the  $\alpha$ -bromo- $\alpha$ -ethylbutyryl cyanate thus obtained to the action of ammonia:  $2\text{CEt}_2\text{Br}\cdot\text{COBr} + 2\text{HgNCO} = \text{Hg}_2\text{Br}_2 + 2\text{CEt}_2\text{Br}\cdot\text{CO}\cdot\text{NCO}$ , and this  $+ \text{NH}_3 = \text{CEt}_2\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ . T. H. P.

**Complex Cyanides of Quadrivalent Tungsten. III.** OSCAR OLSSON (*Zeitsch. anorg. Chem.*, 1914, 88, 49—73. Compare A., 1913, ii, 328; this vol., i, 504).—The following further cyanides containing quadrivalent tungsten are described:  $\text{Ag}_4\text{W}(\text{CN})_8$ , a yellow, amorphous powder;  $[\text{AgNH}_3]_4\text{W}(\text{CN})_8$ , prepared by dissolving the silver salt in concentrated ammonia, separating on cooling as bright yellow crystals;  $\text{Na}_4\text{W}(\text{CN})_8\cdot 2\cdot 5\text{H}_2\text{O}$ , obtained by the action of sodium chloride on the silver salt as small, yellow crystals;  $(\text{NH}_4)_4\text{W}(\text{CN})_8$ , glistening scales;  $\text{Rb}_4\text{W}(\text{CN})_8\cdot 3\text{H}_2\text{O}$ ;  $\text{Cs}_4\text{W}(\text{CN})_8$ ;  $\text{Ti}_4\text{W}(\text{CN})_8$ ;  $\text{Mg}_2\text{W}(\text{CN})_8\cdot 6\text{H}_2\text{O}$ ;  $\text{Ca}_2\text{W}(\text{CN})_8\cdot 8\text{H}_2\text{O}$ ;  $\text{Sr}_2\text{W}(\text{CN})_8$  or  $9\text{H}_2\text{O}$ ;  $\text{Pb}_2\text{W}(\text{CN})_8\cdot 4\text{H}_2\text{O}$ ;  $\text{Mn}_2\text{W}(\text{CN})_8\cdot 8\text{H}_2\text{O}$ ;  $\text{Cd}_2\text{W}(\text{CN})_8\cdot 8\text{H}_2\text{O}$ ;  $[\text{Cd}(\text{NH}_3)_2]_2\text{W}(\text{CN})_8\cdot 2\text{H}_2\text{O}$ ;  $[\text{Cd}(\text{NH}_3)_2]_2\text{W}(\text{CN})_8\cdot 2\text{H}_2\text{O}$ ;  $\text{ZnW}(\text{CN})_8\cdot 4\text{H}_2\text{O}$ ;  $[\text{Zn}(\text{NH}_3)_2]_2\text{W}(\text{CN})_8$ .

The acid,  $\text{H}_4\text{W}(\text{CN})_8\cdot 6\text{H}_2\text{O}$ , is prepared by treating the silver salt with a small excess of cold dilute hydrochloric acid, and saturating the clear filtrate with hydrogen chloride below  $0^\circ$ . The acid is precipitated quantitatively in yellow needles. It is dried in carbon dioxide, and finally in a desiccator over potassium hydroxide. It is a strong acid, decomposing carbonates and yielding a neutral ammonium salt. Its alcoholic solution yields crystalline compounds with pyridine and quinoline. C. H. D.

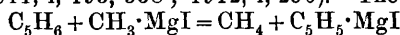
**The Technical Methods for the Preparation of Dicyanodiamide from Calcium Cyanamide from the Point of View of Chemical Kinetics.** G. GRUBE and P. NITSCHKE (*Zeitsch. angew. Chem.*, 1914, 27, 368—378).—A new process for the technical preparation of dicyanodiamide from calcium cyanamide is described, in which the calcium hydroxide already present in the solution of the calcium compound is utilised as catalyst. Since the polymerisation proceeds with a maximum velocity when the concentrations of cyanamide and cyanamidion are equal (A., 1914, i, 152; T., 1914, 105, 576), the hydroxide is fractionally neutralised with hydrochloric acid as the reaction proceeds, in order to satisfy this condition. The calcium chloride formed exerts an additional catalytic accelerating influence in the presence of the hydroxide. The new process has been compared by kinetic experiments with the ammonia and zinc cyanamide processes, and it is shown that under proper conditions, the almost quantitative conversion into dicyanodiamide is possible by the lime and ammonia methods, but that side reactions cause considerable loss in the zinc process. Dicyanodiamide formation in neutral solution in the presence of the almost insoluble zinc cyanamide is a heterogeneous catalysis. The reaction-velocity increases at a proportionally greater

rate than the increase in mass of the catalyst, and does not depend on the rate of diffusion, but is determined by a slow chemical action probably consisting, as in the other cases, in the union of cyanamide and cyanamidion. G. F. M.

**Phytin.** WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1914, **64**, 409—421).—Phytic acid undergoes scission in acid medium at 37° only very slowly, less than 1% being hydrolysed in a day. The hydrolysis is markedly accelerated by light. S. B. S.

**Hydro-aromatic Substances.** W. H. PERKIN, A. W. CROSSLEY, M. O. FORSTER, H. R. LE SUEUR, and A. MCKENZIE (*Rep. Brit. Assoc.*, 1913, 135—136).—A report of recent work on this subject (T., 1913, 103, 1297, 2179). C. H. D.

**Derivatives of cyclopentadiene and its Dimeride.** V. GRIGNARD and CH. COURTOT (*Compt. rend.*, 1914, **158**, 1763—1766).—cyclopentadiene resembles indene and fluorene in its behaviour towards magnesium alkyl haloids, giving a magnesium haloid derivative (compare A., 1911, i, 193, 538; 1912, i, 250). The reaction



takes place best in a mixture of ether and light petroleum (60—80°) at 45—50°, when, on cooling at the end of the reaction, the magnesium derivative separates out as a powder. This derivative readily reacts with iodine and bromine or cyanogen bromide or chloride, but the products, in all cases, rapidly undergo dimerisation. Iodine in toluene solution gives a black, insoluble powder, having the composition  $\text{C}_3\text{H}_5\text{I}$ , but this is evidently a polymeride. Bromine reacts with the magnesiumbromo-derivative in ether at low temperatures to give 3:4:5-tribromo- $\Delta^1$ -cyclopentene, small prisms, m. p. 60°, which is very unstable and is rapidly transformed into the dimeride,  $\text{C}_{10}\text{H}_{10}\text{Br}_6$ , a blackish-brown powder. Attempts to prepare a monobromo-derivative by means of cyanogen bromide only yielded a black powder, which was a mixture of bromo- and cyano-polymerides. Cyanogen chloride yielded the nitrile of bis-cyclopentadienedicarboxylic acid, which on hydrolysis with alcoholic potassium hydroxide yielded the acid (compare Thiele, A., 1901, i, 182). This acid is also obtained directly by the action of dry carbon dioxide on the original magnesium derivative.

With anisaldehyde the magnesium derivative yielded p-methoxyphenylfulvene,  $\begin{matrix} \text{CH}:\text{CH} \\ \text{CH}:\text{CH} \end{matrix} > \text{C}:\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , red crystals, m. p. 70°, and with acetone, dimethylfulvene, b. p. 47°/11 mm. (compare Thiele, *loc. cit.*). With benzophenone the alcohol is, however, obtained, being the first known in this series. Diphenylfulvanol is obtained in colourless crystals, m. p. 123—124°, which are very oxidisable and rapidly resinify on attempts to recrystallise them or under the influence of hydrochloric acid or bromine. In sunlight the alcohol is dehydrated, giving diphenylfulvene, red prisms, m. p. 82° (compare Thiele, *loc. cit.*) W. G.

**Bromination of Benzene and its Homologues, Catalytic Action of Manganese.** L. GAY, F. DUCELLIEZ, and A. RAYNAUD (*Compt. rend.*, 1914, 158, 1804—1806. Compare this vol., ii, 273).—Bromine attacks benzene at 75° in the presence of manganese, but only at 90° in the absence of the metal. Working under similar conditions of temperature, manganese is shown to have a marked catalytic influence. The ratio of recovered benzene to brominated benzene is 8 : 9 in the presence of manganese and 10 : 3 in its absence. Manganese exerts a similar catalytic influence on the bromination of toluene and xylene in the cold, but on working at 80° for toluene and 50° for xylene this action is masked, better results being obtained without the manganese. In no case is the metal attacked. W.G.

**Some Hydrogenations by means of Sodammonium: Hydrocarbons.** P. LEBEAU and M. PICON (*Compt. rend.*, 1914, 159, 70—72).—Using sodium in liquid ammonia under the conditions given for tetrahydronaphthalene (compare this vol., i, 825), the authors have prepared hydrides of a number of hydrocarbons, all of which have been previously described, namely: tetrahydroacenaphthene (compare Bamberger and Lodter, A., 1888, 292), dihydroanthracene (*loc. cit.*), tetrahydrophenanthrene (compare Breteau, A., 1911, i, 625), tetrahydrodiphenyl (*loc. cit.*), and dihydrostilbene. The other product of the reaction is in all cases sodamide. Attempts to hydrogenate amylene, benzene, toluene, cymene, terpinene, terpinolene, carvene, terebene,  $\alpha$ -pinene and menthene by this method were unsuccessful. Fluorene and indene instead of undergoing hydrogenation gave sodium derivatives. W. G.

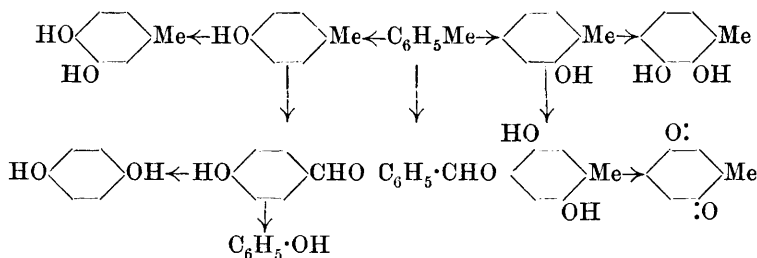
**The Electrochemical Oxidation of Aromatic Hydrocarbons and Phenols.** FR. FICHTER and ROBERT STOCKER (*Ber.*, 1914, 47, 2003—2019. Compare Fichter, A., 1913, i, 1316).—By submitting phenol in a feebly acid sulphate solution to an alternating current between platinum electrodes, Drechsel (A., 1884, 1136; 1888, 1276) was able to produce a mixture of substances which he classified into oxidation products, namely, quinol, catechol, *p*-diphenol, oxalic and formic acids, reduction products, namely, cyclohexanone and succinic acid, and dehydration products of which the only example was phenyl hydrogen sulphate. The authors desired to reproduce these results with a direct current; they discovered that under electrolytic oxidation phenol and benzene yield the same end-products, so that the examination of the behaviour towards electrolytic oxidation was extended to certain homologues and substituted derivatives of phenol and benzene. The substances were generally treated in suspension in 2*N*-sulphuric acid.

It is found that electrolytic oxidation of benzene and its derivatives effects nuclear hydroxylation; the first product from benzene is phenol, which is too easily oxidised to be isolated, and is further converted into catechol and quinol. The former is difficult to detect on account of its passing readily into higher oxidation products, and the isolation of appreciable quantities by Drechsel is attributed to the alterna-

tion of the current tending to check the increase in the oxidation potential of the electrodes. The latter substance passes by oxidation into the relatively stable *p*-benzoquinone, which, if the anode and cathode are separated, together with its degradation product maleic acid, forms the main part of the final product, whilst if no diaphragm is used cathodic reduction reconverts some of the *p*-benzoquinone into quinol. Contrary to the views of Kempf (A., 1907, i, 63; 1906, ii, 24, 25), who regards lead dioxide as the chief agent in electrochemical oxidation at a lead anode, it is found that the same products are obtained whether platinum, lead or graphite electrodes are used. The hypothesis that electrolytic oxidation in sulphuric acid solution depends on the intermediate formation of persulphuric acid is also untenable because the result is qualitatively the same when aqueous phosphoric or perchloric acid is used for the suspension, and it is unlikely that genuine "per-acids" are produced under such conditions from either of these acids.

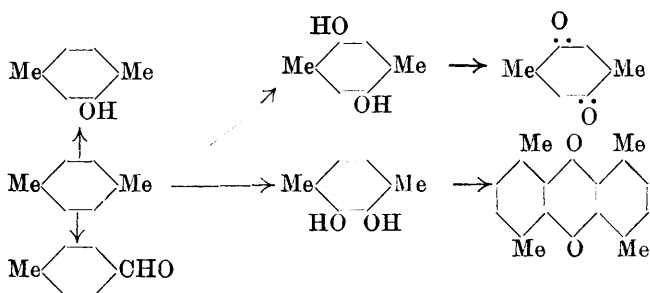
Attention is drawn, by the citation of examples, to the remarkable frequency with which electrolytic oxidation and treatment with hydrogen peroxide yield similar results, and the suggestion is made that an important point of analogy between these agents is the absence of formation of lower oxides which may exert catalytic influence on the oxidation process.

Electrochemical oxidation of toluene in suspension in dilute sulphuric acid was found to give rise to toluquinone, quinol and phenol together with a smaller quantity of benzaldehyde (compare Law and Perkin, T., 1907, 91, 258). The fact that the aromatic nucleus is attacked in preference to the side-chain is in accord with the results of electrochemical chlorination of toluene (compare Cohen, Dawson and Crosland, T., 1905, 87, 1034). In explanation of the above behaviour of toluene the following scheme is suggested:—



in which the final members not included in the experimental products undergo disruptive oxidation. This view of the process is confirmed by examination of the behaviour of *o*- and *p*-cresol on electrolytic oxidation.

*p*-Xylene, in suspension in dilute sulphuric acid, on treatment at a lead dioxide anode, gave in addition to a small quantity of *p*-tolualdehyde (compare Law and Perkin, *loc. cit.*), *p*-xyloquinol and a substance, silky needles, m. p. 161°, probably *p*-xylylene dioxide. The changes are represented by the scheme



Nitrobenzene proved very resistant to anodic oxidation, and the only isolable oxidation product was maleic acid, which was also obtained with *o*- and *m*-nitrophenols; *p*-nitrophenol was completely destroyed. Trichlorophenol gave an unsatisfactory yield of 2:6-dichloroquinol, and thymol gave thymoquinol, together with a mixture of difficultly crystallisable substances from which dithymol could be separated.

The last product is interesting as corresponding with the diphenol obtained by Drechsel, but which the authors have been unable to produce by the electrolytic oxidation of phenol; with the possible exception of this, all the oxidation products named by Drechsel are formed in the electrolytic oxidation of phenol with a direct current. The production of his reduction products was probably to a large extent due to the formation of platinum black on his electrodes; under these conditions, maleic acid would be easily reduced to succinic, and phenol would give *cyclohexanol*, which by subsequent oxidation could pass into *cyclohexanone*.

The authors are, however, unable to confirm the formation of phenyl hydrogen sulphate and bring evidence indicating that the substance described by Drechsel was in reality quinolsulphuric acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_3\text{H}$ .

D. F. T.

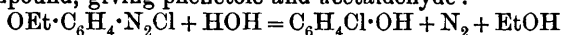
**Separation of the Hydrochlorides of Primary Aromatic Amines and their Derivatives from the Products of Reaction of the Corresponding Nitro-, Nitroamino-, Nitroso-, Azoxy-, Azo-, Hydroxyazo-, and Aminoazo-compounds with Iron and Hydrochloric Acid.** HIRSCH POMERANZ (D.R.-P. 269542).—When the proportion of iron and the proportion and concentration of the hydrochloric acid employed in this reduction are so chosen that the resultant mixture of ferrous chloride, water, free hydrochloric acid, and hydrochloride of the base is just saturated in the cold with respect to ferrous chloride, the hydrochloride of the amine separates almost quantitatively from the liquid. Loss due to oxidation of the liberated amine is thus avoided.

T. H. P.

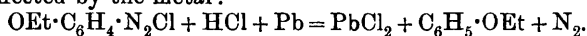
**Diazotisation of Phenetidines.** TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1914, 235—249).—It has been shown by Swarts (A., 1913, i, 842) that considerable quantities of phenetole are formed in addition to fluorophenetoles when *o*- and *p*-phenetidine are diazotised in the presence of hydrofluoric acid and the diazo-compound is subsequently

decomposed; the relative amount of fluoro-compound is greatest when platinum, least when leaden vessels are employed. The reaction has been further investigated by the author, who, however, has generally used solutions of the bases in hydrochloric instead of hydrofluoric acid, since the reaction is found to proceed in an analogous manner in the two cases.

A solution of *o*-phenetidine in hydrochloric acid is diazotised by means of a concentrated solution of sodium nitrite, and the product decomposed by boiling the solution. In these circumstances, decomposition occurs slowly with the production of much resin, from which a definite product cannot be isolated. The portion volatile with steam and insoluble in sodium hydroxide contains phenetole (43%) and *o*-chlorophenetole (47%); the soluble portion consists mainly of the ethyl ether of catechol. In addition, ethyl chloride and acetaldehyde are formed. The formation of the latter is attributed to the hydrolysis of the ethoxy-group with the formation of alcohol, which then reduces the diazo-compound, giving phenetole and acetaldehyde:



and  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl} + \text{EtOH} = \text{C}_6\text{H}_5\text{OEt} + \text{N}_2 + \text{C}_2\text{H}_4\text{O} + \text{HCl}$ . The relative quantities of aldehyde and phenetole are shown to be approximately those required by the equation. In the presence of metallic lead, the proportion of phenetole is increased to 78%, but the quantity of acetaldehyde formed is insignificant, reduction of the diazo-compound being affected by the metal:



A series of experiments has been performed with the object of ascertaining the most favourable conditions for diazotising *o*-phenetidine in the presence of hydrofluoric acid, for which purpose an initial concentration of 55% acid is found best. Subsequent decomposition of the diazo-compound occurs with extreme slowness, but attempts to hasten it by adding the solution to a boiling concentrated solution of potassium fluoride in hydrofluoric acid, or by the use of manganese or antimony fluorides, do not yield better results.

*p*-Phenetidine when diazotised in hydrochloric acid solution and subsequently decomposed behaves in a manner very similar to that of the *o*-compound, except that the auto-reduction, as well as the action of lead, is relatively of less importance.

Elimination of the ethoxy-group appears to take place from the diazo-compound and not from the free base, since phenetole does not yield alcohol when boiled with hydrochloric acid for four hours, and only gives traces of alcohol when hydrofluoric acid is used: analogous results are obtained with *o*-phenetidine, which, however, yields a small quantity of *o*-aminophenol when treated with hydrofluoric acid.

Aldehyde is not formed when aniline is diazotised and the product decomposed in the presence of a small proportion of alcohol. A similar experiment in which *o*-phenetidine is diazotised in the presence of the calculated quantity of hydrochloric acid, and the product decomposed after addition of so much alcohol that its concentration is approximately 10%, shows the formation of considerable amounts of

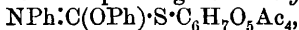
acetaldehyde: the latter is also produced, but in less quantity, without the addition of extraneous alcohol. H. W.

**The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives.** F. S. KIPPING, K. J. P. ORTON, S. RUHEMANN, and J. T. HEWITT [with W. H. GRAY] (*Rep. Brit. Assoc.*, 1913, 136—141).—The behaviour of acetylchloroaminobenzene, which has been previously examined in solutions containing acetic acid, has now been examined in pure aqueous solution. The rate of change in pure water is very slow, and small concentrations of acids produce only a small acceleration. Hydrolysis takes place, followed by reduction of the hypochlorous acid. The transformation of chloroamine into chloroanilides is quite subsidiary. With concentrations of hydrogen chloride above  $N/10$ , chlorine is not hydrolysed, and the formation of chloroanilide is the principal reaction. Other acids do not produce the same effect. The views as to the mechanism of these reactions put forward in previous papers are confirmed (compare Rivett, A., 1913, ii, 202).

C. H. D.

**Thiocarbimides. VI. The Addition of Phenol to Thiocarbimides.** WILHELM SCHNEIDER and FRITZ WREDE (*Ber.*, 1914, 47, 2038—2043).—Some uncertainty exists as to whether phenols can condense with thiocarbimides with the formation of thiourethanes (compare Orndorff and Richmond, A., 1900, i, 157; Eckenroth and Kock, A., 1894, i, 408). By working with lower temperatures than those previously applied, the authors have been able to prepare additive compounds of phenol with phenylthiocarbimide and with allylthiocarbimide.

An equimolecular mixture of phenol and phenylthiocarbimide was kept at  $80^\circ$  for a day and then at the ordinary temperature for several days; after the addition of alcohol and cooling, an aqueous-alcoholic ammoniacal solution of silver nitrate was added, when the *phenyl silver phenyliminothiocarbonate*,  $\text{NPh}\cdot\text{C}(\text{SAg})\cdot\text{OPh}$ , rhombic, bronze-yellow crystals, m. p.  $186^\circ$ , separated. A similar result is obtained if the mixture of phenol and phenylthiocarbimide is merely kept at the ordinary temperature for two months. When treated with acetobromoglucose in chloroform solution the silver salt was converted, in very poor yield, into the corresponding *tetra-acetylglucoside*,



colourless needles, m. p.  $169^\circ$ . The action of hydrogen sulphide on a chloroform solution of the silver salt liberated phenyl phenylthioncarbamate,  $\text{NHPh}\cdot\text{CS}\cdot\text{OPh}$ , colourless needles, m. p.  $142^\circ$  (compare Rivier, A., 1906, i, 948), of feeble odour, which in contact with water undergoes gradual resolution into phenol and phenylthiocarbimide.

By a similar process to the preceding, but using allylthiocarbimide, the *silver* derivative, yellowish-green rhombs, decomp. above  $140^\circ$ , of phenyl allylthioncarbamate was obtained. This on treatment with hydrogen sulphide in chloroform solution gave *phenyl allylthioncarbamate*,  $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{OPh}$ , leaflets or needles, m. p.  $51^\circ$ , which is rather more stable than phenyl phenylthioncarbamate. When heated with alcohol



and excess of ethyl iodide, the silver derivative was converted into *O*-phenyl-*S*-ethyl allyliminothiocarbonate,  $C_3H_5 \cdot N:C(SET) \cdot OPh$ , a colourless liquid of not unpleasant odour, b. p. 150—160°/20 mm. No crystalline tetra-acetylglucoside was obtainable by the action of acetobromoglucose. D. F. T.

**Oxidation of Phenol.** H. WICHELHAUS (*Ber.*, 1914, **47**, 2261).—Commenting on a statement recently made by Pummerer and Frankfurter, to the effect that nothing is known about the oxidation of phenol, the author refers to the production of phenoquinone (*A.*, 1872, 482). J. C. W.

**Catalytic Reactions at High Temperatures and Pressures.**  
**XXXIV. Hydrogenation of Monohydric Phenols.** V. IPATIEV and LUGOVOI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 470—475).—The slowness with which quinol is reduced by hydrogen at high pressure in presence of nickel oxide or reduced nickel and the small yields of quinitol occasioned by the loss of the elements of water and by the partial resinification of the quinol itself have led to the use of simple ethers of phenols in the hope that the methoxy-group would not be eliminated so easily and that resinification would be avoided. Preliminary experiments with the ethers of various phenols showed that such expectation is fulfilled only incompletely and that, although better yields of the normal hydrogenated products are obtained, these are accompanied by secondary products often difficult to remove (this vol., i, 38).

When guaiacol is heated for twelve to fifteen hours at 220—240° with one-tenth of its weight of nickel oxide in an atmosphere of hydrogen at 100 atmospheres, it yields hexahydroguaiacol [2-methoxycyclohexanol] mixed with a little cyclohexane and about 50% of cyclohexyl alcohol. By treatment of the products with alumina and cupric oxide at 250° in an atmosphere of hydrogen at 50 atmospheres, the cyclohexyl alcohol is converted into cyclohexene and may be separated from the 2-methoxycyclohexanol, which is transformed into hexahydrocatechol [cyclohexane-1 : 2-diol].

Hydrogenation of anisole under a pressure of 100 atmospheres in presence of nickel oxide at 240° for twenty-four hours yields cyclohexene, hexahydroanisole [methoxycyclohexane] (about 50%) and cyclohexyl alcohol.

Similarly, the diethyl ether of catechol yields about 50% of the normal hexahydro-derivative,  $C_6H_{10}(OEt)_2$ , apparently in the *cis*- and *trans*-modifications, b. p. 180—190°, and b. p. 190—200°,  $D_{20}^{20}$  0.8997 respectively ; the remainder is converted into cyclohexene. With the dimethyl ether of resorcinol, besides the normal product, a considerable proportion of cyclohexane seems to be formed. The dimethyl ether of quinol gives the normal hydrogenated product, together with a large proportion of methoxycyclohexane. T. H. P.

**The Allylcyclohexanols and Methylallylcyclohexanols, Propyl- and Methylpropyl-cyclohexanones, and cycloHexanols.** R. CORNUBERT (*Compt. rend.*, 1914, **159**, 75—80).—The allyl- and methylallyl-cyclohexanones already described (compare this vol., i, 969)

on reduction with sodium in absolute alcohol yield the corresponding cyclohexanols, and on hydrogenation with active nickel in alcohol at 60° (compare Brochet, this vol., i, 645) the corresponding propylcyclohexanones which have been reduced to the cyclohexanols. The following compounds are described.

1 : 1 : 3 : 3-Tetra-allylcyclohexan-2-ol, a viscous liquid, b. p. 184—185°/24 mm. (corr.), not giving a phenylurethane (compare Haller, A., 1913, i, 630). 1-Methyl-3-allylcyclohexan-2-ol, a mobile liquid, with an odour of menthol, b. p. 105°/15 mm. (corr.), giving a phenylurethane, a very viscous liquid. 1-Methyl-1 : 3 : 3-triallylcyclohexan-2-ol, a very viscous liquid, b. p. 160—161°/15 mm. (corr.), not giving a phenylurethane. 1-Methyl-4-allylcyclohexan-3-ol, a mobile liquid with an odour of menthol, b. p. 110—112°/19 mm., giving a phenylurethane, a very viscous liquid. 1-Methyl-2 : 2 : 4 : 4-tetra-allylcyclohexan-3-ol, a mobile liquid, b. p. 192—193°/21 mm., does not give a phenylurethane. 1-Methyl-3-allylcyclohexan-4-ol, a slightly viscous liquid, b. p. 108°/17 mm. (corr.), giving a phenylurethane, slender needles, m. p. 98—99°. 1-Methyl-3 : 3 : 5 : 5-tetra-allylcyclohexan-4-ol, a slightly viscous liquid, b. p. 173—174°/17 mm. (corr.), does not give a phenylurethane.

1 : 1 : 3 : 3-Tetrapropylcyclohexan-2-one, prisms, m. p. 43°, does not give an oxime, but on reduction gives the corresponding alcohol, a very viscous liquid, b. p. 188°/25 mm. (corr.), not giving a phenylurethane. 1-Methyl-3-propylcyclohexan-2-one is a colourless, mobile liquid with an odour of menthone, b. p. 213·5°/765 mm. (corr.), gives an oxime, m. p. 70°, and on reduction the alcohol, a mobile liquid, b. p. 115°/25 mm., giving a phenylurethane, a very viscous liquid. 1-Methyl-1 : 3 : 3-tripropylcyclohexan-2-one is a colourless, mobile liquid, b. p. 152°/14 mm. (corr.), not giving an oxime, but yielding an alcohol, a very viscous liquid, b. p. 173°/27 mm., which does not give a phenylurethane. 1-Methyl-4-propylcyclohexan-3-one, a colourless, mobile liquid with an odour of menthone, b. p. 217°/765 mm. (corr.), gives an oxime, needles, m. p. 78—82°; and the corresponding alcohol, a mobile liquid, b. p. 107—108°/17 mm., giving a phenylurethane, a very viscous liquid. 1-Methyl-2 : 2 : 4 : 4-tetrapropylcyclohexan-3-one, a colourless, very viscous liquid, b. p. 181°/19 mm. (corr.), does not give an oxime, but is reduced to the alcohol, a viscous liquid, b. p. 185°/18 mm. (corr.), which does not give a phenylurethane. 1-Methyl-3-propylcyclohexan-4-one, a colourless, mobile liquid, with an odour of menthone, b. p. 217°/750 mm. (corr.), giving an oxime, slender needles, m. p. 67—68°, and on reduction the alcohol, a slightly viscous liquid, b. p. 112°/18 mm. (corr.), which yields a phenylurethane, a very viscous liquid. 1-Methyl-3 : 3 : 5 : 5-tetrapropylcyclohexan-4-one, prisms, m. p. 49°, not giving an oxime, but on reduction the alcohol, a very viscous liquid, b. p. 178°/16 mm. (corr.), not giving a phenylurethane.

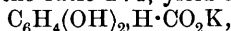
The hydrogenation of the allylcyclohexanones thus gives a ready method of preparing the propylcyclohexanones, which cannot be obtained by direct alkylation with propyl iodide and sodamide. In this hydrogenation the various samples of active nickel prepared appeared to possess a selective action as catalysts, in that they effected the hydrogenation of some compounds and not of others. In the case

of the polyallyl ketones certain nickels provoked the rapid saturation of one or two double linkings, and only a slower saturation of the others, whilst with other nickels no such difference was observable.

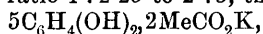
W. G.

**Compounds of Catechol with Alkaline Salts of Carboxylic Acids.** R. F. WEINLAND and WILHELM DENZEL (*Ber.*, 1914, **47**, 2244—2252).—It was recently found that catechol forms complex compounds with its own alkali salts (this vol., i, 525). In the present paper, similar compounds of catechol with the sodium and potassium salts of typical carboxylic acids are described. They cannot be explained by Pfeiffer's views (this vol., i, 834), for, in some cases, the partial valency of a single carbonyl group would have to satisfy several hydroxyl groups. Since catechol does not combine with the free acids, the metallic atom must provide the connecting links, and it is therefore assumed that the substances are like co-ordinated aquo-compounds, in which one molecule of catechol plays the part of two molecules of water.

A solution containing equimolecular proportions of sodium formate and catechol, when left over sulphuric acid, deposits the *compound*,  $C_6H_4(OH)_2 \cdot H \cdot CO_2Na \cdot H_2O$ , in colourless needles and tablets, which are feebly alkaline in concentrated solution. A solution containing sodium formate and catechol in the ratio 1 : 1.75 deposits the *compound*,  $2C_6H_4(OH)_2 \cdot H \cdot CO_2Na$ , in needles or four-sided columns. Potassium formate and catechol in the ratio 2 : 1, yield the *compound*,

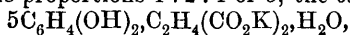


very large, thick, rectangular tablets; in the ratio 1 : 1, the *compound*,  $7C_6H_4(OH)_2 \cdot 4H \cdot CO_2K \cdot H_2O$ , long, thin tablets; and in the ratio 1 : 2.75, the *compound*,  $7C_6H_4(OH)_2 \cdot 2H \cdot CO_2K$ , large, transparent crystals. A 96% alcoholic solution of potassium acetate and catechol in the ratio 1 : 1 deposits the *compound*,  $C_6H_4(OH)_2 \cdot MeCO_2K$ , long, thin tablets, and in the ratio 1 : 2.25 to 2.75, the *compound*,

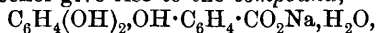


colourless octahedra.

Solutions containing succinic acid, potassium hydroxide and catechol in the proportions 1 : 1 : 1 or 2 or 3, or 1 : 1.5 : 2, deposit the *compound*,  $2C_6H_4(OH)_2 \cdot CO_2H \cdot C_2H_4 \cdot CO_2K$ , in variously shaped, massive crystals, the solutions of which are strongly acid; in the proportions 1 : 2 : 1 or 3, the *compound*,  $3C_6H_4(OH)_2 \cdot C_2H_4(CO_2K)_2 \cdot 4.5H_2O$ , which is feebly alkaline; and in the proportions 1 : 2 : 4 or 5, the *compound*,



irregular, hexagonal columns. Equimolecular proportions of sodium salicylate and catechol give rise to the *compound*,



which is faintly acid in reaction and forms very slender needles.

J. C. W.

**Synthesis of Natural Inositol.** HEINRICH WIELAND and ROBERT S. WISHART (*Ber.*, 1914, **47**, 2082—2085).—The authors have succeeded in reducing hexahydroxybenzene to an inositol, which, of the seven possible isomerides, happens to be the one which occurs most commonly in nature.

The purest hexahydroxybenzene, prepared from carbon monoxide by Nietzki and Benckiser's method, was suspended in water and shaken with palladium black, quite free from hydrochloric acid, in an atmosphere of hydrogen, at 50—55°, until saturation took place. The inositol obtained on evaporation of the clear filtrate was completely identified with the natural substance and also converted into the hexaacetate.  
J. C. W.

**Nitration of the Acyl Derivatives of *m*-Aminophenol.** [Correction.] FRÉDÉRIC REVERDIN (*Ber.*, 1914, **47**, 2216—2218).—In a recent paper (this vol., i, 166) the author reported that he could not confirm Meldola's statement that the product of the action of nitric acid on diacetyl-*m*-aminophenol is a mixture of 4- and 6-nitro-3-acetylaminophenols (compare T., 1914, **105**, 977, footnote). Having now learnt from Meldola the exact experimental details, he finds that the above statement is correct.

Reverdin also described, as the sole product of the nitration at low temperatures, 6-nitrodiacetyl-*m*-aminophenol. He has now found that, even at -7°, both isomerides are formed, accompanied by the monoacetyl derivatives, that is, the free phenols. The above compound, therefore, required digestion with cold sodium carbonate solution in order to remove traces of the corresponding phenol. The m. p. is now given as 149° and not 113°, and the free 6-nitro-3-acetylaminophenol obtained from it is found to have the correct m. p. 220—221°, and not 200°.  
J. C. W.

**The Mechanism of the Action of Magnesium Alkyl Haloids on Esters.** G. STADNIKOV (*Ber.*, 1914, **47**, 2132—2142).—In extension of his investigations of the oxonium compounds produced from magnesium alkyl haloids and ethers (A., 1913, i, 1183, 1335) the author finds that esters and magnesium alkyl haloids form similar oxonium compounds and that the latter possess the constitution suggested by Grignard, namely,  $R \cdot CO \cdot OR' \cdot R'' \cdot MgX$ , for the possible decompositions into  $R \cdot COR' + OR'' \cdot MgX$ ,  $R \cdot CO_2 \cdot MgX + R'R''$  and  $R \cdot CO_2 \cdot MgX + \frac{1}{2}R'R' + \frac{1}{2}R''R''$  respectively, can in some cases be experimentally realised.

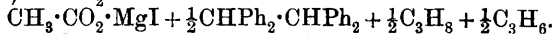
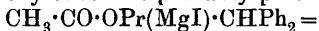
Benzhydryl acetate, b. p. 171—172°/12 mm., prepared by the action of diphenylbromourethane on potassium acetate in acetic acid solution, on treatment with an equimolecular proportion of magnesium ethyl iodide in the cold, gave a colourless precipitate of an oxonium complex which on treatment with water regenerated almost the whole of the ester unchanged.

When benzhydryl acetate was treated in ethereal solution with magnesium ethyl iodide, the former being in excess, the mixture on boiling gave a certain quantity of ethane with a smaller quantity of ethylene, and on subsequent addition of water, besides a further small quantity of these gases, methyldiethylcarbinol, b. p. 122—125°/750 mm., and *s*-tetraphenyldimethyl ether, m. p. 108—109°, were obtained together with unaltered benzhydryl acetate. The result indicated a reaction between one molecule of ester and two of organo-

magnesium compound, the first point of attack in the ester being, not the carbonyl group, but the alkyloxy-group.

An excess of benzhydryl acetate and magnesium *isoamyl* iodide under similar treatment produced methyl*diisoamyl*carbinol, b. p. 112—114°/14 mm., benzhydryl and unaltered benzhydryl acetate, the reaction having proceeded in a normal manner.

Under similar conditions, benzhydryl acetate and magnesium propyl iodide gave during the heating some propane with less propylene and a little hydrogen, whilst on subsequent treatment with water, the mixture yielded tetraphenylethane, m. p. 208°, *s*-tetraphenyldimethyl ether, methyl*di*propylcarbinol, b. p. 159—161°/755 mm., an oily *substance*, b. p. 147—153°, and benzhydryl. The formation of methyl*di*propylcarbinol arises from the normal manner of reaction, whilst the tetraphenylethane is probably produced by a decomposition :



Benzhydryl acetate and magnesium butyl iodide in ethereal solution gave some butane and butylene during the heating and *s*-tetraphenylethane, methyl*di*butylcarbinol, b. p. 84—85°/10 mm., benzhydryl and a *substance*, b. p. 150—160°/12 mm., on subsequent treatment with water. The formation of the tetraphenylethane is attributed to a decomposition corresponding with the last of the three types of decomposition mentioned above.

With magnesium phenyl bromide, benzhydryl acetate gave *s*-tetraphenyldimethyl ether, a *substance*, b. p. 130—145°/9 mm., and *aa* $\beta$ -*triphenylpropylene*,  $\text{CPhMe}\cdot\text{CPh}_2$ , m. p. 121—122°, the formation of the last named being ascribed to a subsequent action of the organo-magnesium compound on the *as*-diphenylacetone produced from the oxonium additive compound by a primary decomposition belonging to the first of the above three types.

Benzyl benzoate and magnesium phenyl bromide reacted in ethereal solution, giving benzoic acid, phenol, benzyl alcohol, triphenylcarbinol, m. p. 164—165°, and triphenylethylene, m. p. 72—73° (compare Staudinger and Kon, A., 1911, i, 876). Again, a decomposition of the primary oxonium compound has probably occurred according to the first of the above possibilities, the resulting phenyl benzyl ketone giving triphenylethylene on reaction with more organo-magnesium compounds, followed by dehydration of the primarily resulting *aa* $\beta$ -triphenylethyl alcohol.

D. F. T.

**Diphenylnitric Oxide, a New Organic Radicle with Quadri-valent Nitrogen.** HEINRICH WIELAND and MORITZ OFFENBÄCHER (*Ber.*, 1914, 47, 2111—2115).—Diphenylhydroxylamine has been oxidised to the compound,  $\text{Ph}_2\text{N}\cdot\text{O}$ , which bears a great resemblance to nitrogen peroxide, with regard both to its colour and its reactivity.

Better results in the preparation of diphenylhydroxylamine are obtained by decomposing the mixture of magnesium phenyl bromide and nitrosobenzene at once, and not after some hours (A., 1912, i, 253). An ethereal solution of the compound is shaken with dry silver oxide at 0°, when a deep red colour develops. After a few minutes, the mixture is dehydrated by sodium sulphate, filtered, diluted with

petroleum, and plunged into a mixture of ether and solid carbon dioxide. About 75% of the theoretical quantity of *diphenylnitric oxide* separates after a short time, in sparkling, deep red needles, m. p. 62° (decomp.), which cannot be kept for more than a day. The compound is uni-molecular in benzene, and is, apparently, unassociated at very low temperatures. It liberates iodine from potassium iodide and changes thereby into diphenylamine, quantitatively, and it decolorises bromine with the formation of tetrabromodiphenylamine. Concentrated acids react explosively, sulphuric acid giving a deep blue solution. The dark red solutions are decolorised at once by nitric oxide or triphenylmethyl.

The discovery of this compound confirms the assumption that the red, highly reactive substance, porphyrexide (Piloty and Schwerin, A., 1901, i, 517, 583), also contains quadrivalent nitrogen, and it may also strengthen the evidence against a ring-formula, with bivalent nitrogen for nitrogen peroxide.

J. C. W.

**Oxonium Compounds.** IV. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 459—469).—Tschelincev and Pavlov's criticisms (A., 1913, i, 461) are refuted and Stadnikov and Kuzmina-Aron's conclusions (A., 1912, i, 971) confirmed by the results of further experiments.

T. H. P.

**Arylsulphuric Acids.** EMIL CZAPEK (*Monatsh.*, 1914, 35, 635—642).—Potassium phenyl sulphate is readily obtained by the following modification of Baumann's method. A mixture of phenol with 60% of potassium hydroxide and 80% of water is treated at 60—63° with finely powdered potassium pyrosulphate (125%) at such a rate that the temperature is maintained between 60° and 70°. The mixture is stirred mechanically for eight to ten hours at this temperature, and is then cooled and repeatedly extracted with boiling 96% alcohol to remove the potassium phenyl sulphate. *Potassium  $\alpha$ -naphthyl sulphate*, m. p. 182°, apparently rhombic, pearly leaflets, is prepared in a similar manner at 40—45°.

Arylsulphuric acids are obtained easily, generally, and in good yields by the following modification of Verley's method. Phenol (50 parts), dissolved in a little pyridine or chloroform, is allowed to flow into a well-stirred, cold mixture of chlorosulphonic acid (60 parts), chloroform (500 parts), and pyridine (100 parts), the temperature being kept below 45°. When the pyridine chlorosulphonate has almost disappeared, the chloroform is removed below 45° in a vacuum, concentrated aqueous potassium hydroxide (80 parts) is added, the pyridine is distilled in a vacuum, and the residue is extracted, firstly with petroleum to remove impurities, and then with boiling alcohol to dissolve the potassium phenylsulphate. Substantially in the same manner have been prepared *potassium menthyl sulphate*, m. p. 190—198°, colourless, silky needles, *potassium bornyl sulphate*, pearly needles or leaflets, *potassium quinolyl 8-sulphate*, slender needles, and *potassium quinolyl 2-sulphate*.

The preceding salts do not react with ferric chloride and are converted into the corresponding sulphonic acids by heating at 150—200°. C. S.

**Cadmium Salicylate.** W. ECHSNER DE CONINCK (*Bull. Soc. chim.*, 1914, [iv], 15, 608—609).—Cadmium carbonate and salicylic acid interact to form cadmium salicylate, which crystallises in plates or needles as monohydrate. In the presence of water at 76—77° it undergoes partial decomposition with the liberation of salicylic acid; at 165—167° it evolves carbon dioxide, with the production of phenol and probably a basic salt,  $C_6H_4 \begin{smallmatrix} \diagup CO_2 \\ \diagdown O \end{smallmatrix} Cd$ ; above 170° it chars.

A. J. W.

**The Hydroxybenzoates.** W. ECHSNER DE CONINCK (*Rev. Gén. Chim. pure appl.*, 1914, 17, 72—75. Compare A., 1907, i, 532, 621, 1042).—A study of calcium salicylate,  $[C_6H_4(OH) \cdot CO_2]_2Ca, 2H_2O$ . The salt is soluble to the extent of approximately 28.46 and 15.50 grams in water and in alcohol at 15.5 and 16.7° respectively. When solutions in these solvents are distilled, no decomposition of the salt occurs, although after heating with water the salt can be obtained in the form of a *trihydrate*. The aqueous solutions acquire a rose-coloured and then a yellow tint on exposure to light. Methyl alcohol is an excellent solvent for the salt.

On heating at 100—115°, the salt loses  $1H_2O$ , and at higher temperatures undergoes decomposition, giving carbon dioxide, phenol, and a so-called basic calcium salicylate,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CO_2 \end{smallmatrix} Ca$ ; the evolution of carbon dioxide commences at 243—244°.

Distillation of a mixture of the salt with such acids as formic, acetic, propionic, gallic, mucic, benzoic, vanillic, and *m*- and *p*-hydroxybenzoic, water also having been added, causes liberation of salicylic acid; hydrogen sulphide, the *o*- and *p*-nitrophenols and picramic acid do not effect such displacement.

After heating in a closed tube for fifteen hours at 215°, no indications of isomeric change with the formation of *m*- or *p*-hydroxybenzoic acid were observable.

D. F. T.

**Preparation of Sodium Acetylsalicylate [*o*-Acetoxybenzoate].** JOHANN A. WÜLFING (D.R.-P. 270326).—*o*-Acetoxybenzoic acid is converted into its sodium salt by treating it, in a powdered dry condition, with the equivalent proportion of anhydrous sodium carbonate in the presence of ethyl acetate.

T. H. P.

**$\omega$ -Bromotoluic Acids.** I. J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 508—511).— *$\omega$ -Bromo-*p*-toluic acid*,  $CH_2Br \cdot C_6H_4 \cdot CO_2H$ , obtained by the interaction of bromine and *p*-toluic acid dissolved in bromoform, crystallises in plates, m. p. 223°, having a vitreous lustre and an irritant action on the mucous membrane; on oxidation with permanganate, it yields terephthalic acid. The *chloro-anhydride*, m. p. 56°, which has an irritating odour, yields the *methyl ester*,  $C_9H_9O_2Br$ ,

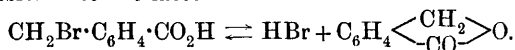
vitreous needles, m. p. 53—53.5°, b. p. 160—161°/17 mm., when treated with methyl alcohol. The action of ethyl alcohol and sulphuric acid on the free acid yields *ethyl ω-ethoxy-p-toluate*,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ , b. p. 277.5—278.5°, 163—165°/18 mm.; the corresponding *acid*,  $\text{C}_{10}\text{H}_{12}\text{O}_3$ , m. p. 78—79°, which gives terephthalic and acetic acids on oxidation, and also its *silver* salt were prepared and analysed.

*ω-Bromo-o-toluic acid*,  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , prepared by the action of hydrobromic acid on phthalide, forms prismatic crystals, m. p. 147°; its *methyl* ester,  $\text{C}_9\text{H}_9\text{O}_2\text{Br}$ , is a viscous liquid,  $D_4^{20}$  1.4136,  $D_4^{25}$  1.3882, which emits a vapour having a marked irritant effect on the eyes and mucous membrane and decomposes with the formation of phthalide on distillation under diminished pressure. T. H. P.

**ω-Bromotoluic Acids.** II. J. S. ZALKIND and A. S. SEMENOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 512—517. Compare preceding abstract).—*ω-Bromo-m-toluic acid*,  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , prepared by brominating *m*-toluic acid in bromoform solution, forms white crystals, m. p. 151—152°, and emits a vapour which produces violent itching of the skin and mucous membrane; on oxidation with permanganate, it yields *isophthalic acid*. Its *ethyl* ester,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ , is an oily liquid, b. p. 160—161°/10 mm.

Since *ω*-bromo-*m*- and -*p*-toluic acids readily exchange their bromine for hydroxyl or ethoxyl, and the *o*-acid gives up hydrogen bromide to form phthalide, the authors have investigated the influence of the carboxyl group on the mobility of the bromine atom. With the *p*- and *m*-acids, the action of water proceeds according to the equation  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O} = \text{HBr} + \text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , and at 50° when a large excess of water is employed, the values of  $k$  calculated from the formula for unimolecular reactions are virtually constant.

In the case of the *o*-acid, the action of water is a reversible reaction, which leads to a chemical equilibrium, two-thirds of the acid undergoing conversion into the lactone:



At 0°, the values of  $k = 1/t \cdot \log[(2-x)/(2-3x)]$  exhibit a gradual but marked diminution, apparently owing to the influence of the increasing number of hydrogen ions on the velocity of the reaction. In the action of water on benzyl bromide,  $\text{CH}_2\text{PhBr} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{Ph} \cdot \text{OH} + \text{HBr}$ , equilibrium is reached when two-thirds of the benzoyl bromide has been changed. Here, too, the values of  $k = 1/t \cdot \log[(2-x)/(2-3x)]$  show gradual diminution.

These results are not all easily explainable, but it is evident that the introduction of a carboxyl group into the molecule of benzyl bromide renders the bromine atom less mobile, this action being most marked in the para-position and least in the meta-position.

T. H. P.

**Action of Magnesium on Ethyl Phenylbromoacetate.** J. S. ZALKIND and A. V. BASKOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 476—478).—The action of magnesium on ethyl phenylbromoacetate in

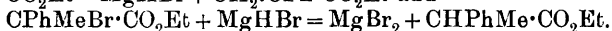


the presence of ether and a crystal of iodine and subsequent decomposition of the product with water yield ethyl  $\alpha$ -diphenylacetoacetate and ethyl phenylacetate, the reactions involved being expressed by the equations: (1)  $\text{CHPhBr} \cdot \text{CO}_2\text{Et} + \text{Mg} = \text{MgBr} \cdot \text{CHPh} \cdot \text{CO}_2\text{Et}$  and this  $+ \text{H}_2\text{O} = \text{CH}_2\text{Ph} \cdot \text{CO}_2\text{Et} + \text{MgBr} \cdot \text{OH}$ ; (2)  $2\text{MgBr} \cdot \text{CHPh} \cdot \text{CO}_2\text{Et} = \text{MgBr} \cdot \text{CHPh} \cdot \text{C}(\text{OEt})(\text{O} \cdot \text{MgBr}) \cdot \text{CHPh} \cdot \text{CO}_2\text{Et}$  and this  $+ 2\text{H}_2\text{O} = 2\text{MgBr} \cdot \text{OH} + \text{Et} \cdot \text{OH} + \text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CO}_2\text{Et}$  (compare Zalkind, A., 1907, i, 22; Reformatski, A., 1907, i, 23; Zeltner, A., 1908, i, 243).

T. H. P.

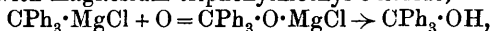
**Action of Magnesium on Esters of  $\alpha$ -Bromo- $\alpha$ -phenylpropionic and Diphenylbromoacetic Acids.** J. S. ZALKIND and (Mlle.) M. S. PESCHERKOVA (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 478—488).—Zalkind and Baskov (preceding abstract) have shown that, like other  $\alpha$ -bromo-esters, ethyl phenylbromoacetate yields derivatives of ethyl acetoacetate when treated with magnesium and subsequently with water. In order to ascertain to what extent this reaction is general for  $\alpha$ -bromo-derivatives of phenyl-substituted acids, the authors have investigated the action of magnesium on ethyl  $\alpha$ -bromo- $\alpha$ -phenylpropionate and diphenylbromoacetate. These esters are highly unstable, the former readily losing a molecule of hydrogen bromide and the latter exchanging a bromine atom for a hydroxyl or ethoxyl group. This mobility of the bromine atom is also manifest in the interaction of the esters and magnesium, which dissolves easily in both of them in presence of dry ether, so that the addition of iodine is unnecessary for the initiation of the reaction.

The decomposition by means of water of the products formed proceeds quite otherwise than with the esters of  $\alpha$ -bromo-acids previously investigated. Thus, with the former of the two esters, the products consist principally of ethyl  $\alpha$ -phenylpropionate (up to 50%) and of 7—9% of ethyl atropate, the main reaction taking place thus:  $\text{CPhMeBr} \cdot \text{CO}_2\text{Et} + \text{Mg} = \text{MgBr} \cdot \text{CPhMe} \cdot \text{CO}_2\text{Et}$  and this  $+ \text{H}_2\text{O} = \text{MgBr} \cdot \text{OH} + \text{CHPhMe} \cdot \text{CO}_2\text{Et}$ . The mechanism of the formation of atropic ester is probably expressed by the equations:  $\text{MgBr} \cdot \text{CPhMe} \cdot \text{CO}_2\text{Et} = \text{MgHBr} + \text{CH}_2 \cdot \text{CPh} \cdot \text{CO}_2\text{Et}$  and

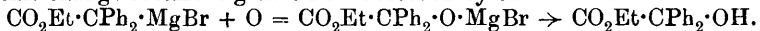


The expected diphenyldimethylacetoacetic ester is obtained in such small proportion that it could not be separated in the pure state.

No acetoacetate derivative at all is obtained from ethyl diphenylbromoacetate, which gives an organo-magnesium compound distinguished by its ready oxidisability. Although the reaction is carried out in a reflux apparatus, so that the vapour of the ether mixes with the air, decomposition of the product of the reaction by means of water gives benzoic acid in 50% yield. Use of an atmosphere of hydrogen causes the amount of benzoic acid to diminish but not to vanish. A similar tendency to oxidation was observed by Schmidlin (A., 1906, i, 392; 1907, i, 26) with magnesium triphenylmethyl chloride,



this change resembling that now observed by the authors:



In the latter case, when the reaction is carried out in hydrogen, the

products consist of diphenylacetic acid (up to 55% yield), benzilic acid, ethoxydiphenylacetic acid and a very small proportion of a crystalline acid, m. p. 275°, the constitution of which was not determined; the ethoxy-acid seems to be formed during the preparation of the original ester from the bromo-anhydride of  $\alpha$ -bromodiphenylacetic acid and alcohol.

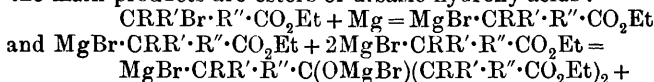
Thus, of these bromoacetic esters, the phenyl derivative yields 65% of ketonic ester and 22% of phenylacetic ester, the phenylmethyl derivative gives about 50% of ketonic ester and 9% of atropic ester, whilst the diphenyl derivative undergoes no condensation. This varying behaviour is regarded as related to the degree of saturation of the fundamental carbon atom and of the bromine atom; as the hydrogen atom of the first ester is displaced by methyl and then by phenyl, the carbon atom attached to the bromine atom becomes increasingly saturated and the bromine atom itself decreasingly so; from this result the diminishing tendency of the carbon to condensation and the increasing mobility of the bromine atom or the magnesium derivative.

*Ethyl  $\alpha$ -bromo- $\alpha$ -phenylpropionate*,  $\text{CMePhBr}\cdot\text{CO}_2\text{Et}$ , prepared from the bromo-anhydride of  $\alpha$ -bromo- $\alpha$ -phenylpropionic acid and alcohol, was obtained as an oily, somewhat impure liquid,  $D_4^{20}$  1.3369.

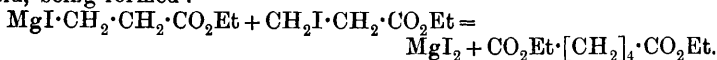
*Ethoxydiphenylacetic acid*,  $\text{OEt}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ , forms crystals, m. p. 114–115°, and has the normal molecular weight in boiling ether. Its silver salt was analysed.

T. H. P.

**Action of Magnesium on Esters of  $\beta$ -Halogenated Acids.** J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 488–504).—The action of magnesium on esters of  $\alpha$ -halogenated acids yields principally ketonic esters, whereas with most carboxylic compounds the reaction goes further and leads to the formation of alcohols. The failure of the latter reaction with  $\alpha$ -bromo-esters may depend on the immediate proximity of the group  $:\text{C}\cdot\text{MgBr}$  to the unsaturated carboxyl group, so that the carbon and the magnesium of the group  $:\text{C}\cdot\text{MgBr}$  become more saturated and less reactive. Greater separation of the halogen from the carboxyl group should therefore be accompanied by increase in the capacity of the organo-magnesium compound to react, and this is actually found to be the case. With  $\beta$ -halogenated esters, indeed, the main products are esters of dibasic hydroxy-acids:



$\text{Br}\cdot\text{Mg}\cdot\text{OEt} \rightarrow \text{CHRR}'\cdot\text{R}''\cdot\text{C}(\text{OH})(\text{CRR}'\cdot\text{R}''\cdot\text{CO}_2\text{Et})_2$ .  
To a slight extent, however, the change proceeds in the direction of the Wurtz-Fittig reaction, esters of dibasic acids, for example, adipic acid, being formed:



The dibasic hydroxy-acids forming the principal products are either viscous liquids or amorphous, colourless solids, which cannot be distilled unchanged even in a vacuum. In spite of the  $\beta$ -position of the hydroxyl to the two carboxyl groups, only the simplest of these acids, obtained from ethyl  $\beta$ -iodopropionate, is able to form a lactone.

*Ethyl β-bromo-β-phenylpropionate*,  $\text{CHPhBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , prepared by the action of hydrobromic acid on ethyl cinnamate, forms a viscous oil with a faint, pleasant odour,  $D_0^0$  1·3751,  $D_4^{20}$  1·3559,  $n_D^{20}$  1·54246. When treated with dry ether, magnesium and a crystal of iodine, it yields ethyl  $\beta\gamma$ -diphenyladipate (9·4%), ethyl  $\beta$ -phenylpropionate (26·5%), and *ethyl γ-hydroxy-βδ-diphenyl-γβ'-phenylethylpimelate* (47·4%),  $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{CH}_2\text{Ph})(\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ . The acid,  $\text{C}_{27}\text{H}_{28}\text{O}_5$ , corresponding with this ester, forms an amorphous, white powder, m. p. 108—111°, and has the normal molecular weight in boiling acetone; its *silver* salt was analysed.

*β-Bromo-β-phenyl-αα-dimethylpropionic acid*,  $\text{CHPhBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , prepared from phenoxypivalic acid and hydrobromic acid, forms prismatic crystals, m. p. 122°, and its *ethyl* ester,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{Br}$ , prepared from the chloro-anhydride and ethyl alcohol, is a colourless, viscous oil, with a pleasant but slightly irritating odour, b. p. (decomp.) 193—194°/44 mm., 163—164°/17 mm.,  $D_0^0$  1·3494,  $D_4^{24}$  1·3274,  $n_D^{24}$  1·54654. The ester reacts with difficulty with magnesium, giving a product which with water yields (1) 2·5% of *ethyl βγ-diphenyl-ααδδ-tetramethyladipate*,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ ,

which forms crystals, m. p. 145·5—146°, and has the normal molecular weight in freezing benzene; (2) 36% of ethyl phenylpivalate, b. p. 235—240° (decomp.), 136—138°/13 mm. and (3) 50% of *ethyl γ-hydroxy-βδ-diphenyl-γβ'-phenylmethylpropyl-ααεε-tetramethylpimelate*,

$\text{CO}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{C}(\text{OH})(\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et})_2$ , m. p. 60—70°; the corresponding acid,  $\text{C}_{33}\text{H}_{40}\text{O}_5$ , an amorphous, white powder, m. p. 74—80°, which has the normal molecular weight in boiling acetone, its *silver* salt,  $\text{C}_{33}\text{H}_{38}\text{O}_5\text{Ag}_2$ , and its *diacetyl* derivative,  $\text{C}_{35}\text{H}_{42}\text{O}_6$ , white, amorphous compound, were prepared.

Ethyl  $\beta$ -iodopropionate and magnesium readily react, giving a product which with water yields: (1) 13·5% of ethyl propionate; (2) 5·6% of ethyl adipate, and (3) 61% of ethyl  $\gamma$ -hydroxy- $\gamma$ -ethylpimelate, which on conversion to the corresponding acid,  $\text{C}_9\text{H}_{16}\text{O}_5$ , undergoes partial conversion into the lactonic acid,  $\text{C}_9\text{H}_{14}\text{O}_4$ . T. H. P.

**Action of Magnesium on Ethyl β-Bromo-β-phenylisobutyrate.** J. S. ZALKIND and S. N. GRABOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 504—507)—This reaction is similar to those obtained with other  $\beta$ -halogenated acids, the products being ethyl  $\alpha$ -benzylpropionate (31%) and ethyl  $\gamma$ -hydroxy- $\beta\delta$ -diphenyl- $\gamma\beta'$ -phenylisopropyl- $\alpha\epsilon$ -dimethylpimelate (55%).

*β-Bromo-β-phenyl-α-methylpropionic acid*,  $\text{CHPhBr}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , prepared by heating  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylpropionic acid in a sealed tube with hydrobromic acid, forms small crystals, m. p. 106—107°, with a faint odour which attacks the mucous membrane. The corresponding *ethyl* ester,  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{Br}$ , is a pale yellow liquid with a faint, but irritating odour,  $D_4^0$  1·1361,  $D_4^{16}$  1·1342,  $n_D^{16}$  1·4958.

*γ-Hydroxy-βδ-diphenyl-γβ'-phenylisopropyl-αε-dimethylpimelic acid*,  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{C}(\text{OH})(\text{CHMe}\cdot\text{CH}_2\text{Ph})\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , is a white, amorphous compound, m. p. 104—105°, and has the normal molecular weight in boiling ether. Its *silver* salt,  $\text{C}_{30}\text{H}_{32}\text{O}_5\text{Ag}_2$ , and the *silver* salt of its *acetyl* derivative,  $\text{C}_{32}\text{H}_{34}\text{O}_6\text{Ag}_2$ , were prepared and analysed. T. H. P.

**Transformation of  $\beta\gamma$ -Unsaturated Acids by Ultra-violet Light.** R. STOERMER and H. STOCKMANN (*Ber.*, 1914, 47, 1793—1795).—As a representative of the  $\beta\gamma$ -ethylenic acids,  $\gamma$ -phenylvinylacetic acid, in benzene solution, has been exposed to ultra-violet light. Although the *allo*-form could not be obtained solid, the crystalline *allo*-amide was isolated and converted by separate illumination into the stable variety.

$\gamma$ -Phenylvinylacetic acid (Fichter, A., 1907, i, 87) is very sparingly soluble in light petroleum, so this solvent was used to extract the *allo*-variety, about 20% of this being formed in a week or two. The crude acid was treated with sodium ethoxide, the dry sodium salt converted into the acid chloride, and this poured into concentrated aqueous ammonia. The brown mass was recrystallised and yielded *allo*-phenylvinylacetamide,  $C_{10}H_{11}ON$ , in white needles, m. p. 85—86°. The stable amide, m. p. 130°, and anilide, m. p. 94·5—95°, were prepared from the corresponding chloride. J. C. W.

**$\beta$ -2-Naphthoylpropionic Acid.** M. GIUA (*Ber.*, 1914, 47, 2115—2116).—Borsche and Sauernheimer have recently described the above acid as the sole product of the condensation of succinic anhydride and naphthalene by aluminium chloride (this vol., i, 839). The author had already shown that both the  $\alpha$ - and  $\beta$ -naphthalene derivatives are obtained in equal quantities when the reaction proceeds slowly in the cold (*Rend. Soc. Chim. ital.*, 1912, 239). The *methyl* ester of the  $\alpha$ -acid is an oil, whilst *methyl*  $\beta$ -2-naphthoylpropionate forms colourless needles, m. p. 74°. J. C. W.

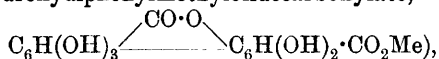
**$\psi$ -Esters of *ortho*-Dicarboxylic Acids.** ALFRED KIRPAL (*Monatsh.*, 1914, 35, 677—696).—By treating  $\alpha$ -ethyl hydrogen hemipinate with thionyl chloride in the cold, or, better, by heating it with thionyl chloride and an excess of carbon tetrachloride on the water-bath (in the absence of carbon tetrachloride, the latter method yields hemipinic anhydride),  $\alpha$ -ethyl hemipinate- $\psi$ -chloride,  $C_6H_2(OMe)_2 \left\langle \begin{smallmatrix} CCl(OEt) \\ CO \end{smallmatrix} \right\rangle O$ , m. p. 102°, colourless prisms, is obtained (compare Egerer and Meyer, A., 1913, i, 269). The ester- $\psi$ -chloride is stable in boiling benzene, but is converted by not too prolonged treatment with cold absolute alcohol into  $\psi$ -ethyl hemipinate,  $C_6H_2(OMe)_2 \left\langle \begin{smallmatrix} C(OEt)_2 \\ CO \end{smallmatrix} \right\rangle O$ , m. p. 64°, colourless prisms or plates. The  $\psi$ -ester changes to the normal ester (m. p. 72°) at its b. p., and is rapidly converted into  $\alpha$ -ethyl hydrogen hemipinate by alcoholic hydrogen chloride; one ethyl group is removed as ethyl iodide even by cold aqueous hydriodic acid (compare Egerer and Meyer, *loc. cit.*). The  $\psi$ -ester is changed to the normal ester by alcoholic sodium ethoxide, slowly at room temperature, almost instantly by heating. That this change is due, not to intramolecular rearrangement, but to the addition of ethyl alcohol and its subsequent elimination in a different manner, is proved by the fact that the  $\psi$ -ethyl ester and methyl-alcoholic sodium methoxide yield exclusively  $\beta$ -methyl  $\alpha$ -ethyl hemipinate, 
$$\begin{array}{c} OMe \cdot C : C(OMe) \cdot C \cdot CO_2Et \\ | \\ CH : CH - C \cdot CO_2Me \end{array}$$
 m. p. 88°, glis-

tening needles. This ester has also been obtained from  $\alpha$ -ethyl silver hemipinate and methyl iodide, and by the action of alcoholic sodium methoxide on normal ethyl hemipinate (again an example of the addition and subsequent elimination of an alcohol).

$\beta$ -Ethyl hydrogen hemipinate and thionyl chloride yield hemipinic anhydride by warming. At room temperature the product is (impure)  $\beta$ -ethyl hemipinate chloride,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{COCl}$ , which behaves like a normal acid chloride, yielding chiefly the normal diethyl ester by treatment with cold alcohol, and  $\beta$ -ethyl hydrogen hemipinate by treatment with water. The  $\beta$ -ester chloride changes to the  $\alpha$ -ester- $\psi$ -chloride, slowly at the ordinary temperature, more rapidly by heating in an indifferent solvent.

Some experiments are recorded on the estimation by Ziesel's method of mobile methoxy- and ethoxy-groups. C. S.

**Gallic Acid.** ERW. SCHWENK (*J. pr. Chem.*, 1914, [ii], 90, 53—60).—An account of unsuccessful attempts to prepare 2:3:4:2':3':4'-hexahydroxydiphenyl-6:6'-dicarboxylic acid, of which ellagic acid is considered to be the anhydride, by oxidising gallic acid and its methyl ester with ferric chloride. Oxidation of methyl gallate in glacial acetic acid solution results in the formation of ellagic acid. The latter acid is also formed when the oxidation is carried out in boiling aqueous solution, but in this case is accompanied by a substance (probably methyl pentahydroxydiphenylmethylenedecarboxylate,



from which it could not be separated.

Ellagic acid is not produced when gallic acid itself is oxidised with ferric chloride.

*Methyl 3:4:5-triacetoxybenzoate*, prepared by heating methyl gallate with acetic anhydride, forms rhomboidal crystals, m. p. 120—122°.

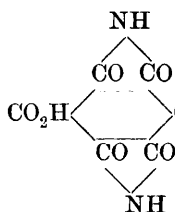
*Ethyl 3:4:5-triacetoxybenzoate* crystallises in rhombs, m. p. 123—125°.

*Methyl dibromogallate* sinters at 155°, m. p. 160—161° (compare Biétrix, A., 1893, i, 343), and on acetylation yields *methyl 2:6-dibromo-3:4:5-triacetoxybenzoate*, which crystallises in white rhombs, m. p. 150—152°. F. B.

**Mellitic Acid.** HANS MEYER and KARL STEINER (*Monatsh.*, 1914, 35, 475—518).—After a review of the history of mellitic acid, the author gives details for the preparation of this substance by oxidising pine-wood charcoal with nitric acid, the yield of crude product being 48% of the charcoal taken (compare Meyer, this vol., ii, 267).

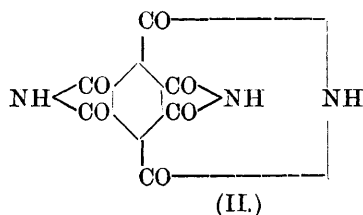
The ammonium salt forms crystals (with  $9\text{H}_2\text{O}$ ) which belong to the rhombic system ( $a:b:c = 1.5443:1:0.5545$ ; compare Wyrubov, *Bull. Soc. chim.*, 1894, [iii], 11, 121). A closer examination of the thermal decomposition of this salt has been made; chemical change commences at 100° and is complete at 200°; above this temperature further decomposition ensues with formation of derivatives of pyromellitic acid. The product at 200° is a yellowish-white powder and can be separated by water, as described by Wöhler, into insoluble

paramide and soluble ammonium euchronate (*Annalen*, 1841, 37, 268). Analysis of the euchronic acid indicates a formula  $C_{24}H_{11}O_{16}N_5$  instead of the earlier  $C_{12}H_4O_8N_2$ ; the acid is tetrabasic, and as diazomethane introduces seven methyl groups, there must also be present three  $\cdot CO \cdot NH \cdot CO \cdot$  groups; on hydrolysis, euchronic acid is converted completely into mellitic acid, whilst when strongly heated it gives pyromellitic acid with partial decomposition. From these results the

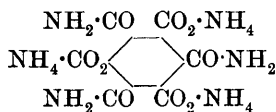


authors deduce for euchronic acid the annexed formula (compare Mathews, A., 1899, i, 56). Paramide, for which mellimide is the better name, is colourless and amorphous when first prepared, but on crystallisation from quinoline is obtained in yellow needles.

When amorphous paramide,  $C_{12}H_3O_6N_3$ , is treated with concentrated ammonia solution, a pentamide,  $C_{12}H_9O_6N_5$ , of mellitic acid is obtained; the addition of only two molecules of ammonia leads the authors to suggest that instead of possessing the structure (formula I), paramide has two of its carbonyl groups linked differently from the remainder, namely, between the para-positions (as, for example, in formula II).



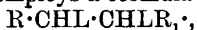
The action of dry ammonia on mellitic anhydride,  $C_{12}O_9$ , at  $120^\circ$  gives a substance, probably a mellitic tri-imide, which is different from paramide, and on heating at  $160$ — $180^\circ$  assumes a deep yellow colour which disappears on cooling; if the anhydride is kept near  $200^\circ$ , the action of ammonia is attended by decomposition with the formation of a deep blue substance. If the mellitic anhydride is in suspension in ether or benzene, dry ammonia converts it into an ammonium salt (annexed formula), a colourless, crystalline powder soluble in water.



The formation and properties of trimethylparamide (compare Meyer and Steiner, A., 1913, i, 204) and of the anhydrides of mellitic acid (A., 1913, i, 368) are discussed. On boiling with methyl alcohol the dianhydride,  $C_{12}H_2O_{10}$ , was converted into a mixture of esters in which a dimethyl ester predominated, whilst the trianhydride,  $C_{12}O_9$ , also gave a mixture of which the only isolable constituent was a tetramethyl ester, crystals, m. p.  $70$ — $110^\circ$ .

D. F. T.

**The Preparation of *l*- and *d*-Cinnamic Acid by Asymmetric Induction.** EMIL ERLÉNMEYER [with G. HILGENDORFF and F. LANDSBERGER] (*Biochem. Zeitsch.*, 1914, **64**, 296—365).—It is shown that optical activity can be “induced” in cinnamic acid when the latter is heated to 168° with optically active tartaric acids. When *d*-tartaric acid is used, a small amount of *l*-cinnamic acid is obtained (which can be dissolved out of the fusion with light petroleum) together with a mixture of the mono- and di-cinnamyl tartrates. The latter on treatment with cold sodium carbonate solution are hydrolysed, and a cinnamic acid preparation can be obtained therefrom, of which  $[\alpha]_D$  reaches  $-20^\circ$ . It is assumed that the cinnamic acid exists in optically active forms before it forms the esters. The cinnamates can also be hydrolysed by heating with water. The optically active preparations of cinnamic acid obtained in this way are free from tartaric acid, as, on heating, they sublime without the smallest trace of charring, and are completely soluble in light petroleum. The cinnamic acid preparations lose their optical activity on sublimation, or on treatment of their solutions with a few drops of sodium hydroxide solution. The dicinnamate can be more advantageously prepared by heating the *d*- or *l*-tartaric acid with cinnamic anhydride. In addition to the ester, cinnamic acid is formed in the reaction and this is optically active, the direction of the rotation depending on the rotation of the tartaric acid used, the *l*-form being obtained from the *d*-tartaric acid, and the *d*-form from *l*-tartaric acid. The cinnamyl tartrate in both cases also yields an optically active acid on hydrolysis. On addition of bromine to the *l*-acid, an optically inactive bromine additive product was obtained. The author develops at length his conceptions of relative asymmetry (compare A., 1911, i, 780), and shows that cases of stereoisomerism in substances containing no asymmetric carbon atom are conceivable when his models are employed. To represent the asymmetry of unsaturated compounds, such as cinnamic acid, he employs a formula of the type



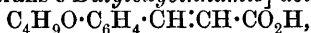
of which twelve “relative” isomerides are possible. In this formula L represents an unoccupied space. The author also recapitulates his various experiments on induced asymmetry. S. B. S.

**Rearrangements of Higher Alkylcoumaric [*o*-Alkyloxy-cinnamic] Acids by Ultra-violet Light.** R. STOERMER and H. LADEWIG (*Ber.*, 1914, **47**, 1795—1803).—In some previous experiments (compare A., 1911, i, 295) it was found that when the hydroxyl-hydrogen atom of coumaric acid is displaced by the methyl or ethyl group, the readiness with which the acid is transformed into the coumarinic acid increases, but falls again with the introduction of the propyl group. It is now found that this characteristic is still further diminished in the case of the butyl radicles, only to rise again with the *iso*amyl group.

An interesting feature about these acids is that many of their salts are soluble in benzene and ether; for example, calcium amyloxy-cinnamate may even be extracted by ether. The heats of combustion and dissociation constants of the acids were recorded in A., 1913, ii, 297. The *iso*amyl isomerides are exceptionally similar in m. p.'s and solu-

bilities in organic media. Owing to their similarity, it was of course impossible to separate the isomerides as such, but their amides differ sufficiently in solubility to be of service. These compounds could only be hydrolysed by Bouveault's method, whereby the labile form was at the same time converted into the stable.

*n*-Butylcoumaric [trans-*o*-Butyloxycinnamic] acid,



was prepared by heating the sodium salt of methyl coumarate with *n*-butyl iodide, followed by hydrolysis of the ester. The pure acid, as obtained from the calcium salt, crystallises from light petroleum (solubility at 17°, 0.447%) in rhombic leaflets, m. p. 89—90°, and exhibits no fluorescence in alkaline solution, which it might do if not free from coumaric acid. The *amide* forms silky, white needles, m. p. 143—144°, and is almost insoluble in light petroleum. *n*-Butylcoumarinic [cis-*o*-Butyloxycinnamic] acid is obtained to the extent of about 70%, when the isomeride is illuminated for ten days or so, or it may be prepared directly from coumarin. It is more soluble than the *trans*-acid (16.4% in light petroleum) and crystallises in small, thick tablets, m. p. 53—54°. Similarly, when the *trans*-amide is exposed to the light for fourteen days in methyl alcohol, 95% is transformed into the *cis*-amide,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}$ , which forms white, matted needles, m. p. 91°. trans-*o*-isoButyloxycinnamic acid forms white crystals, m. p. 98°, solubility in light petroleum, 0.385% at 18°, and the *amide* separates in white needles, m. p. 140°. The *cis*-acid is formed to the extent of about 67% by ten days' illumination, has m. p. 75°, and dissolves in light petroleum to the extent of 4.61% at 18°. The *cis*-amide, m. p. 105°, is formed in 95—99% yield by exposing the isomeride to light.

trans-*o*-isoAmyloxycinnamic acid,  $\text{C}_{14}\text{H}_{18}\text{O}_3$ , was also purified by conversion into the calcium salt. It forms very characteristic rhombic crystals, m. p. 79—80°, from light petroleum (solubility 1.56% at 18°), and the *amide* crystallises in slender, white needles, m. p. 144—145°. The *cis*-acid, prepared directly from coumarin, crystallises from light petroleum (solubility, 1.53%) in sheaves of slender, white needles, m. p. 80—80.5°. The m. p. of a mixture of the acids was depressed nearly 20°. The *cis*-amide forms slender, white needles, m. p. 76—77°. It was prepared directly from the *trans*-acid, by illuminating the isomeride for ten days in methyl alcohol (yield 90%), and also from the mixture obtained by exposing *trans*-amyloxycinnamic acid to the light for twenty days (80% of the calculated yield). The sodium, copper, barium, and calcium salts of the isomeric acids are described. J. C. W.

**Esterifications by Ultra-violet Light.** R. STOERMER and H. LADEWIG (*Ber.*, 1914, 47, 1803—1806).—It has been accidentally discovered that, when alcoholic solutions of *trans*-cyclohexane-1:4-dicarboxylic acid and *trans*-cyclopentane-1:2-dicarboxylic acid are exposed to ultra-violet light, they are partly converted into mono- and di-esters and not transformed into the *cis*-modifications, as was expected. Benzoic acid is also esterified under these conditions (30% in 8 days) and the reaction is still further promoted by the presence of a trace of hydrochloric acid (56% in 8 days). Cinnamic acid is scarcely



affected without the addition of a trace of hydrochloric acid, but the yield of ester may then reach 37% in 8 days.

By illuminating *trans*-cyclohexane-1:4-dicarboxylic acid (Baeyer, A., 1888, 1074) in methyl alcohol for ten days, a 10% yield of the *methyl hydrogen* salt,  $C_9H_{14}O_4$ , was obtained, in small, white needles, m. p.  $125^\circ$ , whilst, after longer exposure, high yields of the dimethyl ester, m. p.  $71^\circ$ , resulted, sometimes mixed with the hemi-ester. Similarly, ten days' illumination of *trans*-cyclopentane-1:2-dicarboxylic acid (Perkin, T., 1894, 65, 572) gave rise to the *methyl hydrogen* salt,  $C_8H_{12}O_4$ , white needles, m. p.  $45^\circ$ , whilst thirty days' exposure to the light resulted in the formation of both esters, in 10% yields.

J. C. W.

**Preparation of Acetoacetanilide-*p*-carboxylic Acid.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 272530).—When ethyl acetoacetanilide-*p*-carboxylate, obtained by heating ethyl *p*-aminobenzoate with ethyl acetoacetate in absence or presence of a suitable diluent, is treated with an alkali hydroxide and subsequently with hydrochloric acid, it is converted into acetoacetanilide-*p*-carboxylic acid.

T. H. P.

**The Preparation of a Lævorotatory Benzaldehyde by Asymmetric Induction by means of *d*-Tartaric Acid; Conversion of the same into *l*-Mandelonitrile and *d*-Mandelic Acid; the Nature of Enzymatic Reactions.** EMIL ERLÉNMEYER [with F. LANDSBERGER and G. HILGENDORFF] (*Biochem. Zeitsch.*, 1914, 64, 382—392).—If a carbonyl derivative is regarded as unsaturated, then, if the author's method is adopted, it can be represented by the formula  $C_6H_5 \cdot CHL \cdot OL$ , where L indicates an unoccupied position. Such a substance should contain an asymmetric carbon atom and be resolvable into optical isomerides. By "induction" by means of *d*-tartaric acid, a *l*-form can be obtained if the acid and aldehyde are heated together in alcoholic solution. The *l*-aldehyde yields with hydrocyanic acid a *l*-nitrile, from which by hydrolysis a *d*-acid is obtained. It is suggested that asymmetric synthesis of the nitrile by means of emulsin is a case of "induction," and that it is by this method that enzymes can act.

S. B. S.

**Reaction of Nitroprussides with Some Ketones. II.** LIVIO CAMBI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 812—820. Compare A., 1913, i, 606).—When a solution of nitroprusside in methyl alcohol containing acetophenone is added at  $0^\circ$  to a solution of sodium methoxide or ethoxide, the salt,  $\left[ \begin{smallmatrix} Fe(CN)_5 \\ C_8H_6O_2N \end{smallmatrix} \right] Na_4, H_2O$ , is precipitated. It is a bright red powder, giving precipitates with solutions of iron and copper salts. The violet *copper* salt,  $\left[ \begin{smallmatrix} Fe(CN)_5 \\ C_8H_6O_2N \end{smallmatrix} \right] Cu_2$ , was prepared. The violet aqueous solution of the sodium salt becomes deep yellow on keeping, and ferroaquopentacyanide and the sodium salt of oximinoacetophenone can be isolated from it. The acid *sodium*

salt,  $\left[ \text{Fe}(\text{CN})_5 \right] \text{C}_8\text{H}_7\text{O}_2\text{N} \text{Na}_3$ , obtained by the action of acid on the sodium salt already mentioned, is a violet powder which yields blue solutions.

Similar compounds can be prepared from other ketones. Bromoacetophenone yields the salt,  $\left[ \text{Fe}(\text{CN})_5 \right] \text{C}_8\text{H}_5\text{O}_2\text{NBr} \text{Na}_4$ , MeOH. Acetylacetone gives the salt,  $\left[ \text{Fe}(\text{CN})_5 \right] \text{C}_5\text{H}_6\text{O}_3\text{N} \text{Na}_4$ .

R. V. S.

**Dimethylallylacetophenone and its Oxidation Products.** J. MEYERINGH and A. HALLER (*Compt. rend.*, 1914, 158, 1957—1961, Compare Haller and Bauer, this vol., i, 549).— $\alpha\alpha$ -Dimethyl- $\alpha$ -allylacetophenone on oxidation in the cold with 3% potassium permanganate containing 1% of potassium hydroxide yields  $\beta$ -benzoyl- $\beta$ -methylpentane- $\delta\epsilon$ -diol, obtained by Ramart-Lucas and Haller from  $\delta\epsilon$ -oxido- $\beta$ -benzoyl- $\beta$ -methylpentane on boiling with water (compare this vol., i, 695). Attempts to prepare a benzoyl derivative or a phenylurethane from the diol by the ordinary methods only yielded the dimeride of  $\delta\epsilon$ -oxido- $\beta$ -benzoyl- $\beta$ -methylpentane (*loc. cit.*). A benzoyl derivative,  $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OBz}$  or  $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CH}(\text{OBz})\cdot\text{CH}_2\cdot\text{OH}$ , m. p. 129°, was, however, obtained by the action of benzoyl chloride in the cold in the presence of pyridine. In the original oxidation, the amount of potassium permanganate used was equivalent to two atoms of oxygen. If the amount is increased to be equivalent to three atoms of oxygen the product is  $\gamma$ -benzoyl- $\alpha$ -hydroxy- $\gamma$ -methylvaleric acid,  $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 152°, which on neutralising with ammonia yields with silver nitrate a silver salt, a white powder, blackening in light. Oxidation of the original acetophenone in warm solution yields a certain amount of the above diol, together with benzoic acid and carbon dioxide.

W. G.

**Syntheses by means of Sodamide.** The Alkylcyclopentanones, Obtained by Hydrogenation of Unsaturated Derivatives Followed or not by Alkylation. A. HALLER and R. CORNUBERT (*Compt. rend.*, 1914, 158, 1739—1743).—2:4-Dibenzylidene-1-methylcyclopentan-3-one on reduction in alcoholic solution with reduced nickel in an atmosphere of hydrogen (compare Brochet, this vol., i, 645) readily yields 2:4-dibenzyl-1-methylcyclopentan-3-one, a viscous liquid, b. p. 232—233°/17 mm., which in ethereal solution on treatment with sodamide, followed by methyl iodide, furnishes 1:3-dibenzyl-1:3:4-trimethylcyclopentan-2-one, m. p. 74°, b. p. 228°/17 mm. The latter ketone on boiling in xylene solution with sodamide yields a compound, m. p. 138—139° (corr.), which is either  $\alpha\delta$ -dibenzyl- $\alpha\beta$ -dimethyl or  $\alpha\delta$ -dibenzyl- $\alpha\gamma$ -dimethylhexoamide.

1:4-Dimethyl-1:3:3-triallylcyclopentan-2-one also undergoes hydrogenation by the above process, giving 1:4-dimethyl-1:3:3-tripropylcyclopentan-2-one, a colourless, viscous liquid, b. p. 145°/15 mm. (corr.),  $D_4^{17}$  0.8955,  $n_D^{17}$  1.4649,  $[\alpha]_D^{17} + 7^\circ 10'$ , which on boiling with sodamide in xylene gives an amide, b. p. 200—205°/17 mm.,  $[\alpha]_D^{18} + 18^\circ 32'$ , which is either  $\beta\gamma$ -dimethyl- $\alpha\alpha$ -dipropyl- or  $\alpha\gamma$ -dimethyl- $\alpha\delta$ -dipropyl-octoamide.

The following conclusions are drawn from the series of researches: (1) cyclopentanone itself does not readily undergo alkylation, but gives condensation products in the presence of sodamide and an alkyl

iodide. (2) This is almost as true of 1-methylcyclopentan-3-one, although moderate yields of 2-derivatives are obtained. The best yields are obtained by using 2-alkyl or 2:5-dialkyl derivatives of cyclopentanone. (3) All the 1:1:4:4-tetra-alkylcyclopentanones, on boiling with sodamide in benzene or toluene yield amides of substituted aliphatic acids. (4) Starting with an active cyclopentanone the successive introduction of 1, 2, 3, or 4 alkyl groups into the positions 1 and 4, with respect to the :CO group, produces a diminution in the specific rotatory power of the substances.

W. G.

**The Allylcyclohexanones and the Methylallylcyclohexanones.** R. CORNUBERT (*Compt. rend.*, 1914, 158, 1900—1903).—The author has prepared all the allyl derivatives of the type  $\cdot\text{CR}_2\cdot\text{CO}\cdot\text{CR}_2$  theoretically possible from cyclohexanone, 1-methylcyclohexan-2-one, 1-methylcyclohexan-3-one and 1-methylcyclohexan-4-one by Haller's method (A., 1913, i, 629).

1-Allylcyclohexan-2-one,  $\text{CH}_2\left\langle\begin{array}{c}\text{CH}_2\cdot\text{CH}_2\text{---} \\ \text{CH}_2\cdot\text{CH}(\text{C}_3\text{H}_5)\end{array}\right\rangle\text{CO}$ , is a colourless, mobile liquid, b. p.  $94^\circ/16$  mm. (corr.), giving an *oxime*, needles, m. p.  $71^\circ$ ; 1:3-diallylcyclohexan-2-one, a colourless, mobile liquid, b. p.  $118\text{--}120^\circ/15$  mm. (corr.), giving an *oxime*, prisms, m. p.  $77^\circ$ ; 1:1:3-triallylcyclohexan-2-one, a colourless, mobile liquid, with an unpleasant odour, b. p.  $147\text{--}148^\circ/15$  mm. (corr.), does not give an *oxime*; 1:1:3:3-tetra-allylcyclohexan-2-one, a colourless, slightly viscous liquid having a disagreeable odour, b. p.  $169\text{--}170^\circ/14$  mm. (corr.), does not give an *oxime*.

1-Methyl-3-allylcyclohexan-2-one, a colourless, mobile liquid, b. p.  $96\text{--}97^\circ/14$  mm. (corr.), giving an *oxime*, microscopic crystals, m. p.  $49^\circ$ ; 1-methyl-1:3-diallylcyclohexan-2-one, a colourless, mobile liquid, b. p.  $125\text{--}126^\circ/15$  mm. (corr.), does not give an *oxime*; 1-methyl-1:3:3-triallylcyclohexan-2-one, a colourless, slightly viscous liquid, b. p.  $150^\circ/15$  mm. (corr.), does not give an *oxime*.

1-Methyl-4-allylcyclohexan-3-one, a colourless, mobile liquid, b. p.  $100\text{--}103^\circ/17$  mm. (corr.), gives an *oxime*, slender needles, m. p.  $80\text{--}86^\circ$ ; 1-methyl-2:4-diallylcyclohexan-3-one, a colourless, mobile liquid, b. p.  $129\text{--}130^\circ/17$  mm. (corr.), gives an *oxime*, prisms, m. p.  $65^\circ$ ; 1-methyl-2:4:4-triallylcyclohexan-3-one, a colourless, slightly viscous liquid, b. p.  $154\text{--}155^\circ/16$  mm. (corr.), does not give an *oxime*; 1-methyl-2:2:4:4-tetra-allylcyclohexanone, a colourless, viscous liquid, with a disagreeable odour, b. p.  $179^\circ/16$  mm. (corr.), does not give an *oxime*.

1-Methyl-3-allylcyclohexan-4-one, a colourless, mobile liquid, b. p.  $105\text{--}106^\circ/16$  mm. (corr.), gives an *oxime*, needles, m. p.  $97\text{--}98^\circ$ ; 1-methyl-3:5-diallylcyclohexan-4-one, a colourless, mobile liquid, b. p.  $131\text{--}133^\circ/17$  mm. (corr.), gives an *oxime*, plates, m. p.  $73^\circ$ ; 1-methyl-3:5:5-triallylcyclohexan-4-one, a colourless, slightly viscous liquid, having a somewhat unpleasant odour, b. p.  $154\text{--}155^\circ/15$  mm. (corr.), does not give an *oxime*; 1-methyl-3:3:5:5-tetra-allylcyclohexan-4-one, a colourless, viscous liquid, with a somewhat unpleasant odour, b. p.  $169^\circ/14$  mm. (corr.), does not give an *oxime*.

The allylation in all cases gives two products separable by fractional distillation, the process being less easy as the allylation proceeds. All the monoallyl derivatives have an odour of menthone and

the yield of them is better the nearer the methyl group is to the ketone group, whilst the products of condensation are greater the more remote the methyl group is. In no case was an oxime obtainable when three or more alkyl groups were present attached to the carbon atoms adjacent to the carbonyl group. W. G.

**The Present State of the Chemistry of Anthraquinone.** ROBERT E. SCHMIDT (*Bull. Soc. chim.*, 1914, [iv], 15, i—xi).—A lecture delivered before the French Chemical Society. W. G.

**Yields of Purpurogallin from the Oxidation of Pyrogallol with Peroxydase and Hydrogen Peroxide.** A. BACH (*Ber.*, 1914, 47, 2125—2126).—The yields of purpurogallin obtained by Bach and Chodat (*A.*, 1904, i, 792) from pyrogallol by oxidation with peroxydase and hydrogen peroxide accord fairly well with the maximum yields obtained by Nierenstein and Spiers (*A.*, 1913, i, 1367), namely, approximately 16%. It has been stated, however, by de Stœcklin (*Diss.*, Geneva, 1907) that yields as high as 50% can be obtained, and that the poorer yields of the former investigators were due to too high a concentration of hydrogen peroxide and too impure a specimen of peroxydase. That this explanation cannot be entirely correct is shown by the formation of a maximum yield of only 26% when the especially pure peroxydase obtained by ultra-filtration (Bach, this vol, ii, 691) is used, for this peroxydase was twenty times as active as that of de Stœcklin; also variation of the concentration of the hydrogen peroxide did not affect the yield to any extent.

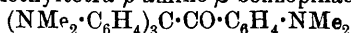
When a solution of purpurogallin in alcohol or acetone is diluted with three volumes of water and treated with peroxydase and hydrogen peroxide, there results a violet coloration which is slowly replaced by a brown. This reaction will detect two parts of purpurogallin in  $10^{-6}$  parts of solvent.

The most important factor for the formation of a good yield of purpurogallin in the oxidation of pyrogallol is probably, therefore, the rapid separation of the purpurogallin in the solid state. D. F. T.

**Dimethylaminodihydroxybenzophenone.** MAX WENZING (*Ber.*, 1914, 47, 2152—2156).—When an intimate mixture of tetramethyldiaminobenzophenone, resorcinol, and zinc chloride is heated, a violet colour is first produced, and on reaching 220° dimethylaniline is set free. The product at the first stage of the reaction dissolves in dilute hydrochloric acid with a reddish-violet colour, and is believed to be an additive compound of the structure  $(\text{NMe}_2 \cdot \text{C}_6\text{H}_4)_2 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , whilst the final product, produced from this by scission of dimethylaniline, is dimethylaminodihydroxybenzophenone,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , yellow needles or leaflets; hydrochloride, colourless prisms, decomp. at 230°; sulphate and oxalate, needles; zincchloride, pale yellow leaflets (with  $2\text{H}_2\text{O}$ ), decomp. at 225°.

The m. p. of the free base was not sharp, crystallisation from dilute solution giving needles, m. p. 165—167°, whilst it was possible to obtain leaflets, m. p. 171—172°, from more concentrated solution. It is suggested that the base may, like benzophenone, be capable of existence in two modifications of different m. p. D. F. T.

**Octamethyltetra-amino- $\beta$ -benzopinacolin and its Reversed Pinacolin Rearrangement.** S. FISCHL (*Monatsh.*, 1914, 35, 519—531).—Octamethyltetra-*p*-amino- $\beta$ -benzopinacolin,



(Fischl, A., 1913, i, 466), is readily formed on heating, with the addition of a small quantity of dilute acid, a benzene solution of the pinacone of tetramethyldiaminobenzophenone. The pinacolin (*platinichloride*, microscopic, orange-yellow, rhombic tablets) when heated with an amyl-alcoholic solution of potassium hydroxide undergoes fission into hexamethyltri-*p*-aminotriphenylmethane and *p*-dimethylaminobenzoic acid, thus demonstrating that the nuclear positions of attachment are the same in the pinacone as in the pinacolin.

Reduction of the pinacone with tin and hydrochloric acid or of the pinacolin with amalgamated zinc and hydrochloric acid (in which case a so-called reversed pinacolin rearrangement occurs; compare Biltz and Seydell, A., 1913, i, 297) gives rise to octamethyltetra-amino-tetraphenylethylene (*platinichloride*, microscopic, orange-yellow, hexagonal prisms or needles; *stannochloride*, needles), which has already been obtained directly from tetramethyldiaminobenzophenone (Willstätter and Goldmann, A., 1906, i, 980). Sodium and boiling *iso*amyl alcohol reduce octamethyltetra-aminotetraphenylethylene to *s*-octamethyltetra-aminotetraphenylethane,  $\text{C}_2\text{H}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_4$ , colourless, lustrous needles, which decompose above  $300^\circ$ ; *platinichloride*, microscopic, orange-yellow prisms. The substance, m. p.  $90^\circ$ , obtained by Schoop by condensation of dimethylaniline with *s*-tetrabromoethane, and described as octamethyltetra-aminotetraphenylethane (A., 1881, 160), is shown to be in reality tetramethyldiaminodiphenylmethane.

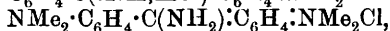
D. F. T.

**The Preparation and Properties of the Compounds Given in the Tables of the Third Paper of Kehrmann, Havas, and Grandmougin [Quinoneimide Dyes].** F. KEHRMANN (*Ber.*, 1914, 47, 2156—2159. Compare Kehrmann, Havas, and Grandmougin, this vol., i, 868).—Details are given as to the preparation of the 1-aminophenazthionium, 3-aminophenazthionium, phenazoxonium, dimethylphenazoxonium, and 3-aminophenazoxonium salts mentioned in the earlier communication (*loc. cit.*).

[With ISAC FRANCEZ.]—The action of warm hydrochloric acid on 3-aminophenazthionium causes a reduction (Pummerer and Gassner, A., 1913, i, 991; this vol., i, 735), and the resulting chloroaminothiodiphenylamine separates as the hydrochloride, which can be oxidised to the corresponding dye by ferric chloride.

D. F. T.

**The Constitution of Auramine.** E. GRANDMOUGIN and S. FAYRE-AMBRUMYAN (*Ber.*, 1914, 47, 2127—2132).—In order to decide between the formulæ  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{:NH}, \text{HCl}) \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$  and



suggested by Graebe and Stock respectively for auramine, the purely chemical evidence being insufficient (compare Semper, A., 1911, i,

577; Strauss and Zeime, A., 1913, i, 992; Strauss and Bormann, A., 1910, i, 281), the authors have submitted the substance to a spectroscopic test; the result is in favour of the former constitution.

Alcoholic solutions of benzophenone, 4:4'-diaminobenzophenone, Michler's ketone, auramine base, auramine acetate and acetylauramine as well as a solution of auramine in concentrated sulphuric acid were examined; certain other derivatives have already been investigated (Grandmougin and Lang, A., 1909, i, 974). Unlike benzophenone, diaminobenzophenone possesses a complete absorption band with its head at  $340\mu\mu$ . In Michler's ketone the band is situated at  $370\mu\mu$ , whilst in auramine base, for which the curve is of the same type, the band is at  $300\mu\mu$ . The absorption spectrum for auramine acetate has maxima at 310, 375 and  $435\mu\mu$ , of which the two latter are the more marked, the deepening in the colour being indicative of salt formation at the chromophoric imino-group. With auramine dissolved in concentrated hydrochloric acid or 50% sulphuric acid, the solution is colourless with a maximum near  $265\mu\mu$ , the dimethylamino-group also having now entered into salt-formation. The spectrum of acetylauramine resembles that of the other members of this group, but has a maximum at  $350\mu\mu$ ; salt formation with this substance occurs at the dimethylamino-group with simultaneous rearrangement to the quinonoid configuration, so that in solution in acids, the spectrum is quite different from those of the preceding substances.

D. F. T.

New Investigations in the Camphor Group. IV. E. RIMINI (*Chem. Zentr.*, 1914, i, 1653—1654; from *Rend. della Soc. Chim. Ital.*, 1914, 27—28).—Traces of a substance of the probable formula  $C_{10}H_{15}Br_3$  are frequently formed during the preparation of bromopernitrosocamphor. *iso*Camphor is converted by reduction with

colloidal palladium into *dihydroisocamphor*. On oxidation, it yields acetone, succinic acid, and  $\alpha$ -ketoglutaric acid. The author is led to propose the annexed formula (I) for *isocamphenone* and hence formula (II) for *isocamphor*. The latter has previously been considered as probable by Wallach.

H. W.

The Electrolytic Reduction of Carvoxime. H. RUPE and K. LÖFFL (*Ber.*, 1914, 47, 2150—2152).—The reduction of carvone and carvoxime by means of hydrogen and a catalyst has already been effected, the results varying somewhat with different conditions (compare Wallach, A., 1911, i, 469; this vol., i, 420; Vavon, A., 1911, i, 730; see also Law, T., 1912, 101, 1061). By reducing carvoxime at a lead cathode in aqueous-alcoholic solution containing sodium hydroxide at  $15^\circ$ , the authors have converted carvoxime into dihydrocarvone, no other reduction product being detected.

D. F. T.

**Thujone and Thujamenthone ; Direct Passage from One to the Other.** MARCEL GODCHOT (*Compt. rend.*, 1914, 158, 1807—1808).—Thujone is readily converted into thujamenthone with an excellent yield by the action of hydrogen in the presence of reduced nickel at 175—180°.

W. G.

**Camphenecamphoric Acid and Hydroxycamphenilanic Acid.** S. V. HINTIKKA (*Chem. Zentr.*, 1914, i, 1573 ; from *Ann. Acad. Sci. Fennicae*, 1914, A, 5, iii, 1—8. Compare this vol., i, 409).—Hydroxycamphenilanic acid, m. p. 182—183°, is prepared in the following manner in a yield of about 15%. Camphene is dissolved in acetone and so much water added that the solution just remains clear. It is then oxidised by the gradual addition of solid potassium permanganate. Acetone, unchanged camphene, and camphenilone are removed in a current of steam. The filtered and concentrated solution is extracted with ether and treated with dry sodium carbonate. The acid is liberated from sparingly soluble sodium salt by means of sulphuric acid.

H. W.

**Constituents of Essential Oils: Effect of High Temperatures on Sesquiterpenes ; Elimination of Terpinene ; Artificial Production of the Blue Compound which is Present in Many Essential Oils.** F. W. SEMMLER and W. JAKUBOWICZ (*Ber.*, 1914, 47, 2252—2259).—Direct evidence in support of the view that terpenes and sesquiterpenes are nearly related has, hitherto, been lacking, for attempts to obtain the former by the decomposition of the latter have failed. It is now shown, however, that at about 330°, and under pressure, some typical sesquiterpenes break down into terpenes and, apparently, isoprene. Of course, these may react among themselves, and, consequently, it is not to be wondered at that isoprene could not be isolated as such. That it is indeed formed is shown by the secondary production of diterpenes. An important conclusion to be drawn is that the heat condensation of simple hydrocarbons, like isoprene and terpinene, has an optimum temperature above which degradation of the complex molecules takes place.

In the case of  $\alpha$ -gurjunene, the blue compound, which is frequently met with in essential oils, was produced.

Ten grams of pure  $\beta$ -gurjunene (this vol., i, 704) were heated in a sealed tube for twelve hours at 330°, when the brown, fluorescent oil was fractionated. The first fraction was boiled with sodium, and then had b. p. 60—65°/10 mm.,  $D_{20}$  0.8520,  $n_D$  1.4800, which agrees with  $\alpha$ -terpinene. This was confirmed by the formation of the nitrosite, m. p. 154°. The second fraction had b. p. 90—130°/10 mm., and was chiefly unchanged  $\beta$ -gurjunene. The final distillate had b. p. 170°/10 mm.,  $D_{20}$  0.9603,  $n_D$  1.54043, and therefore contained a diterpene, probably formed by the condensation of isoprene with  $\beta$ -gurjunene.

$\alpha$ -Gurjunene, with  $n_D$  1.13°, was submitted to the same treatment. The product had a dark blue colour. Fraction I. was colourless, and had b. p. 60—70°/11 mm.,  $D$  0.8643,  $n_D$  1.49143, which corresponds

with a terpene. It did not yield a solid nitrosite or dihydrochloride. Fraction II, b. p. 90—140°/11 mm., became colourless on boiling with sodium, and contained unchanged  $\alpha$ -gurjunene. Fraction III was intensely blue, but lost its colour on boiling with sodium. It contained a diterpene, b. p. 163—175°/13 mm.,  $D_{20}$  0.9495,  $n_D$  1.54125. The blue oil was free from nitrogen.

Cedrene and caryophyllene were also examined. In each case the molecular refraction of the lowest fraction indicated the presence of a terpene, the second fraction contained the unchanged sesquiterpene, and the final distillate agreed with a diterpene. Cadinene, however, a representative of the naphthalene type, was scarcely changed. The lowest fraction had b. p. 120—130°/vacuum,  $D$  0.9025,  $n_D$  1.50829,  $\alpha_D$  -7°, and therefore contained practically no terpene, but chiefly a monocyclic sesquiterpene.

J. C. W.

Cadinene from *Daniella thurifera*. W. LENZ (*Ber.*, 1914, 47, 1989—1991).—So-called *Daniella thurifera* resin, a thin, blackish-brown balsam, can be separated, by distillation with steam, into an oil and a rather soft resin. The oil, which is free from phenolic substances, was fractionally distilled, when fractions were obtained with b. p. ranging from 120° to 290°. After treating with metallic sodium the three fractions obtained between 258° and 275° were again distilled, when two fractions, one colourless, b. p. 259—270°,  $D_{20}^{20.5}$  0.9850,  $\alpha_D^{20.5}$  + 67.83°, the other bluish-green, b. p. 270—271°,  $D_{20}^{20.5}$  0.9845,  $\alpha_D^{19.5}$  + 5.89° (tube, 0.2 cm.), were collected.

When these fractions were dissolved in an equal weight of ether and the solutions saturated in the cold with hydrogen chloride, an abundant crystalline deposit was obtained; after repeated recrystallisation from ethyl acetate, this solid was found to have m. p. 119° (corr.),  $[\alpha]_D^{22.5}$  - 39.82°, and to be identical with cadinene hydrochloride.

D. F. T.

Tobacco Resin. JOSEF VON DEGRAZIA (*Chem. Zentr.*, 1914, i, 1196—1197; from *Fachliche Mitteilungen der österreich. Tabakregie*, 1913, 109—117).—Tobacco resin was thoroughly investigated about fifty years ago by Haid, but his results were not published, and were, in part, lost. A Kentucky tobacco was used, which, on extraction with alcohol, yielded a resin from which the resin acids were precipitated by lime. An essential oil was obtained by distillation with steam, whilst a neutral resin,  $C_{12}H_{20}O_2$ , remained, which was termed *kentuckyn*. Three acids were isolated from the calcium salts of the resin acids, namely, *kentuckylinic acid*,  $C_{23}H_{40}O_5$ , semi-solid, odourless; *kentuckynolic acid*,  $C_{22}H_{34}O_6$ , greenish-brown, soft, with an odour resembling honey, and *kentuckynic acid*,  $C_{22}H_{40}O_7$ , brown, very brittle, odourless. Haid's methods of separating these acids are unknown.

The author has employed the residues from certain Turkish tobaccos. The material is thoroughly extracted with warm water, and the dried material repeatedly treated with alcohol on the water-bath. After protracted cooling, the separated plant wax is removed and the alcohol distilled. Fatty acids are removed from the residue by treatment



with hot water. The yield of purified resin is about 250 grams from 7 kilograms of tobacco.

The dark grey resin is repeatedly warmed with five times its amount of ether. The insoluble portion is worked up according to (1) (see later). The soluble portion, after being partly freed from ether, is thoroughly agitated with 5% potassium hydroxide. The alkaline solution is extracted with ether to remove neutral resin. The portions soluble in ether are freed from nicotine and essential oil by distillation with steam in the presence of alkali. The residue remaining in the flask is *tabakoresen* (V). The saponifiable portions are separated by addition of solid potassium hydroxide and, after acidification, are dissolved in ether. Treatment with alkali also causes the saponification of a resin ester, the corresponding alcohol of which is less soluble in ether than the original ester and is therefore precipitated. By repeated solution and precipitation, the originally green precipitate becomes white (IV). The ethereal solution containing the resin acids is extracted with dilute alkali. Acidification with hydrochloric acid yields a mixture of acids which can be separated by lead acetate. The alcoholic solution of the resin acids is treated with an excess of lead acetate, whereby the *lead* salt of the  $\beta$ -acid (II) is separated as a dark green precipitate. The filtrate contains the  $\gamma$ -acid (III).

The following data are given for the pure products: I.  *$\alpha$ -Tobaccic acid*.—The brown resin which remains after extraction with ether is boiled in alcoholic solution, and the residue, after removal of alcohol, is dissolved in dilute alkali. Acidification of the hot solution precipitates the acid as a powder. It is a brittle, dark brown, odourless, amorphous substance, which is probably identical with Haid's kentuckynic acid. II.  *$\beta$ -Tobaccic acid* is isolated from the lead salt (see above) and forms a dark green, brittle mass which is probably contaminated with chlorophyll; it cannot be purified by means of its salts. (III.)  *$\gamma$ -Tobaccic acid* forms a viscous, brown liquid of unpleasant odour. It does not yield a lead salt. (IV.) *Tabakoresinol* can be obtained by the following process in addition to that previously given. The resin obtained by extraction with alcohol is warmed with water and powdered lime, and finally evaporated to dryness. By this treatment, the free and combined acids are converted into the corresponding calcium salts and the alcohol is liberated. The dry mass is extracted with ether to remove neutral resin, and the residue treated with boiling alcohol from which the resin alcohol separates on cooling. It forms white, microscopic needles, m. p.  $219^{\circ}$  (uncorr.). Analyses agree with the formula  $(C_6H_{10}O)_x$ . The *acetyl* derivative has m. p.  $154^{\circ}$ . (V.) *Tabakoresen*, both quantitatively and also as the odoriferous constituent, is the most important constituent of tobacco resin. In the concentrated condition it is a reddish-brown, viscous mass with an odour of honey. Dilute solutions are golden-yellow. It is not attacked by molten alkali. It has  $D^{18.7}$  0.941,  $n_D^{17}$  1.5169. It commences to boil at  $230^{\circ}$ , but decomposes and cannot be distilled unchanged under diminished pressure. Analyses and determinations of molecular weight lead to the formula  $(C_{19}H_{32}O)_2$ . (VI.) A small quantity of a pleasant smelling essential oil,  $n_D$  1.4882, is also obtained.

H. W.

**Resin Acids Soluble in Water from American Colophony.** LUDWIG PAUL (*Chem. Zentr.*, 1914, i, 1655—1656; from *Chem. Rev. Fett. Harz-Ind.*, 21, 5—8, 36—39, 53—56, 78—80).—American colophony can be separated by means of cold petroleum into a soluble and an insoluble portion. The latter is soluble, the former sparingly soluble, in dilute sodium hydroxide solution, and from the first-named solution the sodium salt of the chief resin acid (abietic acid) is deposited as a slimy precipitate. This is not, however, invariably the chief constituent of colophony, and may be a by-product, depending on whether large, glassy pieces or dust is employed. The acid is soluble in water or forms soapy emulsions; it is precipitated by hydrochloric acid as a curdy mass. The filtrate from the above sodium salt yields a second resin acid, which is readily soluble in sodium hydroxide solution, and does not dissolve in petroleum. The former contains a resinous impurity, which can be removed by repeated solution. A separation of the two chief constituents of colophony can therefore be effected by treatment with petroleum or sodium hydroxide, and the method can also be used for the identification of these constituents. The former acid cannot be completely separated from the latter by repeated solution in alcohol and sodium hydroxide and precipitation with hydrochloric acid. It appears, therefore, that the latter is continuously formed from the former, possibly in the same manner as a hydrate from its anhydride. Similarly, the complete conversion of the former acid into the latter cannot be accomplished. The best method of separating the constituents of colophony consists in treating the substance with twice its weight of petroleum. Large, glassy pieces yield 2%, dust yields up to 50%, of residue, which consists mainly of an acid soluble in water mixed with small quantities of the first acid.

**Distillation of Colophony-Petroleum Filtrates.**—The crude material is a viscous liquid, D ca 0.87. Above 320°, water is violently expelled and two distillates, named respectively light and heavy balsam, are obtained. The former when preserved deposits crystals, m. p. 150—160°, and are probably identical with Tschirch's  $\gamma$ -abietic acid (the substance is only present in small amount and does not appear to be characteristic of colophony). From the difference in the fractions obtained by the distillation of colophony and colophony-petroleum, the author is led to the conclusion that the former is a mixture of substances, whilst the products obtained by the aid of petroleum appear to be uniform. The acid which is soluble in petroleum (and can be obtained as a snow-white powder) has m. p. 74—75°, which rises after a lapse of time. On exposure to air, it forms increasingly large amounts of a residue insoluble in petroleum, probably by absorption of water. The crumbling of glassy pieces of colophony to dust is probably due to the same cause. The m. p. of the acid insoluble in petroleum is variable, generally above 100°.

Chemically, the acid soluble in petroleum resembles colophony. It is converted by washing with hydrochloric acid into the form soluble in water, and in this connexion the absorbed water appears to be particularly active. The behaviour is thus strongly reminiscent of starch.

The chief constituent of American colophony, the resin acid soluble in petroleum, is thus converted by water into a variety of substances, which, to a greater or less extent, exist originally in colophony. The cause of the phenomenon lies in the solubility of these substances in water through which the colophony gradually passes into solution and possibly suffers a degradation of its complex molecule. H. W.

**Mustard Oil Glucosides. IV. Phenylthiourethane-*d*-glucoside.** WILHELM SCHNEIDER and DOUGLAS CLIBBEN (*Ber.*, 1914, 47, 2218—2224).—The silver salt of phenylthiourethane reacts with acetobromoglucose in boiling xylene solution to form *tetra-acetylphenylthiourethane-d-glucoside*,  $\text{NPh}\cdot\text{COEt}\cdot\text{S}\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}$ , which separates in colourless crystals, m. p.  $159^\circ$ ,  $[\alpha]_D^{25} - 2.46^\circ$ , in *s*-tetrachloroethane. As in the case of the corresponding aliphatic thiourethaneglucosides (this vol., i, 669), attempts to remove the acetyl groups and to obtain a crystalline glucoside were unsuccessful. Hydrolysis with baryta water yielded only phenylthiourethane and decomposition products of thioglucose. Alcoholic ammonia at room temperature, however, yielded acetamide and *phenylthiourethane-d-glucoside* as a dextro-rotatory syrup. The latter undergoes hydrolysis when left in aqueous solution, more quickly in acid solution, in two directions. On the one hand, phenylurethane and thioglucose are formed, as is the case with the aliphatic compounds, but, on the other hand, especially in acid solution, the products are phenylthiourethane and dextrose. The latter hydrolysis is met with in the case of the natural mustard oil glucosides, and the phenylthiourethaneglucoside therefore occupies an intermediate position between these and the aliphatic thiourethaneglucosides. Myrosin, however, is without influence on these synthetic glucosides.

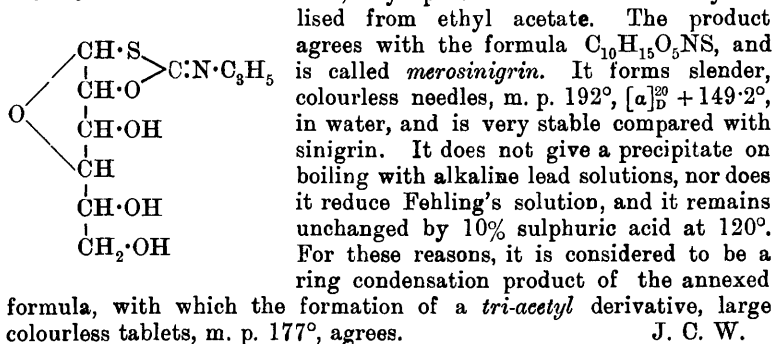
When mixed with alcoholic silver nitrate solution, phenylthiourethane-*d*-glucoside gradually deposits the silver salt of thioglucose, and, on adding ammonia to the filtrate, the original silver salt of phenylthiourethane separates. The glucoside is therefore decomposed in two possible ways. The latter decomposition is in agreement with the formation of mustard oil silver sulphates from the natural glucosides. It is now also shown (following abstract) that thioglucose may be obtained from sinigrin, and, therefore, the relation between the above synthetic glucosides and the natural products is firmly established.

The silver salt of thioglucose (*ibid.*) has been obtained in a purer form by dissolving the crude product in water, precipitating the metal by hydrogen sulphide, concentrating the filtrate in a vacuum, and adding slightly less than the required amount of ammoniacal silver nitrate. The compound forms snow-white flocks, m. p. about  $165^\circ$  (blackening), and is stable. A very slight excess of silver solution causes discoloration. J. C. W.

**Mustard Oil Glucosides. V. Constitution of Sinigrin.** WILHELM SCHNEIDER and FRITZ WREDE (*Ber.*, 1914, 47, 2225—2229).—When a solution of potassium methoxide is added to a hot methyl-alcoholic solution of sinigrin, potassium sulphate separates at once. On adding ammoniacal silver nitrate to the filtrate, the silver salt of

thioglucoſe is precipitated. This proves that the glucoſe molecule is attached to the ſulphur atom in the glucoſide, and the changes may be represented by the ſcheme:  $C_3H_5 \cdot N : C(O \cdot SO_3K) \cdot S \cdot C_6H_{11}O_5 \rightarrow C_3H_5 \cdot N : COMe \cdot S \cdot C_6H_{11}O_5 \rightarrow C_6H_{11}O_5 \cdot SH$ . The experience of the aliphatic thiourethaneglucosides has led Schneider to expect but little from attempts to iſolate the methoxy-compound.

The above change is, however, not the only action of poſſium methoxide on ſinigrin, for, on precipitating the exceſs of ſilver from the filtrate from the above ſilver ſalt of thioglucoſe and evaporating the clear ſolution in a vacuum, a ſyrup remains which can be cryſtallised from ethyl acetate. The product agrees with the formula  $C_{10}H_{15}O_5NS$ , and is called *merosinigrin*. It forms ſlender, colourleſs needles, m. p.  $192^\circ$ ,  $[\alpha]_D^{20} + 149 \cdot 2^\circ$ , in water, and is very ſtable compared with ſinigrin. It does not give a precipitate on boiling with alkaline lead ſolutions, nor does it reduce Fehling's ſolution, and it remains unchanged by 10% ſulphuric acid at  $120^\circ$ . For theſe reaſons, it is conſidered to be a ring condensation product of the annexed



**New Method of Converting Barbaloin into  $\beta$ -Barbaloin.** E. LEGER (*Compt. rend.*, 1914, 158, 1903—1905. Compare this vol., i, 707).—On heating barbaloin with acetic anhydride and ſodium acetate for an hour at  $100$ — $110^\circ$  it is converted into a penta-acetyl derivative, which is really a mixture of penta-acetylbarbaloin and penta-acetyl- $\beta$ -barbaloin. This mixture on ſaponification gives a yellow product ſoluble in a mixture of chloroform and methyl alcohol. The firſt cryſtals deposited from this ſolvent conſiſt of barbaloin, but the mother liquors on evaporation yield  $\beta$ -barbaloin in the form of an amorphous powder. This ſubſtance, ſo prepared, does not undergo iſomeriſation under the influence of acetic anhydride. W. G.

**Production of Anthocyanins and Anthocyanidins.** ARTHUR ERNEST EVEREST (*Proc. Roy. Soc.*, 1914, [B], 87, 444—452).—Anthocyanin was obtained from yellow wallflower, yellow daffodil, white narcissus, yellow or white tulip, white primula, yellow crocus, yellow jaſmin, primroſe and lemon peel by reduction in the cold; no anthocyanidin is produced under theſe conditions, and no oxidation, after reduction, is neceſſary for the production of the anthocyanin pigment, unleſs the reduction is carried too far. N. H. J. M.

**Certain Reactions of the Colouring Matter of the Blackberry (*Rubus Discolor*).** GUIDO VECCHI (*Chem. Zentr.*, 1914, i, 1209; from *Staz. sperim. agrar. ital.*, 47, 60—64).—Determinations of the intensity of the colour ſhow in 2% ſolution a cherry-red colour with a violet ſhade; in 1% ſolution, the colour is ſimilar but weaker; in 0.5%

it is pure red ; in 0.25%, pink ; in 0.05% solution it is colourless in thin layers, pale pink in a layer of 25 cms. The following experiments were effected with a solution of juices (50 c.c.) and water (250 c.c.). A dye is not extracted by light petroleum or ether from the acetic acid or sodium hydroxide solution. Amyl alcohol becomes dark violet, passing to carmine-red on addition of hydrochloric acid. The dye loses its violet tint on addition of mineral acids or acetic acid ; nitric acid gives a golden-yellow, sodium or potassium hydroxide a dark green, ammonia or sodium carbonate a violet colour. Hydrogen peroxide is without action on the solution in hydrochloric acid ; in alkaline solution it causes a colour change through brown to yellow. The acetic acid solution is decolorised by sodium hydrogen sulphite, but addition of an excess of sodium carbonate restores the wine-red colour.

*Lakes from the Dye of the Blackberry.*—Lead acetate gives a greyish-blue precipitate ; silver nitrate has no action in the presence of acetic acid, but gives a chocolate-brown precipitate after addition of sodium carbonate. The filtrate becomes yellow on acidification. Barium chloride in the presence of sodium carbonate causes a grey precipitate, soluble in excess of acetic acid to a wine-red solution ; copper acetate yields a bluish-black coloration, stable towards sodium carbonate and becoming red on addition of acetic acid. Alum and excess of sodium carbonate yield a violet-grey precipitate, and the blackish-violet filtrate becomes bright violet on addition of acetic acid. Zinc chloride yields a dark violet colour which becomes orange-yellow on addition of acetic acid. An excess of sodium carbonate precipitates a grey lake, and the filtrate is colourless. The precipitate is soluble in hydrochloric acid to a red solution, the colour of which can be extracted with amyl alcohol. Zinc chloride and a small amount of sodium hydroxide yield a greyish-violet precipitate which becomes yellowish-white on addition of an excess of alkali. The supernatant liquid is yellow.

H. W.

**Crocetin.** FRITZ DECKER (*Arch. Pharm.*, 1914, 252, 139—160).—From analyses of its salts and molecular-weight determinations of its acetyl derivative, the author draws the conclusion that crocetin, the colouring matter of saffron, has the formula  $C_{10}H_{14}O_2$  (compare Kayser, A., 1885, 59). The ammonium salt,  $C_{10}H_{17}O_2N$ , crystallises from dilute alcohol in lustrous, red needles ; the potassium, sodium, aniline, pyridine, and quinoline salts are also described. The acetyl derivative,  $C_{10}H_{13}O_2Ac$ , prepared by heating the potassium salt with acetyl chloride, crystallises in red needles, m. p.  $174^\circ$ . Crocetin combines with bromine in chloroform solution, yielding a dibromide, yellowish octahedra, m. p.  $103-104^\circ$  (decomp.), and must therefore contain one double linking. On oxidation with bromine in alkaline solution, it yields a compound,  $C_7H_{10}O_2Br_2$ , crystallising in colourless, felted needles.

F. B.

**Lokao Dye.** ADOLF RÜDIGER (*Arch. Pharm.*, 1914, 252, 165—186).—Lokao or China green, a dye which has been entirely displaced by aniline greens, used to be extracted by the Chinese, from the bark of

the boughs and the roots according to some authorities, from the flowers and berries according to others, of *Rhamnus chlorophora* and *Rhamnus utilis*. The commercial product contains nearly 10% of moisture, and leaves 33·5% of ash, consisting chiefly of aluminium and calcium oxides. The author extracts the dye by the French process: solution in 2·5% ammonium carbonate, precipitation by alcohol, repetition of these operations until the ash-content is only 0·1%, solution of the resulting ammonium salt in aqueous ammonium carbonate, and evaporation on the water-bath until crystals begin to separate. The substance thus obtained is *ammonium lokaonate*,  $C_{42}H_{45}O_{25} \cdot NH_4$  (a *di-ammonium* salt,  $C_{42}H_{44}O_{25}(NH_4)_2$ , can also be prepared), from which aqueous oxalic acid liberates lokaonic acid (Cloëz and Guignet's lokain),  $C_{49}H_{46}O_{25}$ , bluish-black substance with a metallic lustre. The acid is a rhamnoside, and its ammonium salt is decomposed by hot dilute sulphuric acid into lokanic acid and a sugar. The sugar, to which Kayser has given the name lokaose and the formula  $C_6H_{12}O_6$ , is proved to be rhamnose,  $C_6H_{12}O_5$ .

Lokanic acid (Cloëz and Guignet's lokaetin),  $C_{36}H_{36}O_{21}$ , is a violet-black, crystalline powder, and yields nitrophloroglucinol, m. p. 203—204°, by treatment with hot nitric acid, and phloroglucinol and delokanic acid by treatment with warm aqueous potassium hydroxide (1 : 1). Delokanic acid,  $C_{12}H_8O_5$ , contains one methoxy-group (as also does lokanic acid), but no hydroxyl groups, and is converted by nitric acid (D 1·4) into oxalic acid and a substance,  $C_8H_7O_5N$ , m. p. 129°, orange-yellow needles, which is possibly 2-nitro-5-methoxybenzoic acid (m. p. 132°). C. S.

**Passage from Oxalacetic Ester to  $\alpha$ -Pyrone Derivatives.** H. GAULT (*Compt. rend.*, 1914, 159, 72—75. Compare A., 1913, i, 953; this vol., i, 384, 484).—Oxalocitrolactone, obtained by the lactonisation of oxalacetic ester (this vol., i, 484) on boiling with concentrated hydrochloric acid, yields oxalic acid, tricarballic acid, a chloro-compound, and an acid compound, m. p. 228°, which the author has shown to be 1 : 2-pyrone-6-carboxylic acid (compare Lapworth, T., 1901, 97, 1276). This compound is probably formed from oxalocitrolactone, by opening of the lactonic ring, followed by saponification, elimination of 2 molecules of carbon dioxide, dehydration, and subsequent cyclisation of the resulting oxalocrotonic acid. W. G.

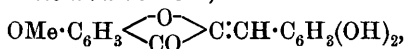
**A New Flavone Synthesis.** H. SIMONIS (*Ber.*, 1914, 47, 2229—2233. Compare A., 1913, i, 890).—The chromones which were originally prepared by condensing phenols with esters of  $\beta$ -ketonic acids in the presence of phosphoric oxide happened to be new. The authors have therefore applied this new synthesis to the preparation of some chromones which other workers have obtained by other means. The method proved to be successful in the condensation of methyl methylacetoacetate and resorcinol to 7-hydroxy-2 : 3-dimethylchromone (Kostanecki and Lloyd, A., 1901, i, 735), a compound which sublimes in long, white needles, but failed in the case of ethyl acetoacetate and phenol. It was assumed that the latter ester is transformed almost entirely into the ketone in the presence of phenol, and, therefore, the

synthesis was modified by making use of the sodium derivative of the ester. This was fully justified, for the addition of phosphoric oxide to a suspension of ethyl sodioacetoacetate and phenol in toluene resulted in the formation of 2-methylchromone (Bloch and Kostanecki, A., 1900, i, 502). Flavone was also readily synthesised by adding alternately phosphoric oxide and ethyl sodiobenzoylacetate to a solution of phenol in xylene, the mixture being vigorously stirred and finally heated to 160° for two hours.

J. C. W.

**Conversion of Benzylidenecoumaranones into Flavonols.** K. VON AUWERS and P. POHL (*Annalen*, 1914, 405, 243—294).—The reaction whereby dibromobenzylidene-4-methylcoumaran-2-one is converted into 6-methylflavonol by hot alcoholic potassium hydroxide (Auwers and Müller, A., 1909, i, 45) proves to have only a limited applicability for the synthesis of flavonol derivatives, and unfortunately gives the worst results in the cases of the naturally occurring members.

The condensation of resorcinol dimethyl ether and chloroacetyl chloride by aluminium chloride and carbon disulphide yields *ω*-chloro-2-hydroxy-4-methoxyacetophenone,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{OMe}$ , m. p. 116°, colourless needles, which is converted into paeonol by reduction with zinc and glacial acetic acid. Blom and Tambor's so-called *α*-bromoresacetophenone dimethyl ether, prepared in a similar manner from bromoacetyl bromide and resorcinol dimethyl ether (A., 1905, i, 916), is shown to consist chiefly of the monomethyl ether, since it also yields paeonol by reduction. By boiling with alcohol and hydrated sodium acetate, *ω*-chloro-2-hydroxy-4-methoxyacetophenone yields 5-methoxycoumaran-2-one, m. p. 119—120°, colourless needles (described by Blom and Tambor [*loc. cit.*] as 3-methoxycoumaranone, m. p. 125°, yellow needles). At 50—60° in alcohol containing a little concentrated hydrochloric acid, 5-methoxycoumaranone condenses smoothly with protocatechualdehyde to form 3':4'-dihydroxy-5-methoxybenzylidenecoumaran-2-one,



m. p. 228—229° (decomp.), greenish-yellow needles (*diacetate*, m. p. 152—153°), and with vanillin to form 4'-hydroxy-3':5-dimethoxybenzylidenecoumaran-2-one, m. p. 195—195.5°, yellow rhombohedra (Blom gives m. p. 194°, brown leaflets), either of which reacts with methyl sulphate to form 3':4':5-trimethoxybenzylidenecoumaranone, m. p. 183—184° (Blom and Tambor give 189°).

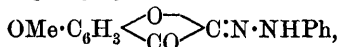
With the ultimate object of synthesising fisetin, the authors converted the preceding diacetate into its dibromo-additive compound; however, this and also the dibromide of 3':4':5-trimethoxybenzylidenecoumaranone proved to be too unstable to be converted into flavonol derivatives. The *dibromide*,



m. p. 191—192° (decomp.), of 5-methoxy-1-benzylidenecoumaranone is more stable than the two preceding dibromides and is converted in

boiling alcohol by *N*/10-sodium hydroxide into *α*-bromo-5-methoxy-1-benzylidenecoumaran-2-one,  $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C} : \text{CPhBr}$ , m. p. 176—177°, yellow, pearly, hexagonal leaflets, and 7-methoxyflavonol in the ratio about 4:1; the acetate of 7-methoxyflavonol has m. p. 176° (Kostanecki gives 140°: A., 1904, i, 443).

The authors employ three criteria to differentiate between flavonols and the isomeric benzoylcoumaranones; the former (I.) have a higher m. p.; (II.) form in concentrated sulphuric acid yellow solutions with a blue fluorescence; (III.) do not yield characteristic derivatives with diazonium salts. The *benzoate*, m. p. 104—105°, long, colourless needles, of *ω*-chloro-2-hydroxy-4-methoxyacetophenone, obtained in poor yield from the hydroxy-ketone and benzoyl chloride, is converted in benzene solution by prolonged boiling with potassium carbonate into 1-benzoyl-5-methoxycoumaran-2-one, m. p. 94—95°, yellow needles, which unlike the isomeric methoxyflavonol reacts with benzenediazonium chloride in very dilute alkaline solution to form 5-methoxycoumaran-1:2-dione-1-phenylhydrazone,



m. p. 248—249°, golden-yellow leaflets.

The dichlorides of benzylidenecoumaranones have been examined in the hope that they would be more stable than the dibromides. Unfortunately, mixtures of chlorinated products are obtained even with a molecular proportion of chlorine at 0°. By treatment with dry chlorine (6 mols.) in chloroform at 0°, 5-methoxy-1-benzylidenecoumaran-2-one yields 4-chloro-5-methoxy-1-benzylidenecoumaran-2-one dichloride,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Cl} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CCl} \cdot \text{CHClPh}$ , m. p. 227—228°, colourless needles. Since a boiling alcoholic solution of this substance (and also of the corresponding dibromide) is converted into 6-chloro-7-methoxyflavonol, m. p. 197·5—198·5°, faintly yellow needles, by *N*/10-sodium hydroxide, whilst the unchlorinated analogue yields mainly *α*-bromo-5-methoxy-1-benzylidenecoumaran-2-one by such treatment (see above), it is obvious that the nuclear chlorine atom facilitates the formation of the flavonol derivative, and the determination of its position is of great importance. This has been accomplished as follows: 5-Nitro-2-aminophenol is converted successively by the Sandmeyer reaction, by methylation, and by reduction into 6-chloro-*m*-anisidine, the solid diazonium sulphate of the latter is decomposed by dilute sulphuric acid at 150°, and the resulting 2-chloro-1-resorcinol methyl ether, b. p. 141—152°/13 mm. (once by chance a sample, m. p. 79—80°, has been obtained), is converted by methyl sulphate and warm alkali into 4-chlororesorcinol dimethyl ether, b. p. 135—137°/17—18 mm. This ether condenses with chloroacetyl chloride in the presence of aluminium chloride and carbon disulphide to form 5:ω-dichloro-2-hydroxy-4-methoxyacetophenone,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Cl}(\text{OH}) \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , m. p. 178·5—180°, colourless needles, which is also produced by the chlorination of ω-chloro-2-hydroxy-4-methoxyacetophenone in chloroform. By boiling



with alcohol and hydrated sodium acetate, 5:ω-dichloro-2-hydroxy-4-methoxyacetophenone is converted into 4-chloro-5-methoxycoumaran-2-one,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Cl} \left\langle \begin{smallmatrix} \text{O} \\ \text{CO} \end{smallmatrix} \right\rangle \text{CH}_2$ , m. p. 170—172° (decomp.), pale yellow needles, which condenses with benzaldehyde in alcohol containing a few drops of 8% sodium hydroxide at 50—60° to form 4-chloro-5-methoxy-1-benzylidenecoumaran-2-one, m. p. 172·5—173°, colourless or faintly yellow needles; the dibromide of the latter has m. p. 219°, and the dichloride, m. p. 227—228°, is identical with that obtained above by the chlorination of 5-methoxy-1-benzylidenecoumaran-2-one, and is converted into 6-chloro-7-methoxyflavonol by boiling alcohol and *N*/10-sodium hydroxide.

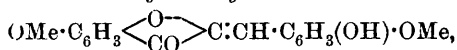
6-Chloro-7-methoxyflavonol is proved to be a flavonol, not the isomeric benzoylcoumaranone, by the three criteria mentioned above. 4-Chloro-1-acetyl-5-methoxycoumaran-2-one, m. p. 162—163°, colourless needles, prepared from the acetate, m. p. 93—94°, of 5:ω-dichloro-2-hydroxy-4-methoxyacetophenone for comparative purposes (the benzoyl derivative, which is isomeric with 6-chloro-7-methoxyflavonol, is very difficult to prepare), forms a greenish-yellow solution in concentrated sulphuric acid, and reacts with a benzenediazonium salt in very dilute alkaline solution to yield 4-chloro-5-methoxycoumaran-1:2-dione-1-phenylhydrazone,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Cl} \left\langle \begin{smallmatrix} \text{O} \\ \text{CO} \end{smallmatrix} \right\rangle \text{C}:\text{N} \cdot \text{NHPh}$ , m. p. about 215—220°, orange, crystalline powder.

The following substances are prepared by methods similar to those recorded above. The condensation of quinol dimethyl ether and chloroacetyl chloride in carbon disulphide on the water-bath yields only ω-chloro-2-hydroxy-5-methoxyacetophenone, m. p. 81—81·5°, stout, yellow needles or irregular leaflets, when freshly prepared aluminium chloride is used, but results in the formation of a mixture of this substance and ω-chloro-2:5-dimethoxyacetophenone, m. p. 87—88°, colourless needles, when stored aluminium chloride is employed.

4-Methoxycoumaran-2-one, m. p. 92·5—93·5°, flesh-coloured leaflets, forms a red solution in concentrated sulphuric acid; its aqueous solution exhibits a strong blue fluorescence.

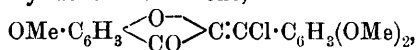
4-Methoxy-1-benzylidenecoumaran-2-one, m. p. 131—132°, yellow needles, forms a dibromide,  $\text{C}_{16}\text{H}_{12}\text{O}_3\text{Br}_2$ , m. p. 142—143°, colourless needles, and a dichloride, m. p. 127—128°, colourless needles, which yield 50—60% and 80% respectively of 6-methoxyflavonol in the usual manner.

4'-Hydroxy-3':4-dimethoxy-1-benzylidenecoumaran-2-one,



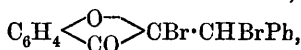
m. p. 160·5—161·5°, long, yellow needles, prepared from 4-methoxycoumaranone and vanillin, is converted by methyl sulphate and warm aqueous potassium hydroxide into 3':4':4-trimethoxy-1-benzylidenecoumaran-2-one, m. p. 171·5—172°, greenish-yellow needles. The action of chlorine on the trimethyl ether yields, according to the experimental conditions, a trichloro-derivative, m. p. 177—178°, a

substance, m. p. 215—216°, which is probably impure  $\alpha$ -chloro-3':4':4'-trimethoxy-1-benzylidenecoumaranone,

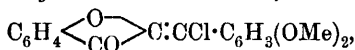


and a crude *dichloride*, m. p. 145—153°; from the last substance, 3':4':6-trimethoxyflavonol is obtained in 25% yield.

Benzylidenecoumaran-2-one forms a *dibromide*,



m. p. 147.5—148.5°, colourless needles, from which flavonol can be obtained in 32% yield. 4'-Hydroxy-3'-methoxy-1-benzylidenecoumaran-2-one, m. p. 203°, golden-yellow needles, prepared from coumaranone and vanillin, is converted by methylation into 3':4'-dimethoxy-1-benzylidenecoumaran-2-one, m. p. 159—160°, greenish-yellow needles. By chlorination (1 mol.) in chloroform at 0°, the dimethyl ether yields the *dichloride*, which, however, partly decomposes into  $\alpha$ -chloro-3':4'-dimethoxy-1-benzylidenecoumaran-2-one,



m. p. 211—212°, yellow needles, by crystallisation from alcohol or acetic acid. The *dibromide*, m. p. about 142°, pale yellow, crystalline powder, is somewhat more stable; it gives only a poor yield of 3':4'-dimethoxyflavonol.

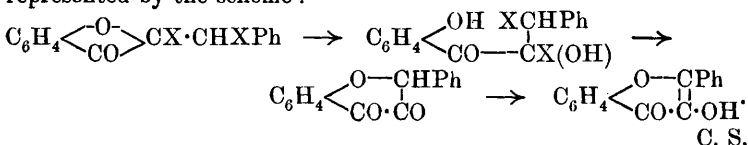
1-Benzylidene-5-methylcoumaran-2-one, m. p. 153°, colourless, pearly leaflets, prepared from benzaldehyde and 5-methylcoumaran-2-one, forms a *dibromide*,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{Br}_2$ , m. p. 153—154°, colourless needles, which is not unchanged by repeated crystallisation and is converted by boiling alcohol and *N*/10 sodium hydroxide (2 mols.) into a mixture of  $\alpha$ -bromo-1-benzylidene-5-methylcoumaran-2-one, m. p. 135—136°, yellow needles, and 7-methylflavonol, m. p. 160°, faintly yellow needles (*acetate*, m. p. 122—123°, colourless needles). The isomeric 1-benzoyl-5-methylcoumaran-2-one, m. p. 84—86°, rosettes of yellow needles, prepared from  $\alpha$ -bromo-1-benzylidene-5-methylcoumaran-2-one and sodium hydroxide in boiling aqueous alcohol, forms a yellow, non-fluorescent solution in concentrated sulphuric acid (the solution of 7-methylflavonol is yellow with a blue fluorescence) and reacts with benzenediazonium chloride in very dilute alkali to form 5-methylcoumaran-1:2-dione-1-phenylhydrazone,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C} : \text{N} \cdot \text{NHPh}$ ,

m. p. 239°, golden-yellow, pearly leaflets.

A survey of the preceding results shows that the production of a flavonol derivative is facilitated when the benzylidenecoumaranone dihaloid contains a methyl or methoxy-group or a chlorine atom in the para-position to the oxygen atom of the coumaranone ring, and is retarded by a methyl or methoxy-group in the meta-position, or by two methoxy-groups in the benzylidene nucleus.

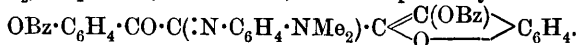
Since dimethoxybenzylidenecoumaranone dihaloids readily lose hydrogen haloid with the formation of  $\alpha$ -haloiddimethoxybenzylidenecoumaranones, and also give poor yields of flavonol derivatives, the explanation of the formation of the latter advanced by Auwers and

Müller (*loc. cit.*), which involves the intermediate production of  $\alpha$ -haloidbenzylidenecoumaranones, must be incorrect. It is shown experimentally that  $\alpha$ -haloidbenzylidenecoumaranones do not yield flavonols by treatment with dilute alkali. Consequently, a flavonol is produced from a benzylidenecoumaranone dihaloid only when the rupture of the coumaranone ring occurs more readily than the elimination of hydrogen haloid. Probably the course of the reaction is represented by the scheme :



**Oxindigo** [2 : 2'-Diketo- $\Delta^{1:1'}$ -dicoumaran]. K. FRIES, A. HASSELBACH, and L. SCHRÖDER (*Annalen*, 1914, 405, 346—372). —2 : 2'-Diketo- $\Delta^{1:1'}$ -dicoumaran (oxindigo) (Fries and Hasselbach, A., 1911, i, 150) is extensively decomposed by alkaline reducing agents, but yields well-defined reduction products in acid solution. By reduction with zinc dust and boiling acetic anhydride, it yields 2 : 2'-diacetoxy-1 : 1'-biscoumarone (oxindigo-white diacetate),  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}(\text{OAc}) \end{array} \text{C} \cdot \text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}(\text{OAc}) \end{array} \text{C}_6\text{H}_4$ , m. p. 221° (sintering at 210°), needles, which is readily re-oxidised to oxindigo. By boiling with zinc dust and glacial acetic acid, 2 : 2'-diketo- $\Delta^{1:1'}$ -dicoumaran yields a substance,  $\text{C}_{16}\text{H}_{12}\text{O}_4$ , m. p. 119°, almost colourless prisms, which cannot be oxidised to oxindigo and is probably 2 : 2'-dihydroxy- $\Delta^{1:1'}$ -dicoumaran,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH}(\text{OH}) \end{array} \text{C} \cdot \text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH}(\text{OH}) \end{array} \text{C}_6\text{H}_4$ .

In contrast to its nitrogen and sulphur isologues, 2 : 2'-diketo- $\Delta^{1:1'}$ -dicoumaran easily reacts additively with primary amines. (The only recorded case of a similar reaction in the series of indigoid dyes is that of gallorubin [Feuerstein and Brass, A., 1904, i, 344], which also contains the coumaran ring). The additive compounds have the formula  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CO} \end{array} \text{C}(\text{NHR}) \cdot \text{CH} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_4$ , and are decomposed into their two generators by mineral acids. 1-Anilino-2 : 2'-diketo-1 : 1'-dicoumaran,  $\text{C}_{22}\text{H}_{15}\text{O}_4\text{N}$ , m. p. 209°, yellow needles, is prepared from oxindigo and aniline in boiling benzene. The additive compound with *p*-aminodimethylaniline, m. p. 203°, is identical with the condensation product of 2-coumaranone and 1-*p*-dimethylaminoanil-coumaran-1 : 2-dione (Fries and Hasselbach, *loc. cit.*). It is soluble in aqueous alcoholic sodium hydroxide without undergoing any profound change, and is recovered by acidifying the solution with acetic acid. By shaking the alkaline solution with benzoyl chloride, a substance,  $\text{C}_{28}\text{H}_{28}\text{O}_6\text{N}_2$ , m. p. 220°, is obtained, which is probably



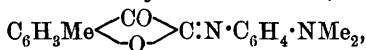
This substance forms a red solution in concentrated sulphuric acid, which yields oxindigo and *p*-aminodimethylaniline by dilution with water, and is converted by a mixture of glacial acetic and concentrated

hydrochloric acids into *p*-aminodimethylaniline and a *substance*,  $C_{80}H_{18}O_7$ , m. p.  $148^\circ$ , yellow prisms, which doubtless has the formula  $OBz \cdot C_6H_4 \cdot CO \cdot CO \cdot C \begin{smallmatrix} \diagup C(Obz) \\ \diagdown O \end{smallmatrix} C_6H_4$ , because its hydrolysis by sodium acetate yields oxindigo, and, moreover, as an  $\alpha$ -diketone the substance reacts with *o*-phenylenediamine to form a *quinoxaline*,  $C_{36}H_{22}O_5N_2$ , m. p.  $102^\circ$  (decomp.), greyish-yellow powder.

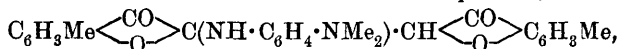
By heating with hydrogen chloride in glacial acetic acid in a sealed tube in the water-bath, 2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran yields *o*-hydroxyphenylglyoxylic acid and a *substance*,  $C_{16}H_{10}O_4$ , sintering at  $228^\circ$ , m. p.  $255^\circ$  (decomp.), dark red, metallic crystals, which is isomeric with, but apparently not nearly related to, the diketodicoumaran, forms a *sodium salt*,  $C_{16}H_9O_4Na$ , and *acetyl derivative*, m. p.  $242^\circ$ , red crystals, and is changed in boiling nitrobenzene into an isomeric *substance*,  $C_{16}H_{10}O_4$ , m. p.  $223^\circ$ , red crystals (*acetyl derivative*, m. p.  $153-154^\circ$ , citron-yellow crystals).

2:2'-Diketo-5:5'-dimethyl- $\Delta^{1:1'}$ -dicoumaran,  $C_{18}H_{12}O_4$ , m. p.  $296^\circ$  (decomp.), stout, yellow needles, has been prepared from 5-methylcoumaran-2-one, and 4:4'-dichloro-2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran,  $C_{16}H_6O_4Cl_2$ , yellow crystals sintering at  $288^\circ$ , m. p.  $320^\circ$ , from 4-chlorocoumaran-2-one, by series of reactions quite similar to those whereby 2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran is produced from 2-coumaranone (Fries and Hasselbach, *loc. cit.*).

1-*p*-Dimethylaminoanil-5-methylcoumaran-2-one,

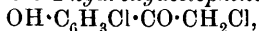


m. p.  $152^\circ$ , forms red crystals from alcohol or large prisms with bluish-black shimmer from benzene. The condensation product,



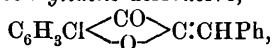
m. p.  $245^\circ$  (decomp.), reddish-brown needles, yields *p*-aminodimethylaniline and dimethyloxindigo by treatment with acetic and concentrated hydrochloric acids. Dimethyloxindigo is reduced to 2:2'-diacetoxy-5:5'-dimethyl-1:1'-dicoumarone, m. p.  $205^\circ$ , colourless needles, by zinc dust and acetic anhydride, and to 2:2'-dihydroxy-5:5'-dimethyl- $\Delta^{1:1'}$ -dicoumaran, m. p.  $172^\circ$ , faintly yellow prisms (*diacetate*, m. p.  $137^\circ$ ), by zinc dust and glacial acetic acid. By treatment with hydrogen chloride in glacial acetic acid at  $100^\circ$ , dimethyloxindigo yields 2-hydroxy-*p*-tolylglyoxylic acid and a *compound*,  $C_{18}H_{14}O_4$ , m. p.  $246^\circ$  (decomp.), dark red crystals.

*p*-Chlorophenol and chloroacetyl chloride react at  $130-140^\circ$  to form *p*-chlorophenyl chloroacetate, m. p.  $36^\circ$ , b. p.  $181^\circ/45$  mm., which is converted into 5: $\omega$ -dichloro-2-hydroxyacetophenone,

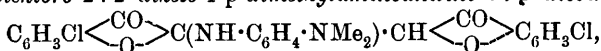


m. p.  $65^\circ$ , colourless needles, by aluminium chloride at  $140-150^\circ$  and subsequent treatment with ice.

5: $\omega$ -Dichloro-2-hydroxyacetophenone is converted by boiling alcohol and hydrated sodium acetate into 4-chlorocoumaran-2-one, m. p.  $117^\circ$ , leaflets, which forms a *benzylidene derivative*,



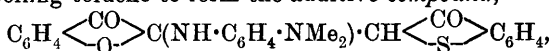
m. p. 169°, pale yellow needles. 4-*Chloro-1-p-dimethylaminoanil-coumaran-2-one*,  $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}:\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m. p. 168—169°, forms red needles with a golden lustre. The condensation product, 4:4'-*dichloro-2:2'-diketo-1-p-dimethylaminoanilino-1:1'-dicoumaran*,



m. p. 214° (decomp.), crystallises in brownish-red needles. C. S.

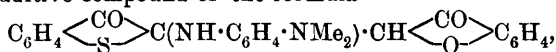
**2-Thionaphthen-2-coumaroneindigo** [Thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one]. K. FRIES and E. BARTHOLOMÄUS (*Annalen*, 1914, 405, 373—394).—Thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one

(2-thionaphthen-2-coumaroneindigo),  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$ , sintering at 272°, m. p. 292°, red needles with a faint yellowish-green reflex, is prepared by a method quite analogous to that used in the preparation of 2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran (preceding abstract). 1-*p*-Dimethylaminoanilcoumaran-1:2-dione and 3-oxythionaphthen react in boiling toluene to form the additive compound,

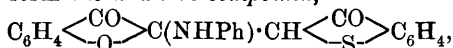


m. p. 220° (decomp.), reddish-brown needles; this substance, which is also produced from 2-coumaranone and thionaphthenquinone-*p*-dimethylamino-2-anil (Pummerer, A., 1910, i, 510), is decomposed into *p*-aminodimethylaniline and thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one by mineral acids.

The fact that the same additive compound is obtained in each of the preceding reactions, although the second method might be expected to yield an additive compound of the formula

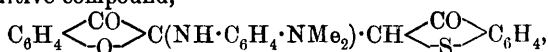


does not invalidate the explanation previously given of the course of the formation of oxindigo (preceding abstract) and similar indigoid dyes. The authors are of opinion that in all cases, where such dyes are prepared by methods similar to that here mentioned, the first product is an additive compound, which decomposes very rapidly into the indigoid dye and an amine; only in exceptional cases (oxindigo, preceding abstract; gallorubin, Feuerstein and Brass, A., 1904, i, 344) are such additive compounds stable. In this case, the two products of decomposition of the additive compound are thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one and *p*-aminodimethylaniline, which, however, readily unite, as is shown experimentally, to form the additive compound,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{CH} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$ , actually isolated. Thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2-one also combines with aniline to form the additive compound,



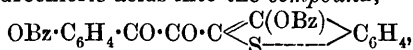
m. p. 170—173° (decomp.), ruby-red crystals, and is reduced by zinc dust and acetic anhydride to 3:2'-*diacetoxythionaphthen-2:1'-coumarone*  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OAc}) \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}(\text{OAc}) \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p. 193°, colourless needles.

The additive compound,



is soluble in aqueous alcoholic sodium hydroxide, the *disodium* salt,  $\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_2\text{SNa}_2$ , brown needles, being formed. The *dimethyl ether*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{C} \begin{array}{c} \text{C(OMe)} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C}_6\text{H}_4$ , m. p.  $204^\circ$  (decomp.), reddish-yellow plates, and corresponding *dibenzoyl* derivative, m. p.  $204.5^\circ$ , brick-red, rhombic crystals, are prepared by the action of methyl sulphate and benzoyl chloride respectively on the alkaline solution.

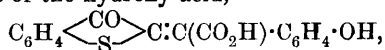
The dibenzoyl derivative is converted by boiling glacial acetic and concentrated hydrochloric acids into the *compound*,



m. p.  $182^\circ$ , faintly yellow needles, and *p*-aminodimethylaniline; the former is converted into thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one by diluting its solution in concentrated sulphuric acid with water.

The *compound*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C}_6\text{H}_4$ , m. p.  $169^\circ$ , brownish-red needles, has been obtained (i) by hydrolysing the preceding dibenzoate,  $\text{C}_{30}\text{H}_{18}\text{O}_6\text{S}$ , by *N*/2-sodium hydroxide and boiling alcohol; (ii) from thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one in a similar manner, or by boiling it with glacial acetic and concentrated hydrochloric acids (by more prolonged heating, a *substance*, m. p.  $280^\circ$ , colourless prisms, is obtained), and (iii) synthetically from ethyl *o*-hydroxyphenylglyoxylate and 3-oxythionaphthen in the presence of boiling alcoholic sodium ethoxide. The compound reacts with *o*-phenylenediamine to form the *quinoxaline*,  $\text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ , m. p.  $263^\circ$  (decomp.), brownish-red needles, and is converted into thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one by heating at about  $187^\circ$  or by solution in concentrated sulphuric acid. It is oxidised by alkaline potassium ferricyanide presumably to 3-oxythionaphthen-2-carboxylic acid and "thioindigo" is produced.

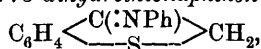
Coumaran-1:2-dione and 3-oxythionaphthen in glacial acetic acid at about  $80^\circ$  are converted by concentrated sulphuric acid into *thionaphthenquinone- $\Delta^{2:2'}$ -coumaran-1'-one*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C} : \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$ , m. p.  $242^\circ$ , red needles, which forms a blood-red solution in aqueous-alcoholic sodium hydroxide; the solution becomes pale yellow when it is acidified by acetic acid, and yields the indigoid compound when it is acidified with concentrated hydrochloric acid. Doubtless the red and the yellow solutions contain respectively the disodium and the monosodium salts of the hydroxy-acid,



formed by the rupture of the lactone ring; the hydroxy-acid itself could not be isolated.

3-Oxythionaphthen and ethyl oxalate condense in the presence of alcoholic sodium ethoxide to form, after acidification, 3-*hydroxythio*-

*naphthen-2-glyoxylic acid*,  $C_6H_4 \begin{smallmatrix} \diagup C(OH) \\ \diagdown S \end{smallmatrix} \diagup C \cdot CO \cdot CO_2H$ , orange needles, m. p.  $173^\circ$  (decomp.), or yellow needles containing  $H_2O$ . It forms a violet solution in concentrated sulphuric acid, yields a *potassium* salt, citron-yellow needles, and *ethyl* ester, m. p.  $94^\circ$ , yellowish-brown needles, and reacts with boiling aniline to form oxanilide, the *anil*, m. p.  $179^\circ$ , brownish-yellow needles, of 3-hydroxythionaphthen-2-aldehyde, and 3-keto-2:3-dihydrothionaphthen-3-anil,



m. p.  $87^\circ$ .

C. S.

**Azomethines Derived from Phenylisooxazolone.** ANDRÉ MEYER (*Bull. Soc. chim.*, 1914, [iv], 15, 609—613).—An ineffectual attempt to prepare aminophenylisooxazolone by reduction of oximinophenylisooxazolone, and to oxidise it to a symmetrical rubazonic acid. Reduction of oximinophenylisooxazolone in dilute alcoholic solution with tin and hydrochloric acid yields benzylamine hydrochloride; the platinichloride has m. p.  $197$ — $198^\circ$  (decomp.). Reduction with zinc and acetic acid produces benzonitrile and benzylamine, with a small proportion of a substance, probably aminophenylisooxazolone, which could not be isolated.

A. J. W.

**N-Demethylcodeine.** OTTO DIELS and ERNST FISCHER (*Ber.*, 1914 47, 2043—2047).—Ethyl azodicarboxylate combines quite generally with amines, producing colourless additive products (Diels and Fritzsche, A., 1911, i, 957; Diels and Paquin, A., 1913, i, 839), the hydrolysis of which offers a method for the dealkylation of amines; thus the crystalline additive compound of ethyl azodicarboxylate and dimethylamine on warming with dilute acids undergoes fission into ethyl *s*-hydrazinedicarboxylate, formaldehyde, and methylamine.

It has been found that such substances as methylpiperidine, atropine, morphine and codeine can be demethylated in this way, and the results with the last-named base are described.

Codeine readily condenses with ethyl azodicarboxylate in methylalcoholic or acetone solution, and the action needs to be moderated by cooling; the *additive* compound is a yellow, amorphous powder, which on warming with *N*-hydrochloric acid is resolved into formaldehyde, ethyl *s*-hydrazinedicarboxylate, and the hydrochloride of a substance,  $C_{17}H_{19}O_3N$ , designated *N-demethylcodeine*, derived from codeine by the removal of methyl from the nitrogen atom. *N*-Demethylcodeine forms small, hexagonal leaflets, m. p.  $185^\circ$ ; *hydrochloride*, needles, decomp. near  $314^\circ$ ; *diacetyl* derivative, needles (from benzene), m. p.  $176$ — $178^\circ$ .

D. F. T.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT (*Arch. Pharm.*, 1914, 252, 89—138).—A recapitulation and extension of previous work on the constitution of ephedrine and  $\psi$ -ephedrine (this vol., i, 78, and earlier abstracts).

On oxidation with potassium ferricyanide in alkaline solution, ephedrine yields benzaldehyde, ammonia and methylamine, together with *benzylidene-ephedrine*, which separates from ether in lustrous, long,

broad needles, m. p. 72—73°, and is also formed by the condensation of benzaldehyde and ephedrine in the presence of aqueous sodium hydroxide. The benzylidene compound yields a reddish-yellow, amorphous *platinichloride*, and a golden-yellow, microcrystalline *aurichloride*,  $2C_{17}H_{19}ON \cdot HCl \cdot AuCl_3$ . It is also formed by the oxidation of ephedrine with potassium permanganate or with chlorine and bromine in alkaline solution.

*Benzylidene-ψ-ephedrine*, obtained by the oxidation of ψ-ephedrine or by the direct condensation of benzaldehyde and ψ-ephedrine in the presence of aqueous sodium hydroxide, crystallises in transparent, tabular or leafy crystals, m. p. 65°, and forms a reddish-yellow *platinichloride*. Both the benzylidene compounds are readily resolved by warm hydrochloric acid into their components, and receive the following provisional constitution :



Although ephedrine and ψ-ephedrine readily undergo interconversion when heated with hydrochloric acid at 100°, their hydrochlorides remain unchanged when heated with water at 200—205°.

On distillation in an atmosphere of carbon dioxide, ephedrine and ψ-ephedrine hydrochlorides decompose into propiophenone, ammonia, methylamine and trimethylamine. When heated with phosphorus pentabromide, both bases are converted into α-bromo-β-methylaminopropylbenzene,  $CHPhBr \cdot CHMe \cdot NHMe$ , which forms a *hydrobromide*, crystallising in colourless, transparent leaflets or plates, m. p. 174·5° (decomp.); the *hydrochloride* also crystallises in leaflets or plates, m. p. 176—177°; the *platinichloride* forms small, lustrous, reddish-yellow leaflets, m. p. 188—189° (decomp.); the *aurichloride*, yellow leaflets, m. p. 138—139°.

The above-mentioned hydrobromide has  $[\alpha]_D^{19} - 92\cdot54^\circ$  in aqueous solution, and  $-92\cdot79^\circ$  in alcoholic solution.

The rotation in aqueous solution gradually diminishes, and finally becomes positive, owing to the conversion of the bromo-hydrobromide into ψ-ephedrine hydrobromide, m. p. 179°, which is accompanied by a small amount of ephedrine hydrobromide, m. p. 205°.

When heated with acetic anhydride the hydrobromide yields an *acetyl* derivative,  $CHPhBr \cdot CHMe \cdot NHMeAc$ , crystallising in colourless columns, m. p. 175°,  $[\alpha]_D^{15} + 80\cdot0^\circ$  in aqueous solution.

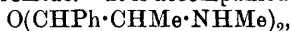
On treatment with silver nitrate in aqueous solution the acetyl derivative is converted into acetyl-ψ-ephedrine, which has m. p. 101—102° and forms a *platinichloride*.

β-Methylaminopropylbenzene,  $CH_2Ph \cdot CHMe \cdot NHMe$ , obtained by reducing the bromo-derivative (above) with zinc and hydrochloric acid, forms a *hydrochloride* (colourless, tabular crystals, m. p. 172°,  $[\alpha]_D^{15} + 19\cdot14^\circ$  in aqueous solution), a *platinichloride* (reddish-yellow needles, m. p. 202°), and an *aurichloride*, crystallising in twisted needles, m. p. 126°; it is accompanied by methylamine and propylbenzene.

When kept for fifteen minutes in sulphuric acid solution at the ordinary temperature, both ephedrine and ψ-ephedrine give rise to the compound,  $\begin{array}{c} CHPh \cdot O \cdots SO_2 \\ | \\ CHMe \cdot NH_2Me \end{array} > O$ . This forms columnar or tabular, colour-

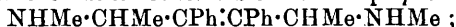


less crystals, m. p.  $244^{\circ}$ ,  $[\alpha]_D^{15} + 109.09^{\circ}$  in aqueous solution, and is also obtained by the action of silver sulphate on  $\alpha$ -bromo- $\beta$ -methylamino-propylbenzene hydrobromide. It is accompanied by a compound,



which forms a *platinichloride*,  $C_{20}H_{28}ON_2 \cdot H_2PtCl_6 \cdot 3H_2O$  (small needles, m. p.  $225-227^{\circ}$ ), and an *aurichloride*,  $B_2HAuCl_4$ , lustrous needles, m. p.  $183-184^{\circ}$ .

If the action of the sulphuric acid is continued for five days, ephedrine and  $\psi$ -ephedrine are converted into a yellow, amorphous substance, which the author considers to be an *apoeephedrine*,



the *aurichloride*, *platinichloride*, *dibromide* and additive compound with mercuric chloride are all amorphous.

On treatment with bromine in chloroform solution, ephedrine and  $\psi$ -ephedrine give rise to the corresponding hydrobromides.

The above results confirm the author's view that ephedrine and  $\psi$ -ephedrine are stereoisomerides having the constitution



F. B.

**Preparation of Double Halogen-hydracid Salts of Alkaloids of the Morphine Series.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 270575).—These double salts may be obtained by crystallisation from solutions containing equimolecular proportions of the separate salts, in presence or in absence of a precipitating agent. Descriptions are given of: *morphine narcotine hydrochloride*, short prisms, m. p. about  $200^{\circ}$ ; *codeine narcotine hydrochloride*, prisms, m. p.  $200^{\circ}$  (decomp.); and *morphine narcotine hydrobromide* ( $+ 2H_2O$ ), needles, sintering and turning brown at  $170^{\circ}$ .  
T. H. P.

**A Base,  $C_{13}H_9ON$ , from the Action of Aluminium Chloride on *o*-Nitrobenzyl Chloride and Benzene.** KARL DRECHSLER (*Monatsh.* 1913, 35, 533—560).—In the action of aluminium chloride on a mixture of benzene and *o*-nitrobenzyl chloride, a yellow solid, needles, m. p.  $169^{\circ}$ , is obtained as a by-product (Freund, A., 1897, i, 68); this substance, which gives solutions with a blue fluorescence, has the composition  $C_{13}H_9ON$ ; it gives a *hydrochloride*, pale yellow needles, m. p.  $169^{\circ}$  (decomp.), and a *mercurichloride*, golden-yellow leaflets, m. p.  $225-232^{\circ}$  (decomp.). Ebullioscopic determination of the molecular weight in benzene indicates that  $C_{13}H_9ON$  represents the molecular formula.

When treated in acetic acid solution with sodium nitrite solution, the above base does not appear to undergo diazotisation in the usual manner, for on the addition of water it is reprecipitated unchanged; the solution on warming, however, gives a substance,  $C_{13}H_{11}O_4N_2$  [possibly  $CO_2H \cdot C_6H_4 \cdot NPh \cdot N(OH)_2$ ], microscopic, yellow needles, m. p.  $365^{\circ}$ , which is soluble in solutions of alkalis, and on reduction by distillation with zinc dust, by sodium amalgam and alcohol or by tin and hydrochloric acid gives acridine or dihydroacridine. The action of nitrous

acid on the boiling alcoholic solution of the yellow base yielded a *substance*, yellow needles, m. p. 223—233° (possibly 10-hydroxyacridone).

The reduction of the yellow base,  $C_{13}H_9ON$ , by heating with zinc dust or by sodium amalgam and alcohol gave rise to acridine; attempts or acetylate the base by heating with acetic anhydride or acetic acid produced acridone, which was also obtained as a by-product in the action of nitrous acid on a hot solution of the base in hydrochloric or acetic acid. From these results the author draws the conclusion that the

yellow base is *N*-phenylanthranil,  $C_6H_4\begin{smallmatrix} \text{CO} \\ | \\ \text{NPh} \end{smallmatrix}$ , which structure can be made to accord with the general behaviour of the substance.

The author discusses the probable method of formation of this substance and also of acridine, which is another by-product, in the original Friedel-Craft's reaction. A third by-product in the original synthesis is a colourless *base*,  $C_{13}H_{11}N$ , needles, m. p. 83°; *hydrochloride*, silky needles, m. p. 205—208°; *sulphate*, sparingly soluble; *acetyl derivative*, colourless needles, m. p. 212—213°; *mercurichloride*, yellow.

D. F. T.

**Preparation of 2-Phenylquinoline-4-carboxylic Acid.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (Austrian Patent, 63525).—2-Phenylquinoline-4-carboxylic acid is obtained by the interaction of benzylideneaniline and pyruvic acid, this being effected by heating the condensation product of aniline and benzaldehyde with pyruvic acid in alcoholic solution.

T. H. P.

**Phenyloxindole.** R. STOLLÉ (*Ber.*, 1914, **47**, 2120—2122).—Chloroacetodiphenylamide,  $CH_2Cl\cdot CO\cdot NPh_2$  (Frerichs, A., 1903, i, 610), when heated with aluminium chloride to 160—180° undergoes intramolecular condensation with the formation of *phenyloxindole*,  $C_6H_4\begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{NPh} \end{smallmatrix} > CO$ , colourless leaflets, m. p. 121°; *benzylidene derivative*, yellow needles, m. p. 121°. Phenylisatin condenses with phenyloxindole in boiling acetic acid solution containing a little hydrochloric acid, the product being *diphenylisoindigotin* (compare Wahl and Bayard, A., 1909, i, 330), reddish-brown needles, m. p. near 305°. It was not found possible to prepare phenyloxindole by heating *phenylisatin-hydrazone*, which was obtained in yellow needles, m. p. 192°, from the interaction of phenylisatin and hydrazine hydrate in boiling alcoholic solution.

*Chloroacetoethylanilide*, m. p. 35°, b. p. 165°/21 mm., obtained from chloroacetyl chloride and ethylaniline in ethereal solution, when heated with aluminium chloride at 160° was gradually converted into ethyloxindole, needles, m. p. 97°.

The substance, m. p. 38°, obtained by Auwers and Arndt (A., 1909, i, 175) by the action of chloroacetyl chloride on *p*-thiocresol and described as *p*-thiocresyl chloroacetate,  $C_6H_4Me\cdot S\cdot CO\cdot CH_2Cl$ , is in reality *p*-tolylthiolacetyl chloride,  $C_6H_4Me\cdot S\cdot CH_2\cdot COCl$ , and on hydrolysis yields *p*-tolylthiolacetic acid which is already known.

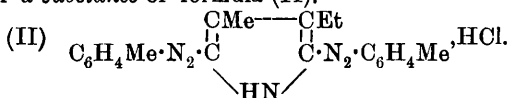
D. F. T.

**New Condensation Products of Carbazoles and Phthalic Anhydrides.** BADISCHE ANILIN- & SODA-FABRIK (Fr. Patent, 463508).—When carbazole or its derivatives substituted either at the nitrogen atom or in the nucleus are heated with phthalic anhydride or its derivatives in the presence of concentrated or slightly diluted sulphuric acid, condensation products are obtained which either are colouring matters or serve for the production of these. In certain cases, it is advantageous to submit the crude condensation products to subsequent treatment with a hypochlorite. T. H. P.

**Hæmopyrrole and the Scission of Hæmin by Oxidation.** AMANDUS HAHN (*Zeitsch. Biol.*, 1914, 64, 141—160).—A comprehensive review of the investigations into the oxidation products of hæmin, culminating in the synthesis of hæmatic acid (Küster and Weller, this vol., i, 442) and of the researches on the constituent pyrroles of hæmopyrrole oil. In connexion with the latter subject, the most recent paper under review is dated August, 1912, but important communications have since appeared (compare Fischer and Eismayer, this vol., i, 886). J. C. W.

**Synthesis of Hæmopyrrole.** I. J. GRABOWSKI and L. MARCHLEWSKI (*Ber.*, 1914, 47, 2159—2161).—The authors give the term "hæmopyrrole I" to that constituent of crude hæmopyrrole which gives a red azo-dye with diazonium salts (A., 1912, i, 923), and has been shown to be 2-methyl-5-ethylpyrrole (compare also Piloty and Stock, A., 1912, i, 1015). The presence of this substance in hæmopyrrole renders necessary a revision of earlier discussions as to the nature of the latter substance (compare Fischer and Bartholomäus, A., 1912, i, 646).

2-Methyl-5-ethylpyrrole has now been synthesised by dry distillation of methylethylmaleinimide with zinc dust and calcium hydroxide in a current of carbon dioxide. The distillate was extracted with ether, and the solution treated with *p*-toluenediazonium chloride when a mixture of reddish-brown and blue crystals was obtained on evaporation. The latter, m. p. 252°, were separated by their much greater solubility in chloroform, and were found to consist of the substance (I), whilst the former, (I) 
$$\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\overset{\text{CMe}\cdot\text{CE}}{\underset{\text{NH}}{\text{C}}}\text{—}\text{NH}\cdot\overset{\text{CMe}\cdot\text{CEt}}{\underset{\text{NH}}{\text{C}}}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}, \text{HCl},$$
 which were needle-shaped, m. p. 256°, were of composition agreeing with that of a substance of formula (II).



Treatment of crude hæmopyrrole with *p*-toluenediazonium chloride gives two products agreeing in all respects with the synthetic substances described above. D. F. T.

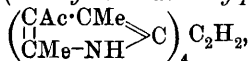
**The Constitution of the Blood and Bile Pigments.** III. HANS FISCHER and K. EISMAYER (*Ber.*, 1914, 47, 2019—2027. Compare Fischer and Bartholomäus, A., 1913, i, 209, 1236).—It is already known that formaldehyde will condense with substituted pyrroles, giving dipyrromethane derivatives (Fischer and Bartholomäus, *loc.*

*cit.*; Piloty, Stock and Dormann, this vol., i, 755). The authors have therefore applied glyoxal in place of formaldehyde in the hope of obtaining tetrapyrrole derivatives.

Formaldehyde and hæmopyrrole readily condense together when heated in alcoholic solution containing a little hydrochloric acid, the product being di(4:5-dimethyl-3-ethylpyrryl)methane, m. p. 108° (Piloty, Stock and Dormann, this vol., i, 327, give 99.5—100°); *picrate* needles, m. p. 186° (decomp.). Condensation of glyoxal with hæmopyrrole under similar conditions gives rise to the same substance, which is not a leuco-compound but a dye, the *hydrochloride* (a red, crystalline solid with a green lustre) imparting a yellow colour to cotton.

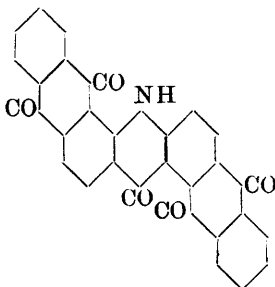
In a similar manner formaldehyde condenses with methyl phonopyrrolecarboxylate, the result being much less satisfactory if the free acid is used. The product is di(4:5-dimethyl-3-*o*-carboxymethyl-ethylpyrryl)methane (for formula of free acid see Piloty, Stock and Dormann, *loc. cit.*). This substance, which was obtained in 50% yield from glyoxal and methyl phonopyrrolecarboxylate even in neutral solution, forms brownish-yellow crystals with a green lustre, m. p. 110—112°; *hydrochloride*, small rods with a greenish-red metallic lustre, soluble in chloroform to a deep red solution; *picrate*, m. p. 192° (decomp.). The constitution of this base was confirmed by molecular-weight determination in alcoholic solution and by its oxidation (with lead dioxide and sulphuric acid) and reduction (with a mixture of hydriodic and acetic acids) to hæmatic acid and phonopyrrolecarboxylic acid respectively. On warming with sodium methoxide solution, the compound was hydrolysed to the corresponding acid (compare Piloty, Stock and Dormann, *loc. cit.*)

The action of glyoxal on 3-acetyl-2:4-dimethylpyrrole follows a different course, *s-tetra*(3-acetyl-2:4-dimethylpyrryl)ethane,



being readily formed on the addition of a little hydrochloric acid to an alcoholic solution of these substances. This product, which is closely related to the non-isolated leuco-compound of Willstätter and Fischer's aetioporphyryin (A., 1913, i, 1251), was obtained as the *hydrochloride*, prisms, decomp. at 210—225°. D. F. T.

**Diphthaloylacridones.** ALFRED ECKERT and OTTOKAR HALLA (*Monatsh.*, 1914, 35, 755—763).—1:2:6:7-Diphthaloylacridone



(annexed formula), red needles, is obtained directly and in almost quantitative yield by boiling 1-aminoanthraquinone-2-carboxylic acid, 2-chloroanthraquinone, sodium acetate, and a little cuprous chloride in nitrobenzene for fifteen hours. It forms a greenish-yellow solution in concentrated sulphuric acid, and the flocculent precipitate obtained by the addition of water readily yields a vat which dyes cotton reddish-yellow (in the massive state, the acridone forms a vat only with great difficulty).

The constitution of 1:2:6:7-diphthaloyl-

acridone is proved as follows. 3-Bromo-2-aminoanthraquinone, m. p. 307°, orange-yellow leaflets, prepared by boiling 1:3-dibromo-2-aminoanthraquinone, pyridine, and iron filings with glacial acetic acid, forms an *acetyl* derivative, m. p. 259°, almost colourless leaflets, and a *benzylidene* derivative, pale yellow leaflets. The latter condenses with 1-aminoanthraquinone-2-carboxylic acid under the conditions mentioned above to form a substance,  $C_{36}H_{18}O_5N_2$ , brownish-red, microscopic needles, by the hydrolysis of which is obtained 9-amino-1:2:6:7-diphthaloylacridone; by boiling the diazonium sulphate of this with alcohol, a diphthaloylacridone, identical with that described above, is obtained.

1-Aminoanthraquinone-2-carboxylic acid condenses with 1-chloroanthraquinone under the conditions described above to form 1:2:8:9-diphthaloylacridone, copper needles with a blue reflex.

Attempts to oxidise the methyl group in 2-methyl-1:2'-dianthrimide have been unsuccessful. When the substance is fused with potassium hydroxide and lead oxide (compare D.R.-P. 192436) a product is obtained which is quite different from 1:2:6:7-diphthaloylacridone.

C. S.

#### Preparation of Halogenated 5:5-Dialkylbarbituric Acids.

ALFRED EINHORN (D.R.-P. 272611).—When 5:5-dialkylbarbituric acids are heated with halogens under pressure, in some cases with addition of an indifferent organic diluent, they are converted into halogenated derivatives containing the halogens in the alkyl groups. These derivatives are soluble in dilute alkali carbonate or ammonia solution, from which they are precipitated unchanged by addition of acid.

*Bromo-5:5-diethylbarbituric acid* forms nodular masses of needles, m. p. 172–174°.

*Dibromo-5:5-dipropylbarbituric acid* forms needles, m. p. 176°.

*Chloro-5:5-diethylbarbituric acid* forms vitreous prisms, m. p. 199–200°.

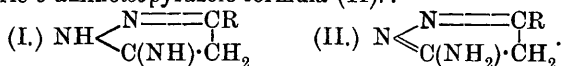
T. H. P.

**Incompatibility of Melubrin with Preparations which contain Aldehydes. Estimation of Aldehydes.** MARC TIFFENEAU (*Chem. Zentr.*, 1914, i, 1368; from *Bull. Sci. Pharmacol.*, 21, 71–73).—Melubrin,  $C_{11}H_{11}O_2N \cdot NH \cdot CH_2 \cdot SO_3Na \cdot H_2O$ , is gradually decomposed in aqueous solution into aminoantipyrine,  $C_{11}H_{11}O_2N \cdot NH_2$ , and sodium methanalsulphonate. For this reason its solutions give the same condensation products with aromatic aldehydes as aminoantipyrine itself. *Anisylideneaminoantipyrine*, *piperonylideneaminoantipyrine*, and *vanillylideneaminoantipyrine* have m. p.'s 168°, 229° and 198° respectively. This behaviour of melubrin renders it incompatible with preparations which contain aromatic aldehydes; on the other hand, it gives excellent results in the estimation of benzaldehyde and its homologues. For this purpose, two molecules of melubrin are required for each molecule of aldehyde. Condensation is effected in aqueous or feebly alcoholic solution. The condensation products are soluble in alcohol and are decomposed into their constituents by boiling dilute mineral acids.

H. W.

**Bimolecular Nitriles.** E. VON MEYER (*J. pr. Chem.*, 1914, [ii], 90, 1—52).—A continuation of previous work (A., 1908, i, 909) on the properties and reactions of dinitriles,  $R \cdot C(NH) \cdot CH_2 \cdot CN$ .

I. [With RICHARD FRIEDRICH].—*Derivatives of Iminopyrazoline and Aminopyrazole.*—Benzoacetodinitrile and *p*-toluacetodinitrile react with hydrazine hydrate in alcoholic solution at 150—200°, yielding 5-iminopyrazolines (I), the salts of which are derived from the tautomeric 5-aminoisopyrazole formula (II).:



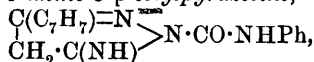
5-Imino-3-*p*-tolylpyrazoline (I,  $R = C_6H_4Me$ ), prepared from *p*-toluacetodinitrile, crystallises in white needles, m. p. 143°, and forms a *hydrochloride*, crystallising in pearly, lustrous leaflets, m. p. 252°. That the hydrochloride has the constitution represented in (II) ( $R = C_6H_4Me$ ) has been established by its behaviour towards nitrous acid. On successive treatment with sodium nitrite and sodium acetate in aqueous solution, it yields a very unstable, crystalline *diazocompound*, which explodes when rubbed, or when heated at 121°. The *diazonium chloride* crystallises in light yellow needles, explodes at 157° without melting, and is remarkably stable in aqueous solution; it couples with  $\beta$ -naphthol in alcoholic solution, yielding an *azo-dye*, crystallising in yellowish-red needles, m. p. 237°.

5-Imino-3-*p*-tolylpyrazoline reacts with nitrous acid in alcoholic solution to form a reddish-brown, amorphous *nitroso-compound*, and with acetic anhydride at the ordinary temperature, yielding a *mono-*

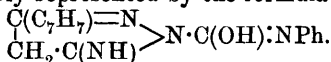
*acetyl* derivative,  $\text{NAc} \begin{array}{c} \diagup \text{N}=\text{C} \cdot C_6H_4Me \\ \diagdown \text{C}(\text{NH}) \cdot \text{CH}_2 \end{array}$ , felted, white needles, m. p.

221°. The *diacetyl* derivative,  $\text{NAc} \begin{array}{c} \diagup \text{N}=\text{C} \cdot C_6H_4Me \\ \diagdown \text{C}(\text{NAc}) \cdot \text{CH}_2 \end{array}$ , white prisms, m. p. 163°, is obtained by heating the iminopyrazolone with an excess of acetic anhydride.

1-Phenylcarbamylyl-5-imino-3-*p*-tolylpyrazoline,

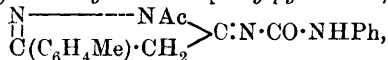


prepared from the iminopyrazoline and phenylcarbimide in hot xylene solution, crystallises in lustrous, silky, white needles, m. p. 173°, yields an *acetyl* derivative (slender needles, m. p. 161°), and when heated above its m. p. is converted into an *isomeride*, which separates from dilute alcohol as a micro-crystalline powder, m. p. 206°, and yields an *acetyl* derivative, m. p. about 204°. The constitution of the isomeride is probably represented by the formula



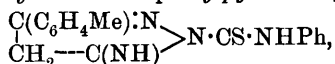
In agreement with this view, it is found that only the acetyl derivative of the less fusible isomeride is capable of yielding a *silver* salt on treatment with silver nitrate in alcoholic solution.

1-Acetyl-5-phenylcarbamylylimino-3-*p*-tolylpyrazoline,



prepared by the interaction of phenylcarbimide and the monoacetyl derivative of 5-imino-3-*p*-tolylpyrazoline in benzene solution, crystallises in slender needles, m. p. 177°, and is isomeric with the preceding acetyl derivatives.

1-Phenylthiocarbamyl-5-imino-3-*p*-tolylpyrazoline,



obtained by heating the iminopyrazoline with phenylthiocarbimide, crystallises in stout prisms, m. p. 196°.

The hydrochloride of 5-imino-3-*p*-tolylpyrazoline reacts with benzenediazonium chloride in aqueous solution, yielding 5-imino-3-*p*-tolyl-4-pyrazolonephenylhydrazone,  $\text{NH} \begin{array}{c} \text{N}=\text{C} \cdot \text{C}_6\text{H}_4\text{Me} \\ | \\ \text{C(NH)} \cdot \text{C:N} \cdot \text{NHPh} \end{array}$ , which crystallises in golden-yellow needles, m. p. 233°, forms a yellow *silver* salt, and yields in hydrochloric acid solution a *dial*zo-compound which couples with resorcinol to form a brown *azo*-dye.

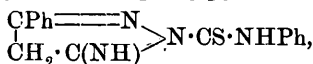
1-Carbamyl-5-imino-3-*p*-tolylpyrazoline,  $\begin{array}{c} \text{C}(\text{C}_6\text{H}_4\text{Me})\text{:N} \\ | \\ \text{CH}_2\text{---C(NH)} \end{array} \text{N} \cdot \text{CO} \cdot \text{NH}_2$

obtained in the form of its *hydrochloride* by the interaction of semicarbazide hydrochloride and *p*-toluoacetodinitrile in alcoholic solution, crystallises in white leaflets, m. p. 186°, and is hydrolysed by hydrochloric acid to 5-imino-3-*p*-tolylpyrazoline.

5-Imino-3-phenylpyrazoline (I. above, R = Ph), prepared from benzoacetodinitrile and hydrazine hydrate, separates from alcohol in lustrous, pearly leaflets, m. p. 119°, and forms a *hydrochloride*, which can be diazotised and is, therefore, derived from the tautomeric 5-amino-3-phenylisopyrazole (II. above, R = Ph); the *diazonium chloride* explodes at 98°, and couples with resorcinol, yielding a reddish-yellow *azo*-dye.

On treatment with nitrous gases in boiling glacial acetic acid solution, 5-imino-3-phenylpyrazoline yields an amorphous, reddish-brown *nitrosoacetyl* derivative,  $\begin{array}{c} \text{N} \text{---} \text{N} \cdot \text{Ac} \\ | \\ \text{CPh} \cdot \text{CH}_2 \end{array} \text{C:N} \cdot \text{NO}$ . With acetic anhydride it forms a *diacetyl* derivative, white needles, m. p. 151°, and a *monoacetyl* derivative, stout prisms, m. p. 162°, which forms a white *silver* salt.

1-Phenylthiocarbamyl-5-imino-3-phenylpyrazoline,

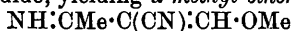


prepared by heating the iminophenylpyrazoline with phenylthiocarbimide at 100°, has m. p. 187°.

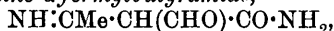
II. [With P. ESSER.]—*Condensation of Dinitriles with Esters*.—Under the influence of sodium or potassium ethoxide, dinitriles condense with the ethyl esters of formic, phenoxyacetic, and oxalic acids, yielding compounds of the type  $\text{NH} \cdot \text{CR} \cdot \text{CH}(\text{CN}) \cdot \text{COR}$ , where R = H,  $\cdot\text{CH}_2\text{OPh}$ , and  $\cdot\text{CO}_2\text{Et}$  respectively.

$\beta$ -Imino- $\alpha$ -formylbutyronitrile,  $\text{NH} \cdot \text{CMe} \cdot \text{CH}(\text{CHO}) \cdot \text{CN}$ , prepared by condensing ethyl formate with acetodinitrile by means of potassium ethoxide in ethereal solution, and acidifying the aqueous solution of

the resulting *potassium* salt, has m. p. 109°. The *potassium* salt reacts with methyl iodide, yielding a *methyl ether*,



(long needles, m. p. 40°), and when kept in aqueous solution is slowly hydrolysed to  $\beta$ -imino- $\alpha$ -formylbutyramide,

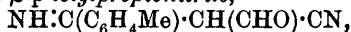


which separates from alcohol in needles, m. p. 269°.

$\alpha$ -Formyl- $\beta$ -phenyliminobutyronitrile,  $\text{NPh}:\text{CMe}\cdot\text{CH}(\text{CHO})\cdot\text{CN}$ , obtained from *N*-phenylacetodinitrile and ethyl formate in a similar manner, has m. p. 102°.

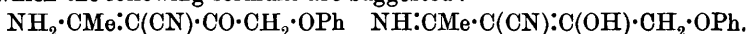
$\beta$ -Imino- $\alpha$ -formyl- $\beta$ -phenylpropionitrile,  $\text{NH}:\text{CPh}\cdot\text{CH}(\text{CHO})\cdot\text{CN}$ , from benzoacetodinitrile, crystallises in needles, m. p. 106°, and is readily hydrolysed to the corresponding amide; the *potassium* salt yields, with methyl iodide, a *methyl ether*,  $\text{NH}:\text{CPh}\cdot\text{C}(\text{CN})\cdot\text{CH}\cdot\text{OMe}$ , having m. p. 84°.

$\beta$ -Imino- $\alpha$ -formyl- $\beta$ -p-tolylpropionitrile,



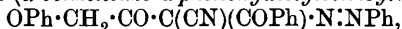
prepared from *p*-tolylacetodinitrile, has m. p. 122°, and forms a *phenylhydrazone*, m. p. 188°; on treatment with benzenediazonium chloride and sodium acetate in alcoholic solution, it is converted into a yellow azo-compound ( $\alpha$ -benzeneazo- $\alpha$ -formyl- $\alpha$ -p-toluoylacetonitrile), m. p. 120°,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}(\text{CHO})(\text{CN})\cdot\text{N}:\text{NPh}$ . Ethyl phenoxyacetate readily condenses with acetodinitrile in ethereal solution in the presence of *potassium* ethoxide, yielding  $\beta$ -imino- $\alpha$ -phenoxyacetylbutyronitrile, m. p. 96°,  $\text{NH}:\text{CMe}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , together with an *isomeride*, m. p. 123°, which constitutes the main product of the reaction. The more fusible  $\alpha$ -isomeride is present in the condensation product in the form of its *potassium* salt, and is isolated by extraction with water and subsequent acidification with hydrochloric acid.

The insoluble residue consists of the less fusible  $\beta$ -isomeride, for which the following formulæ are suggested :



In agreement with the first formula it is found that the  $\beta$ -isomeride does not form a *potassium* salt.

Benzoacetodinitrile and ethyl phenoxyacetate give rise to  $\beta$ -imino- $\alpha$ -phenoxyacetyl- $\beta$ -phenylpropionitrile,  $\text{NH}:\text{CPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , which also exist in two isomeric forms. The  $\alpha$ -isomeride has m. p. 87°, and is present in the condensation product in the form of its *potassium* salt; on treatment with benzenediazonium chloride it is converted into an azo-compound ( $\alpha$ -benzeneazo- $\alpha$ -phenoxyacetylbenzoylacetonitrile),

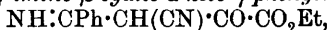


which crystallises in golden-yellow leaflets, m. p. 110°. The  $\beta$ -isomeride has m. p. 114°, and constitutes the main product of the reaction.

*p*-Toluacetodinitrile yields  $\beta$ -imino- $\alpha$ -phenoxyacetyl- $\beta$ -p-tolylpropionitrile,  $\text{NH}:\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , which was isolated in only one (the  $\beta$ -) form, having m. p. 148°. Ethyl  $\gamma$ -imino- $\beta$ -cyano- $\alpha$ -ketovalerate,  $\text{NH}:\text{CMe}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , prepared from acetodinitrile and ethyl oxalate, has m. p. 90° and is readily hydrolysed to the corresponding *acid*, m. p. 168°, an aqueous solution of which, on acidification with hydrochloric acid, slowly deposits  $\gamma$ -imino- $\alpha$ -keto-



*β*-carbamylvaleric acid, m. p. 268°,  $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO}\cdot\text{CO}_2\text{H}$ . The silver and ammonium salts of the two last-named acids are mentioned. Ethyl *γ*-imino-*β*-cyano-*α*-keto-*γ*-phenylbutyrate,



obtained in the form of its potassium salt from benzoacetodinitrile and ethyl oxalate, has m. p. 90°, and on treatment with ammonia in ethereal solution yields the corresponding amide, m. p. 199° (decomp.); the potassium salt is hydrolysed in acid solution to *γ*-imino-*α*-keto-*β*-carbamyl-*γ*-phenylbutyric acid,  $\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , m. p. 259°.

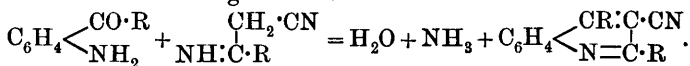
The following compounds were prepared from *p*-toluoacetodinitrile in a similar manner: *γ*-imino-*β*-cyano-*α*-keto-*γ*-*p*-tolylbutyric acid, white needles, m. p. 283°; ethyl ester, m. p. 142°, and amide, slender needles, m. p. 206°. Both the acid and ester are hydrolysed by boiling aqueous sodium hydroxide to oxalic acid and *β*-imino-*β*-*p*-tolylpropionamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , which has m. p. 177°, and is also obtained by heating *p*-toluoacetodinitrile with alcoholic potassium hydroxide.

*β*-Imino-*α*-formyl-*β*-phenyl-*α*-methylpropionitrile,



prepared from benzopropiodinitrile and ethyl formate in the presence of potassium ethoxide, crystallises in leaflets, m. p. 133°, and forms a yellowish-white potassium salt.

III. [With G. HAENSEL.]—*Derivatives of β-cyanoquinoline*.—*o*-Aminobenzaldehyde, *o*-aminoacetophenone, and isatic acid undergo condensation with dinitriles, yielding derivatives of 3-cyanoquinoline, as shown in the following scheme:



3-Cyano-2-phenylquinoline-4-carboxylic acid, prepared by heating benzoacetodinitrile with isatic acid in alcoholic solution in the presence of zinc chloride, crystallises in slender, white needles, m. p. 267—268°.

3-Cyano-2-*p*-tolylquinoline-4-carboxylic acid, obtained in a similar manner from *p*-toluoacetodinitrile, forms white prisms, m. p. 215°.

When heated in glacial acetic acid solution at 150°, *o*-aminoacetophenone and acetodinitrile yield 3-cyano-2:4-dimethylquinoline, which crystallises in white needles, m. p. 161—162°, yields a picrate (yellow needles, m. p. 203°), and is hydrolysed by concentrated hydrochloric acid at 180° to 1:4-dimethylquinoline-3-carboxylic acid, white needles, m. p. 231°, and the corresponding amide, small needles, m. p. 198°; the acid yields a hydrochloride, which forms prismatic crystals, and is readily hydrolysed by water.

3-Cyano-2-phenyl-4-methylquinoline, prepared from benzoacetodinitrile and *o*-aminoacetophenone in a similar manner, crystallises in long, white needles, m. p. 166—167°; 2-phenyl-4-methylquinoline-3-carboxylic acid forms white needles, m. p. 284—285° (decomp.); the amide crystallises in clusters of needles, m. p. 189—190°.

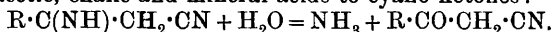
3-Cyano-2-*p*-tolyl-4-methylquinoline crystallises in yellow needles, m. p. 133°.

When heated at 120°, *o*-aminobenzaldehyde condenses with aceto-

dinitrile, yielding 3-cyano-2-methylquinoline, white needles or prisms, m. p. 131°.

3-Cyano-2-phenylquinoline, prepared from benzoacetodinitrile and o-aminobenzaldehyde in alcoholic solution at 180°, forms white needles, m. p. 193—194°, and is hydrolysed by hydrochloric acid to 2-phenylquinoline-3-carboxylic acid, small needles, m. p. 230° (decomp.).

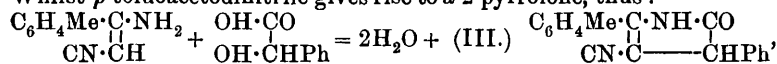
IV. [With P. BERGE, R. OEHLER, and E. SCHLETTER].—*Action of Various Acids on Dinitriles*. In aqueous solution dinitriles are hydrolysed by acetic, oxalic and mineral acids to cyano-ketones:



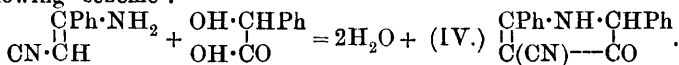
The action has been quantitatively followed in the case of acetodinitrile, benzoacetodinitrile, and *p*-toluoacetodinitrile by determining the diminution in the concentration of the acid. It is found that acetodinitrile is much more readily hydrolysed than the two remaining nitriles, the rates of hydrolysis being in the ratio 30 : 4 : 7 in the order given.

The interaction of dinitriles and anhydrous organic acids depends on the nature of the acid and nitrile, and also on the conditions under which the reaction is carried out. Cyanacetic,  $\alpha$ -hydroxyisobutyric, succinic, glycollic, and malic acids give rise to aminocyanopyridines:

$2R \cdot C(NH) \cdot CH_2 \cdot CN = NH_3 + N \begin{smallmatrix} C(NH_2) \cdot CH \\ \diagup \quad \diagdown \\ CR = C(CN) \end{smallmatrix} CR$ . The water simultaneously produced by the action of the ammonia on the acid may lead to a partial or complete displacement of the amino-group by hydroxyl. If the reaction is carried out in alcoholic solution, displacement of the amino-group by the ethoxy-group may also take place. A remarkable difference in the behaviour of benzoacetodinitrile and *p*-toluoacetodinitrile towards mandelic acid has also been observed. Whilst *p*-toluoacetodinitrile gives rise to a 2-pyrrolone, thus:



benzoacetodinitrile is converted into a 3-pyrrolone, as shown in the following scheme:



When heated with anhydrous cyanoacetic acid at 140°, acetodinitrile yields 6-amino-3-cyano-2 : 4-dimethylpyridine, which is accompanied by a substance,  $C_{12}H_{10}O_2N_2$ , crystallising in needles, m. p. 220°; if the components are not anhydrous, 3-cyano-6-hydroxy-2 : 4-dimethylpyridine is produced.

The action of succinic acid on *p*-toluoacetodinitrile in alcoholic solution at 150° leads to the formation of 3-cyano-6-hydroxy-2 : 4-di-*p*-tolylpyridine,  $N \begin{smallmatrix} C(OH) \text{---} \text{---} CH \\ \diagup \quad \diagdown \\ C(C_6H_4Me) : C(CN) \end{smallmatrix} C \cdot C_6H_4Me$ , m. p. 265°, together with a small amount of 6-amino-3-cyano-2 : 4-di-*p*-tolylpyridine, m. p. 165°, which forms a *picrate*, m. p. 205°.

When heated with glycollic acid in alcoholic solution, benzoacetodinitrile is converted into 3-cyano-6-ethoxy-2 : 4-diphenylpyridine, slender needles, m. p. 141—142°; if the reaction is carried out in a sealed tube at 150°, the ethoxy-derivative is accompanied by 6-amino-

3-cyano-2:4-diphenylpyridine, which crystallises with  $\frac{1}{2}\text{H}_2\text{O}$  in needles, m. p.  $213^\circ$ , and yields a deep yellow *picrate*.

3-Cyano-6-hydroxy-2:4-diphenylpyridine, prepared by heating benzoacetodinitrile with  $\alpha$ -hydroxyisobutyric acid in alcoholic solution at  $150^\circ$ , crystallises in lustrous, silky needles, m. p.  $192^\circ$ , with previous sintering at  $143^\circ$ .

The above-mentioned 3-cyano-6-ethoxy-2:4-diphenylpyridine is converted by the action of hydrochloric acid at  $200^\circ$  into 6-hydroxy-2:4-diphenylpyridine, which crystallises in slender needles, m. p.  $208^\circ$ .

4-Cyano-3-phenyl-5-p-tolyl-2-pyrrolone (formula III above), prepared by heating *p*-toluoacetodinitrile and mandelic acid in equimolecular proportions in alcoholic solutions at  $150^\circ$ , forms slender needles, m. p.  $200^\circ$ , with previous softening at  $150^\circ$ . It yields a yellow *picrate*, and when heated with hydrochloric acid at  $200^\circ$  is transformed into 3-phenyl-5-p-tolyl-2-pyrrolone,  $\text{NH} \begin{array}{c} \text{C}(\text{C}_6\text{H}_4\text{Me})\text{:CH} \\ \text{CO} \text{---} \text{CHPh} \end{array}$ , slender, white needles, m. p.  $235\text{--}237^\circ$

The interaction of benzoacetodinitrile and mandelic acid under similar conditions leads to the formation of 4-cyano-2:5-diphenyl-3-pyrrolone (formula IV above), which crystallises from alcohol in white needles, m. p.  $230^\circ$ , with previous softening at  $200^\circ$ , and yields an *acetyl* derivative (pale yellow prisms, m. p.  $134^\circ$ ), a *phenylhydrazone*, slender, grey needles (decomp.  $260^\circ$ ), and an *oxime*, crystallising in pale yellow needles, which decompose above  $170^\circ$  without melting.

When heated with concentrated hydrochloric acid at  $200^\circ$ , the cyanodiphenylpyrrolone is converted into 2:5-diphenyl-3-pyrrolone, white needles, m. p.  $205^\circ$ . It is hydrolysed by alcoholic potassium hydroxide to 4-carbamyl-2:5-diphenylpyrrolone,  $\text{NH} \begin{array}{c} \text{CHPh}\cdot\text{CO} \\ \text{CPh}=\text{C}\cdot\text{CO}\cdot\text{NH}_2 \end{array}$ , which crystallises in small prisms, m. p.  $255^\circ$  (decomp.).

4-Cyano-5-phenyl-2-methyl-3-pyrrolone,  $\text{NH} \begin{array}{c} \text{CPh}=\text{C}\cdot\text{CN} \\ \text{CHMe}\cdot\text{CO} \end{array}$ , prepared from lactic acid and benzoacetodinitrile, forms small needles, m. p.  $170^\circ$  (decomp.), yields an *acetyl* derivative, m. p.  $185^\circ$  (decomp.), and when heated with hydrochloric acid is transformed into 5-phenyl-2-methyl-3-pyrrolone, pale yellow needles, m. p.  $215^\circ$ , with partial decomposition.

Attempts to condense benzoacetodinitrile with oxalic acid in alcoholic solution at  $100^\circ$  resulted in the formation of  $\omega$ -cyanoacetophenone; at  $170^\circ$ , 3-cyano-6-hydroxy-2:4-diphenylpyridine is produced.

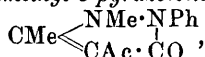
F. B.

**Preparation of 2- or 3-Antipyrilquinoline-4-carboxylic Acids.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270487).—These compounds, obtained by the interaction of 4-acetyl-1-phenyl-2:3-dimethylpyrazolone or its homologues with isatin in alkaline solution, show the actions both of 1-phenyl-2:3-dimethyl-5-pyrazolone and of the quinoline-4-carboxylic acids and find therapeutic application.

2-Antipyrilquinoline-4-carboxylic acid, m. p.  $266\text{--}268^\circ$ , and

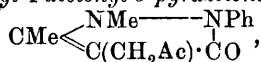
3-antipyryl-2-methylquinoline-4-carboxylic acid or 2-methylantipyryl-quinoline-4-carboxylic acid, m. p. 238—239°, are described.

4-Acetyl-1-phenyl-2:3-dimethyl-5-pyrazolone,



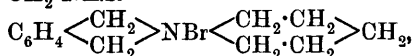
obtained by the action of acetyl chloride on 1-phenyl-2:3-dimethyl-5-pyrazolone in presence of ammonium chloride, forms colourless crystals, m. p. 150—151°, and gives a red coloration with ferric chloride in aqueous solution.

1-Phenyl-2:3-dimethyl-4-acetonyl-5-pyrazolone,

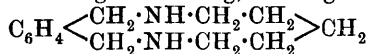


m. p. 87°, gives a red coloration with ferric chloride in aqueous solution and is obtained by the action of chloroacetone and sodium hydroxide on 1-phenyl-3-methyl-5-pyrazolone and methylation of the 1-phenyl-3-methyl-4-acetonyl-5-pyrazolone thus obtained. T. H. P.

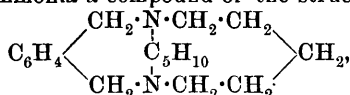
**The Interaction of Bicyclic Ammonium Compounds and Secondary Cyclic Bases. The Stereochemistry of Tervalent Nitrogen.** M. SCHOLTZ (*Ber.*, 1914, **47**, 2162—2170).—It is known from the earlier work of the author that *o*-xylylene bromide reacts with secondary amines, giving rise to substituted ammonium bromides of the type  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{NRR}'\text{Br}$ , which on heating with ammonia produce bases with two secondary amino-groups as indicated by the formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{NHR} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{NHR}' \end{array}$ . With the product,



obtained from *o*-xylylene bromide and piperidine, the action of ammonia causes a widening of the ring, forming a structure



(A., 1898, i, 305, 383, 471, 565, 567). By allowing xylenepiperidinium bromide to react with piperidine a compound was obtained to which the structure  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NC}_5\text{H}_{10})_2$  was ascribed, but if the behaviour of xylenepiperidinium bromide towards piperidine is the same as towards ammonia a compound of the structure

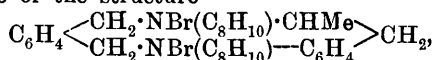


might be expected. A decision between these two alternative formulæ by direct methods is not easy, but with compounds of an analogous nature, the occurrence of isomerism has been observed, which is explicable only by the latter representation (compare Scholtz and Wolfrum, A., 1910, i, 771).

In the same manner as piperidine, 2-methyldihydroindole reacts with *o*-xylylene bromide in the presence of alkali hydroxide in hot alcoholic solution, giving *o*-xylylene-2-methyldihydroindolium bromide,

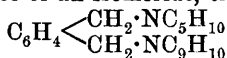
$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{NBr} \begin{smallmatrix} \text{CHMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH}_2$ , colourless, tetragonal prisms (with  $1\text{H}_2\text{O}$ , from water), which melts in its water of crystallisation at  $135\text{--}140^\circ$ , and, after re-solidifying, melts again at  $207^\circ$ ; the anhydrous substance crystallises from a mixture of chloroform and ether in hexagonal tablets; the more sparingly soluble *iodide*, obtained by precipitation from the bromide by potassium iodide, forms stellar aggregates of needles, m. p.  $220^\circ$ ; the *chloride*, obtained from the bromide by the action of silver chloride, forms hexagonal tablets, m. p.  $210^\circ$ .

When the above bromide is heated with aqueous ammonia for ten hours at  $200^\circ$  in a sealed tube, *propylenephénylen-*o*-xylylenediamine*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{NH} \cdot \text{CHMe} \\ \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH}_2$ , is obtained as an almost colourless, viscous oil, b. p.  $250\text{--}255^\circ/16\text{ mm.}$ , with slight decomposition. The presence of two secondary amino-groups in this substance was confirmed by treating with *o*-xylylene bromide and alkali hydroxide when a *bromide* of the structure

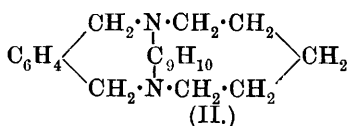
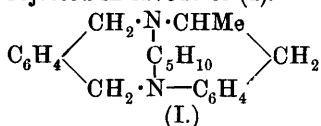


colourless prisms, m. p.  $112^\circ$ , was obtained, and was converted by successive treatment with silver oxide and chloroplatinic acid into the *platinichloride*, orange-yellow needles, m. p.  $177^\circ$  (decomp.).

2-Methyldihydroindole, when heated for eight hours at  $200^\circ$  with *o*-xylylenepiperidinium bromide in alcoholic solution, gave rise to ( $\alpha$ ) *o*-xylylenepiperidyl-2-methyldihydroindyl, colourless needles, m. p.  $87^\circ$  (*dimethiodide*, colourless needles, m. p.  $173^\circ$ , with decomp.), for which, on account of the existence of an isomeride, the structure



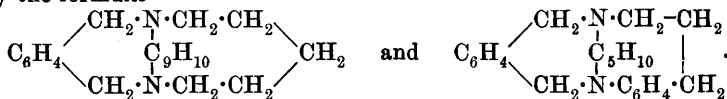
is rejected in favour of (I).



When *o*-xylylene-2-methyldihydroindolium bromide and piperidine were heated together in the presence of water, an *isomeride* ( $\beta$ ) of the preceding substance was obtained in colourless prisms, m. p.  $102^\circ$ ; this is a strong, reducing agent, liberating silver from silver nitrate in the presence of acetic acid; it forms a *methiodide*, tablets, m. p.  $200^\circ$ ; *perchlorate*, sparingly soluble prisms, m. p.  $182^\circ$ . Both the  $\alpha$ - and  $\beta$ -isomerides give deep red solutions in nitric acid. The existence of isomerism is attributed to the situation of the three valencies of tervalent nitrogen in one plane, one of the isomerides possessing the structure represented by formula (I), whilst the other may be represented by formula (II).

In an analogous manner to the preceding, tetrahydroquinoline reacts with *o*-xylylenepiperidinium bromide in the presence of alcohol at  $200^\circ$ , giving  $\alpha$ -*o*-xylylenepiperidyltetrahydroquinolyl, whilst the  $\beta$ -isomeride was produced by the interaction of *o*-xylylenetetrahydroquinolinium

bromide, colourless needles, m. p. 233° (previously described as an oil, Scholtz and Wolfrum, *loc. cit.*), and piperidine in the presence of water at 200°. The existence of these isomerides is again explained by the formulæ



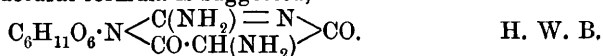
The  $\alpha$ -isomeride was an oil; *dimethiodide*, leaflets, m. p. 78°; *picrate*, orange-yellow needles, m. p. 116–117°. The  $\beta$ -isomeride forms colourless prisms, m. p. 89°; *methiodide*, stellar aggregates of needles, m. p. 206°; *perchlorate*, rhombic tablets, m. p. 196°.

The isomerism in each case was confirmed by molecular-weight determination. It is remarkable that, not only do the isomerides differ in physical properties but also in chemical, the  $\alpha$ -isomerides behaving as di-acid bases, whilst the  $\beta$ -compounds are only mon-acid. All these bases exceed brucine in their sensitiveness towards nitric acid, giving an intense red coloration even in dilute solution, a similar effect being also produced by other oxidising agents.

D. F. T.

**Vicine.** P. A. LEVENE (*J. Biol. Chem.*, 1914, **18**, 305–311).—The author supplements the work of Johnson and Johns on this compound (this vol., i, 366, 579). Crystalline vicine obtained from vetch meal has m. p. 242° and  $[\alpha]_D^{25} - 11.7^\circ$ . On heating at 100° with 20% sulphuric acid, divicine sulphate,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , appeared as a crystalline deposit. The compound differed from the sulphates of 4:5-diamino-tetrahydropyrimid-2:6-dione and of 2:5-diaminotetrahydropyrimid-4:6-dione, both of which were prepared by Traube's method (A., 1900, i, 416); but it is regarded as more closely allied to the latter than to the former, because of its behaviour towards nitrous acid and urea (uric acid formation).

After the removal of the divicine sulphate, dextrose was recognised in the filtrate, and vicine is therefore regarded as a nucleoside composed of 2:5-diaminotetrahydropyrimid-4:6-dione and dextrose. The following structural formula is suggested,



**The Diketotriazines.** J. BOUGAULT (*Compt. rend.*, 1914, **159**, 83–85).—The author has prepared a number of diketotriazines of the type  $\text{R} \cdot \text{C} < \begin{array}{c} \text{N} - \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} > \text{CO}$  by the action of warm dilute alkali on the semicarbazones of the corresponding  $\alpha$ -ketonic acids, the reaction being  $\text{R} \cdot \text{C} < \begin{array}{c} \text{N} - \text{NH} \\ \text{CO}_2\text{H} \quad \text{NH}_2 \end{array} > \text{CO} = \text{H}_2\text{O} + \text{R} \cdot \text{C} < \begin{array}{c} \text{N} - \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} > \text{CO}$ . The diketotriazines are crystalline substances, insoluble in water, but soluble in alcohol. Their melting points are much higher than those of the corresponding semicarbazones, and they can often be sublimed unaltered. They are acid, and on titration in alcoholic solution with phenolphthalein as indicator they behave as monobasic acids. They yield alkali salts and alkyl derivatives. The monoalkyl

derivatives obtained by the action of the monopotassium salts on alkyl iodides are crystalline, have lower melting points than the diketotriazines, and are more soluble in organic solvents. They also exhibit slight acidity towards phenolphthalein. The dialkyl derivatives are similarly prepared and have lower melting points than the monoalkyl derivatives. Alkalis decompose the monoalkyl derivatives, giving the corresponding alkylamines. The following diketotriazines have been prepared: *diketodimethylethyltriazine*,  $\text{CMe}_3 \cdot \text{C}_3\text{H}_2\text{O}_2\text{N}_3$ , m. p.  $285^\circ$ ; *diketophenyltriazine*,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_3\text{Ph}$ , m. p.  $262^\circ$ ; *diketop-methoxyphenyltriazine*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_2\text{ON}_3$ , m. p.  $273^\circ$ ; *diketobenzyltriazine*,  $\text{CH}_2\text{Ph} \cdot \text{C}_3\text{H}_2\text{O}_2\text{N}_3$ , m. p.  $208^\circ$ ; *diketophenylethenyltriazine*,  $\text{CHPh} \cdot \text{CH} \cdot \text{C}_3\text{H}_2\text{O}_2\text{N}_3$ , m. p.  $266^\circ$ ; *diketopiperonaethenyltriazine*,  $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_3\text{H}_2\text{O}_2\text{N}_3$ , m. p.  $282^\circ$ .

The method appears to be general, except for the fact that all attempts to prepare diketomethyltriazine (compare Thiele and Bailey, A., 1899, i, 169) in this way were unsuccessful. W. G.

**Quinonoid Oxidation Products of Dianisidine and their Polymerisation.** JAMES MOIR (*South African J. Sci.*, 1914, March).—By the rapid addition of a slight excess of concentrated aqueous ferric chloride to a solution of dianisidine in an excess of dilute hydrochloric acid below  $25^\circ$ , a substance,  $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_4\text{Cl}_2$ , bluish-black crystals, is immediately and almost quantitatively obtained, which is regarded as the *hydrochloride* of the quinhydrone of dianisidine and the unknown 3 : 3'-dimethoxydiphenokinonedimine. The corresponding *hydrobromide*,  $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_4\text{Br}_2$ , purple crystals, *basic nitrate*,  $\text{C}_{28}\text{H}_{31}\text{O}_4\text{N}_4(\text{NO}_3)$ , violet-black paste, *sulphate*,  $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_4(\text{SO}_4)$ , almost black substance, and *dichromate*,  $\text{C}_{28}\text{H}_{30}\text{O}_4\text{N}_4 \cdot 2\text{H}_2\text{Cr}_2\text{O}_7$ , blackish-violet cake, are described. These salts yield dianisidine by reduction with stannous chloride, undergo various colour changes by treatment with water and with acids, and yield by treatment with alkalis or aqueous ammonia, dianisidine and a base,  $\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_4$ , m. p.  $220$ — $240^\circ$ , dark brick-red substance. The base yields only dianisidine by reduction with hot stannous chloride, and forms olive basic salts and purple acid salts. The author regards it as a polymerised, 3 : 3'-dimethoxydiphenokinonedimine having the formula



and suggests that Willstätter and Kalb's diphenokinonedimine (A., 1905, i, 361) has a similar constitution. An attempt to prepare 3 : 3'-dimethoxydiphenokinonedimine by oxidising dianisidine in chloroform by lead peroxide resulted in the formation of the base,  $\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_4$ , together with a small amount of a higher polymeride,  $\text{C}_{42}\text{H}_{42}\text{O}_6\text{N}_6(?)$ , m. p.  $245^\circ$ . C. S.

**The Direct Fixation of Metals by Proteins.** A. BENEDICENTI and S. REBELLO-ALVES (*Biochem. Zeitsch.*, 1914, 65, 107—116).—A preliminary account is given of the solvent action of serum and egg-albumin on finely divided iron. This action takes place when all the carbon dioxide which can be removed by a pump has been eliminated, and also when the serum has been submitted to prolonged dialysis. The action is not a new suspension phenomenon, and the iron taken

up is partly masked. Various possible explanations of the action are offered by the authors. S. B. S.

**Composition of the Insoluble Gases Formed by the Decomposition of Organic Substances.** R. H. JESSE (*Chem. Zentr.*, 1914, i, 1682; from *University of Illinois, Bulletin*, 1912, 9, 47—61).—A gas explosion in a sewer has caused the author to compare the composition of the gas with that formed in other reservoirs. Methane was present to the extent of 85% in the sewer, compared with 70—73% in the reservoir. When compared with the figures of other investigators, the composition of the gases is shown to vary within wide limits, particularly with regard to nitrogen and carbon dioxide. The origin of the gases is to be found in the hydrolysis of proteins, which are peptonised and also converted into amino-acids, leucine, tyrosine and aromatic compounds. Gas is not evolved at this stage. Further, the amino-acids are converted into fatty or aromatic acids with formation of nitrogen and ammonia. The acids obtained by the decomposition of protein substances are transformed into simpler acids with evolution of hydrogen and methane. Carbamide is converted into carbon dioxide and ammonia, which is transformed into the carbonate; cellulose evolves carbon dioxide and hydrogen or methane, and yields fatty acids. Butyric and lactic acids are formed from starch and sugar, whereby, also, carbon dioxide, hydrogen and water are produced. In addition, fats undergo aerobic decomposition, and hydrogen sulphide and mercaptan are produced from organic sulphur compounds. H. W.

**Influence of the Mineralisation of the Caseins on their Solubility.** L. LINDET (*Compt. rend.*, 1914, 159, 122—124. Compare A., 1913, i, 1116, 1414).—The soluble caseins of colostrum contain less inorganic salts than those of milk. The soluble caseins of milk contain from 4.61—8.36% of phosphoric acid and from 7.22—14.97% of lime, whilst those of colostrum contain only from 0.6—1.4% of phosphoric acid and from 0.37—1.49% of lime. Further, the solubility of the caseins in milk serum, or even in water, is greater when they contain less mineral matter. W. G.

**The Conjugated Sulphuric Acid from Tendomucoid.** P. A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1914, 18, 237—240. Compare A., 1913, i, 917, 1006).—The analysis of the conjugated sulphuric acid obtained from tendomucoid shows that the components of this acid are identical with those of chondroitin-sulphuric acid, namely, chondrosamine, and glycuronic, acetic and sulphuric acids. Since the ratio of nitrogen to carbon was also 1:14, and the substance contained only one acetyl group in its molecule, the identity of the conjugated sulphuric acid from tendomucoid with that of chondroitin-sulphuric acid from cartilage is regarded as established. The melting point of the glycuronic acid osazone hydrazone obtained from either substance should be 122° (decomp.) instead of 115° as previously reported. H. W. B.



**The Chemistry of Proteolytic Ferments.** E. HERZFELD (*Biochem. Zeitsch.*, 1914, 64, 103—105).—By dialysing a certain quantity of pepsin in aqueous solution, a definite amount of substances yielding the ninhydrin reaction is obtained in the dialysate. When dialysed in 0.18% hydrochloric acid, less of such substances are obtained. The same phenomenon is observed in the case of peptones. The degrading action of pepsin in water and 0.18% hydrochloric acid is about the same. Peptone solution, both in water and in acid, also degrades proteins to the same extent in both solutions, but the peptone must be derived from the same protein as the substrate; thus, a peptone from egg-albumin will degrade this protein, whereas silk peptone will not. Trypsin in aqueous solution on dialysis gives in the dialysates substances yielding the ninhydrin reaction, but less of these are obtained from trypsin when dissolved in sodium carbonate. Trypsin will degrade proteins more rapidly in the presence of carbonates than in pure water. The same happens in the case of amino-acids, which degrade proteins; in this case the specificity is not so marked as in that of the peptones. On the ground of these experiments, the author puts forth the theory that pepsin owes its action to the peptones it contains, and trypsin to the amino-acids, and as peptones and amino-acids can act catalytically (in traces) in degrading proteins, there is no ground for regarding pepsin and trypsin as ferments. Similar generalisations are made with regard to other ferments. S. B. S.

**The Conditions of Action of Pepsin.** L. MICHAELIS and A. MENDELSSOHN (*Biochem. Zeitsch.*, 1914, 65, 1—15).—The optimal hydron concentration for peptic activity is about  $4 \times 10^{-2}$ . Salts cause a small transference of this point toward the less acid position. Pepsin is a ferment which follows the ordinary dissociation laws, and the free cation is the proteolytically active constituent. This peptic activity can still be detected when the hydron concentration reaches  $10^{-5}$ , and from this point onwards the precipitating (rennin) action increases, and the pepsin in an electric field wanders to the anode. These facts seem to indicate that the rennet action of pepsin is due to the anion. There is no evidence of a special casease which digests the casein clot in a medium which is only very slightly acid. S. B. S.

**Ferments. I. Estimation of Fermentative Change by means of the Interferometer. I. Application of the "Interferometric Method" to the Study of Protective Ferments.** PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1914, 91, 440—449).—In experiments such as Abderhalden's test for pregnancy the activity of the protective ferments leads to the formation of peptones which dissolve in the serum. The author's method for detecting such changes is to measure by means of the interferometer the change in concentration which occurs in the serum in consequence of the solution in it of the peptones. R. V. S.

**Mechanism of Oxidative Changes. III.** HEINRICH WIELAND (*Ber.*, 1914, 47, 2085—2111. Compare A., 1913, i, 1304).—In the

last communication, it was shown that certain typical biological oxidations are really processes of dehydrogenation; in other words, the catalytic action of the ferments concerned does not consist in an activating of oxygen, but rather in such an activating of the hydrogen atoms involved, that they are readily taken up by appropriate "acceptors."

The behaviour of aldehydes in presence of ferments is of especial interest. Three types of reactions have been recognised, namely, oxidation of the aldehyde, accelerated reduction of a third substance, such as methylene-blue or *p*-benzoquinone, and intramolecular redistribution of the aldehyde into the corresponding acid and alcohol. It is considered that these processes can be explained by the action of a single ferment, a "dehydrase," and that the assumption of separate oxydases, reductases, and mutases is therefore unnecessary. The aldehyde reacts in the form of its hydrate, and the ferment activates two of the hydrogen atoms, which are then taken up by an "acceptor." This may be oxygen or methylene-blue, etc., or it may be the non-hydrated aldehyde, which would account for the mutase action, thus,  $R \cdot CH(OH)_2 + R \cdot CHO = R \cdot CO_2H + R \cdot CH_2 \cdot OH$ . What the end result may be, whether it manifests itself as an oxidation or reduction or "mutation" or a mixture of these effects, depends on the concentration and speed of reaction of the various "acceptors." These conclusions are illustrated quantitatively in the case of Schardinger's milk ferment and salicylaldehyde.

In the first place, when salicylaldehyde and fresh, unboiled milk are left in an atmosphere of nitrogen, salicylic acid and saligenin are formed. In air or oxygen, more acid and less alcohol are formed, since the oxygen competes with the aldehyde-anhydride as an "acceptor" of the activated hydrogen of the aldehyde-hydrate. In presence of methylene-blue, in an atmosphere of nitrogen, still less alcohol is formed, the speed at which the dye takes up the hydrogen being much greater than in the case of oxygen. Against the assumption that all these effects are to be referred to the action of one ferment on salicylaldehyde, two objections may be raised, both of which have been answered. In the first place, it is necessary to show that salicylic acid and saligenin themselves are not affected by the ferment, in the presence of air or methylene-blue, which is, indeed, the case. Then it might be argued that a ferment specific to, say, the mutase action, would be damaged or destroyed by the presence of, say, methylene-blue. It is well known that the milk enzyme soon becomes inactive and this is especially so in the presence of the aldehyde, oxygen, or methylene-blue. A kinetic study of the above reactions shows, however, that the decrease in activity follows the same course in each case. This would not be expected if three different enzymes were at work, and is, therefore, evidence in support of the "dehydrase" theory.

Further studies were made on the influence of the concentration of the aldehyde on the reactions. The effect on the reaction depends, not only on the speed at which the aldehyde is activated, this being raised by increased concentration, but also on the speed at which the "acceptor" combines with the hydrogen. The mutase effect in a

nitrogen atmosphere is considerably influenced, but not so the oxidation in oxygen, since this gas acts very slowly as an "acceptor." It is therefore possible, under certain conditions of concentration, that more salicylic acid will be formed in nitrogen than in oxygen. Methylene-blue, however, acts as an "acceptor" about eight times as fast as oxygen, so the reduction of the dye is considerably accelerated by raising the concentration of the aldehyde, within certain limits.

Reference must be made to the original for details of the very many experiments. Underlying them all, was the separation and estimation of salicylic acid and saligenin. For this purpose, the warm mixture was treated with 4*N*-sulphuric acid and left overnight. An aliquot part of the filtrate from the casein (usually 150 c.c.) was shaken with 120, 100, 80, and then 50 c.c. of ether, and the extract was dried and concentrated to 5 c.c. in a 30 c.c. bottle. The unchanged aldehyde was then removed as the bisulphite compound and the salicylic acid was extracted from the ethereal solution by sodium hydrogen carbonate, and the saligenin by sodium hydroxide. The respective aqueous solutions were decomposed by sulphuric acid, extracted with ether, and the extracts were dried and evaporated. The substances were obtained pure enough to weigh, but their purity was controlled by titration. For the estimation of saligenin, an approximately 0.4% solution was treated with an excess of 0.2—0.3*N*-bromine water, and, after twenty seconds, the excess was determined iodometrically. Under these conditions, a constant amount of 5.38 equivalents of bromine is absorbed by saligenin. It is extremely difficult to recover the whole of these compounds from milk, but 60—65% of the acid and 90% of the alcohol may be regularly separated by the above method. J. C. W.

**Mineral Water and Catalysis. Action of Philothion on Treatment with Water from Sulphur Springs.** J. DE REY-PAILHADE (*Chem. Zentr.*, 1914, i, 1210; from *Bull. gén. Thérap.*, 1913, No. 18, 8 pp. Compare A., 1906, i, 999).—The rôle of hydrogenating ferments and the specific action of the sulphur in waters from sulphur springs on philothionic hydrogen are discussed. Hydrogen sulphide is formed in the stomach by the action of the sulphur of the gastric juice on the water, and, occasionally, separation of free sulphur occurs. The latter, in contact with the philothion of the epithelial cells, forms hydrogen sulphide, which is added to that derived from the decomposition of sulphides. The hydrogen sulphide passes rapidly into the circulation, and, in a more oxidising medium, is converted into water and free sulphur, the latter being very finely divided or, possibly, in colloidal or atomic form. The sulphur is carried by the blood into all the organs, and again combines with philothionic hydrogen to yield hydrogen sulphide, whilst the philothionic hydrogen is regenerated by abstraction of hydrogen from the food. The cycle of operations is continuously repeated, and thus the philothionic hydrogen behaves as a hydrogenating catalyst, yielding hydrogen sulphide, whilst, on the other hand, the sulphur behaves as an oxidising catalyst, since it ultimately forms water from the free oxygen and the hydrogen of the food. Whereas the sulphur of the food is incapable of reacting with philothionic hydrogen and is thus

without influence, that supplied in the sulphur water increases the oxidation of the hydrogen in the foodstuffs. H. W.

**Preparation of Arseno-metallic Derivatives.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270258. Compare this vol., i, 345, 761).—In the preparation of these compounds, the use of ready-formed arseno-compounds may be avoided, as they may be formed by reduction of the corresponding substituted arsenic acids or oxides in presence of metallic salts. T. H. P.

**Preparation of Methylglycylphenylarsinic Acid and its Reduction Product, Bismethylglycylarsenobenzene.** LES ÉTABLISSEMENTS POULENC FRÈRES and KARL OECHSLIN (Fr. Patent, 462276).—*Methylglycylphenylarsinic acid*,  $\text{AsO}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained by hydrolysis of its esters by means of excess of sodium hydroxide at about  $60^\circ$  and subsequent acidification, forms small, white crystals, and when heated does not melt, but yields carbon dioxide and dimethylaminophenylarsinic acid, which decomposes at  $280\text{--}300^\circ$ . On reduction by means of sodium hyposulphite at a high temperature, it is converted into *bismethylglycylarsenobenzene*,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{As} \cdot \text{As} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ . T. H. P.

**Preparation of Additive Metallic Derivatives of Arseno-phosphorus and Arseno-antimony Compounds.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270259).—Additive compounds of metallic salts with organic arseno-phosphorus and arseno-antimony compounds may be obtained by methods similar to those described earlier (this vol., i, 345, 761). They are very similar to the arseno-metallic derivatives and are of therapeutic value. T. H. P.

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## Physiological Chemistry.

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**The Basal Gaseous Metabolism of Normal Men and Women.** FRANCIS G. BENEDICT, LOUIS E. EMMES, PAUL ROTH, and H. MONMOUTH SMITH (*J. Biol. Chem.*, 1914, **18**, 139—155).—The authors record the respiratory exchanges of a large number of healthy persons, male and female, with the corresponding temperature and pulse rate. The observations were usually made for periods of fifteen minutes, the average of several periods, taken on the same or different days, being recorded. A discussion of the results is not appended.  
H. W. B.

**The Sensitiveness of Oxygen Respiration [of the Cell Granule] towards Indifferent Narcotics.** OTTO WARBURG (*Pflüger's Archiv*, 1914, **158**, 19—28).—The respiratory function of the granules contained in a centrifugalised extract of liver with

dilute potassium chloride solution is depressed 50% by the following concentrations of narcotics expressed in milli-mols. per litre: methyl carbamate, 960; urethane, 360; propyl carbamate, 150; isobutyl carbamate, 33; isoamyl carbamate, 14. On the other hand, the aqueous extract of liver, containing material dissolved out of the granules, has less respiratory power than the suspension of granules, and considerably greater concentrations of the narcotics must be employed to bring about a 50% depression of respiratory power, namely, methyl carbamate 2000 milli-mols. per litre, urethane 740, propyl carbamate 500, isobutyl carbamate 90, isoamyl carbamate 40. The granules, therefore, are not enzymes, but organised structures (organisms). H. W. B.

**Elimination of Carbon Dioxide during Manual Labour.** GÖSTA BECKER and J. W. HAMÄLÄINEN (*Chem. Zentr.*, 1914, i, 1359; from *Skand. Archiv. Physiol.*, 31, 198—240).—The elimination of carbon has been determined for a series of manual workers who were employed at their respective occupations in a large breathing chamber for three experiments, each lasting two hours. Experiments were performed on two workers for each occupation, and a remarkable similarity was found in the elimination of carbon by different persons similarly employed. The varying demands of different occupations on the bodily strength of the workers are well marked by the figures obtained for the carbon elimination. They are least, for example, for cobblers and tailors, greatest for masons and sawyers. The average of the carbon elimination (in grams) in the middle of the working period is 15.63 or 15.56 for cobblers, 11.27 or 12.31 for tailors, 37.07 or 33.28 for masons, and 45.50 or 40.96 for wood sawyers. Of female workers, sempstresses (7.5 or 8.0) are at one end of the scale, washerwomen (25.91 or 16.91) at the other end. H. W.

**The Intake of Methyl Alcohol in Inspiration.** A. LOEWY and R. VON DER HEIDE (*Biochem. Zeitsch.*, 1914, 65, 230—252).—Rabbits and dogs were exposed in a respiration chamber to air containing various quantities of methyl alcohol vapour. These amounts could be regulated by passing air through methyl alcohol in various dilutions in water. The air was measured by a meter, and the amount of alcohol was estimated at the beginning and end of the experiment. The toxic effects were noticed, and the alcohol in the animal bodies was estimated at the end of the experiment. In the presence of only 0.2% of alcohol in the air, quite appreciable quantities were taken up by the organism. With alcohol of this tension, and up to 0.5%, the saturation of the animal body is reached in two hours. With higher concentrations, the times required for saturation are markedly longer, and when the tension reached 2½% the maximal amount is not taken up even after eight hours. Fat animals, under similar conditions, take up less alcohol than lean ones. This is due to the small solubility in lipoids of methyl alcohol; the coefficient of distribution between oil and water is about 2½ : 100. S. B. S.

**The Absorption and Dissociation of Carbon Dioxide by the Human Blood.** JOHANNE CHRISTIANSEN, C. G. DOUGLAS, and J. S. HALDANE (*J. Physiol.*, 1914, 48, 244—271).—Under normal conditions, the curve representing the relation between the amount of carbon dioxide taken up by fresh, defibrinated blood and the pressure of the gas is a very definite constant for the same individual, and does not vary very much for different individuals. At 40 mm. pressure, 100 volumes of oxygenated human blood take up about 50 volumes of gas, and at 80 mm. about 15 volumes more. Blood which has been deprived of oxygen takes up more carbon dioxide than oxygenated blood under the same pressure. Oxygen tends, therefore, to drive out the carbon dioxide, and the action depends on the saturation of the hæmoglobin. A curve is given showing the extent of this action with varying pressures of carbon dioxide. By means of these facts, an explanation is offered as to the method by which carbon dioxide is driven out of the lungs by oxygenation. With the help of these and other data, it is also shown how it is possible to calculate the carbon dioxide pressure of the venous blood reaching the lungs, and the rate of blood flow through these organs. S. B. S.

**The Rate of Disappearance of Ammonia from the Blood in Normal and in Thyroidectomised Animals.** CLARA JACOBSON (*J. Biol. Chem.*, 1914, 18, 133—137. Compare A., 1910, ii, 324; 1911, ii, 632).—The author has determined the rate of disappearance of ammonia from the circulating blood after intravenous injections of ammonium carbonate, the renal vessels being ligatured to prevent escape through the kidney. The ammonia was estimated by a modification of Folin's method, the normal quantity present in cat's blood being 0.6 mg. per kilo. body-weight.

So rapidly does ammonia disappear from the blood, that five minutes after the injection of ammonium carbonate equivalent to 100 mg. of ammonia per 100 c.c. of blood, the ammonia content of the blood is scarcely above normal. No perceptible difference is observed in the case of parathyroidectomised animals, and even when the liver is also excluded the ammonia content of the blood five minutes after the injection is not more than 8 mg. per 100 c.c. of blood. H. W. B.

**The Distribution of Glycogen in the Blood During Resorption of Carbohydrates from the Small Intestine.** OSW. POLIMANTI (*Biochem. Zeitsch.*, 1914, 64, 490—494).—A dog was killed during the height of digestion after a diet rich in carbohydrates, and the amount of glycogen in various parts of the circulation was determined. The following quantities were found in 100 grams of blood: in the carotid artery, 58.21 mg.; in the *vena cava abdominalis*, 34.25; and in the portal vein, 96.75. The author expresses the opinion that the synthesis of glycogen takes place in the intestinal wall. S. B. S.

**The Fermentative Properties of the Blood. IV. The Proteoclastic Properties of the Formal Elements of the Blood.**

LUDWIG PINCUSOHN and KURT RÜDIGER VON ROQUES (*Biochem. Zeitsch.*, 1914, **64**, 1—12. Compare A., 1913, i, 788, 1404; this vol., i, 895).

—The proteoclastic action of the blood corpuscles (intact and lysed) from various species on different organs was investigated, the Abderhalden dialysis method being employed. It was found invariably that no proteoclastic action could be detected when ninhydrin was used as the reagent. S. B. S.

**The Esterase of Blood. VI. Comparative Experiments with the Lipase of the Pancreas and the Esterase of the Blood.** P. RONA and Z. BIEN (*Biochem. Zeitsch.*, 1914, **64**, 13—29. Compare this vol., i, 341).—The optimal activity of the pancreatic lipase lies between  $p=8.3$  and 9, a region distinctly more alkaline than that found for blood lipase. The anions are the active portion. The acid dissociation constant is  $1.8 \times 10^{-7}$ , as compared with  $1 \times 10^{-6}$  for the blood lipase. The two lipases are not therefore identical. The action of the pancreatic lipase is accelerated by calcium, barium, magnesium, and manganese salts, which are without action on the blood lipase. Sodium fluoride inhibits the blood-lipase action to a much larger extent than it does that of the pancreatic lipase. The latter appears to act in a heterogeneous, the former in a homogeneous, system. S. B. S.

**Fibrin in its Relation to Problems of Biology and Colloidal Chemistry. The Problem of Blood Coagulation. IV. Formation of Gels in Liquid Plasma and Transudates obtained by the Action of Acids; the Reversibility of these Gels and the Properties of their Sols. The Significance of Alkalescence as a Factor in Delaying or Checking Coagulation.** E. HEKMA (*Biochem. Zeitsch.*, 1914, **64**, 86—102. Compare this vol., i, 754, 895).—Gel formation in natural fluids containing fibrinogen (transudates, etc.) can be slowed or inhibited by the addition of alkalis, but can be caused to take place, on the other hand, by the addition of acids or acid salts, until the liquid is near the neutral point. Such natural fluids behave towards acids and alkalis in the same way as the artificially prepared alkaline hydrosol of fibrin. The gels produced from such preparations, and those prepared from natural liquids by acids, are quite similar in their properties. The gels produced by "spontaneous" clotting of natural fluids and by serum from natural fluids and alkali hydrosols are also similar. All the gels produced by various methods are reversible. It is presumed that gel-formation is in all cases due to the same protein. S. B. S.

**Fibrin in its Relation to Problems of Biology and Colloidal Chemistry. The Problem of Blood Coagulation. V.** E. HEKMA (*Biochem. Zeitsch.*, 1914, **65**, 311—331. Compare this vol., i, 754, 895, and preceding abstract).—The author supplements his previous work with certain experiments on the influence of salts on gel-formation from plasma and transudates. S. B. S.



**The Physico-chemical Mechanism of Hæmolysis by Specific Hæmolysins. II. The Electrical Conductivity of Sensitised Corpuscles and the Action of Inorganic Ferments or Metal-sols on them.** UPENDRA NATH BRAHMACHARI (*Biochem. J.*, 1914, 8, 227—229. Compare this vol., i, 347).—The adsorption of amboceptor by erythrocytes is followed by a diminution in the electrical conductivity of the corpuscles, due to the combination of the amboceptor with the corpuscular wall.

Metal sols, as well as other catalysts, such as animal charcoal, platinum black, and colloidal iodine, do not bring about any hæmolysis of sensitised corpuscles. H. W. B.

**Influence of a Number of Foods on the Secretion of the Digestive Glands.** OSKAR WOLFSBERG (*Zeitsch. physiol. Chem.*, 1914, 91, 344—371).—Meat, meat extract, and milk cause an increase in secretion in the proportion to the quantity of food introduced, whilst potato, butter, bread, and probably sugar do not. The increased secretion is due to "extractives," which activate the hormone of the pyloric mucous membrane. The amount of secretion caused by a given stimulus in given circumstances is approximately constant. When the amount of secretion is doubled, the time required to empty the stomach is not doubled; it is often hardly increased. R. V. S.

**The Dynamic Side of Biochemistry.** F. GOWLAND HOPKINS (*Rep. Brit. Assoc.*, 1913, 652—668).—Presidential address to Section I (Physiology). Metabolism deals mainly with simple molecules, and a very large part of the chemical dynamics of the cell consists of simple reactions catalysed by independent specific enzymes.

C. H. D.

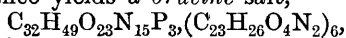
**The Relationships of Lactic Acid to Carbohydrate Metabolism. I. The Appearance of Lactic Acid in the Urine of Rabbit in Phosphorus Poisoning.** OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1914, 64, 131—155).—No increase in the lactic acid was observed in the urine of rabbits which had been fed on greens when doses of 0.005 to 0.20 gram of phosphorus were administered. On the other hand, such an increase took place when much sugar was administered, either immediately after poisoning or in the terminal stages of the toxic action. The increase, however, was small compared with the amount of sugar ingested, and this fact gives the impression that the acid is not a direct product of sugar metabolism, but is perhaps derived from a "lactacidogen." There was no relationship between the amount of lactic acid in the urine and the alimentary glycosuria. Glycer-aldehyde ingestion caused no increase in lactic acid, and dextrose-phosphates caused only such an increase as could be due to the combined sugar. S. B. S.

**The Relationships of Lactic Acid to Carbohydrate Metabolism. II. The Lactic Acid Secretion in the Urine of Rabbits which have been Submitted to Low Temperature.** OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1914, 64, 156—171).—Rabbits

in which the body-temperature has been reduced to  $30^{\circ}$  by immersion in a cold bath excrete lactic acid in the urine. This phenomenon will happen several times with the same animal, provided only that a sufficient interval has elapsed between the intervals of cooling. It seems, therefore, that the animal does not possess an unlimited supply of material yielding lactic acid (lactacidogen). If the animal is submitted to the cooling process when on a diet rich in sugar, it tends readily to excrete the acid, but if the same animal is cooled when in a condition of starvation, after adrenalin injection (so that the body is deficient in carbohydrates), then the increased excretion of lactic acid will disappear. The excretion of lactic acid appears to depend in some way, therefore, on the condition of the supply of carbohydrate in the animal. In one experiment the administration of excess of sugar, without cooling, produced an increased secretion of lactic acid. S. B. S.

**The Influence of a Vitamine-free Diet on the Carbohydrate Metabolism.** CASIMIR FUNK and COUNT ERWIN VON SCHÖNBORN (*J. Physiol.*, 1914, 48, 328—331).—Pigeons kept on a vitamine-free diet develop hyperglycæmia, with a diminution of the glycogen of the liver. The hyperglycæmia is especially marked in a sugar-free diet, which is followed by the disappearance of the liver glycogen. The addition of vitamine from yeast to such a diet produced in three cases a marked diminution of sugar in the blood and a formation of glycogen in the liver. Vitamine appears, therefore, to affect the carbohydrate metabolism. In the case of the fat-free diet, the glycogen of the liver is increased. S. B. S.

**Nuclein Metabolism. I. Digestion of Yeast Nucleic Acid by Human Duodenal Juice. Isolation of Triphosphonucleic Acid.** S. J. THANNHAUSER (*Zeitsch. physiol. Chem.*, 1914, 91, 329—335).—The product of this digestion (prolonged for seventy-two hours under toluene) does not contain nucleosides or free purine bases, but free phosphoric acid is present. From the mixture a substance, termed *triphosphonucleic acid*, can be isolated. It has the composition  $C_{32}H_{49}O_{23}N_{15}P_3$ ,  $[\alpha]_D^{17} - 19.6^{\circ}$ . The rotatory power and the titratable acidity of different preparations is the same. The substance yields a *brucine* salt,



which crystallises in prisms, m. p.  $200-205^{\circ}$ . When hydrolysed with ammonia in an autoclave, triphosphonucleic acid yields guanosine, adenosine, and cystidine. R. V. S.

**Nuclein Metabolism. II. Metabolism Experiments with Adenosine and Guanosine.** S. J. THANNHAUSER and A. BOMMES (*Zeitsch. physiol. Chem.*, 1914, 91, 336—343).—In rabbits, injection of adenosine or guanosine is followed by an increased excretion of allantoin corresponding with 40% of the substance injected. In healthy men the injection is followed by an increase in the excretion of uric acid (75—82% of the corresponding amount), but no

increase takes place in the uric acid of the blood. In a case of severe gout, no increase in uric acid excretion was observed; in a less severe case a delayed increase in the excretion of uric acid took place. In cases of gout, the amount of uric acid in the blood rises after each injection. In three out of four cases of gout, injection was followed by an attack of gout.

R. V. S.

**Purine Metabolism. I. The Effect of Adrenaline on the Elimination of Allantoin in the Dog.** W. FALTA (*Chem. Zentr.*, 1914, i, 1360; from *Zeitsch. expt. Path. Ther.*, 15, 356—358. Compare Abl, this vol., i, 111).—Experiments show a considerable (about 30%) increase in the elimination of allantoin during the adrenaline periods. Elimination of uric acid is slightly increased.

H. W.

**The Nutrition of Mice on Diets containing Simple Food-stuffs.** F. RÖHMANN (*Biochem. Zeitsch.*, 1914, 64, 30—62).—An account is given of a long series of experiments on diets containing a mixture of pure proteins (caseinogen, egg-albumin, edestin) with starch, fat, and salts. It was found that whereas several such diets were sufficient for the maintenance of adult animals, they were unsuitable for young individuals, in which often, after a short period of development, growth ceased. Certain additions to the diet, such as malt extract and yeast, greatly increased the efficiency, even when administered to young animals. It is claimed that by the last experiments (carried out in 1902) it was demonstrated for the first time that it was possible to rear animals on an artificial diet compounded of simple food-stuffs. A long series of experiments on the value of different proteins is also described; too many factors are, however, involved for any definite conclusions to be drawn. Proteins containing phosphorus (nucleo-proteins) and lecithin were not found to be indispensable. The author discusses the results obtained by Osborne and Mendel in a similar series of experiments, and puts forward a claim for priority.

S. B. S.

**Experiments with Diets which are Qualitatively Insufficient.** S. OSEKI (*Biochem. Zeitsch.*, 1914, 65, 158—176).—Rye bread prepared with water is a far more efficient diet for mice than bread prepared from fine wheat flour. The addition, however, of milk, pressed yeast, cruder rye and wheat flours, and the extracts of the same can increase the nutritive value of the fine wheat bread, and even make it equivalent to that of the rye bread. The accessory food substances contained in the rye bread can be readily extracted with water, but not with alcohol and ether, and are apparently, therefore, not identical with the food adjuvants which have been obtained from milk.

S. B. S.

**Suitability of Hardened Fats for Use as Human Foods.** K. B. LEHMANN (*Chem. Zeit.*, 1914, 38, 798—799).—Hardened fats prepared from earthnut, cottonseed and sesame oils were found to

contain from 0.1 to 6 mg. of nickel per kilo. of fat, quantities which are considerably less than those found occasionally in foods prepared in nickel utensils; this slight metallic contamination is not injurious to health, and the author is of opinion that hardened fats may be used as substitutes for the ordinary edible fats, this conclusion being confirmed by the fact that feeding experiments with hardened fats yielded satisfactory results. W. P. S.

**The Chemical Determinants of Growth.** CASIMIR FUNK and ARCHIBALD BRUCE MACALLUM (*Zeitsch. physiol. Chem.*, 1914, **92**, 13—20. Compare Osborne and Mendel, A., 1913, i, 1128).—The authors were unable to maintain rats for more than forty-seven days on an artificial diet of purified casein, starch, sugar, lard and salts, together with butter. The conclusion drawn is that the "protein-free" milk used by Osborne and Mendel in their experiments must contain the growth vitamine, since the rats fed by these experimenters on a similar diet plus "protein-free" milk were maintained practically as long as rats fed on ordinary food.

The authors also describe the effect of feeding chickens with polished rice with and without the addition of cod-liver oil. Without the addition, the chickens die of polyneuritis within two months. The addition of the cod-liver oil prevents polyneuritis, but does not promote growth, showing the presence of anti-polyneuritic vitamine and absence of growth vitamine respectively. The seven months' old chicken has not increased in weight during the last five months, and possesses no secondary sexual characters. A striking photograph showing the relative sizes of chickens fed on polished rice and cod-liver oil, and on a normal diet, is appended. H. W. B.

**The Movements of the Intestinal Villi.** B. F. HAMBLETON (*Amer. J. Physiol.*, 1914, **34**, 446—447).—Microscopical observations have been made by the author on the movements of the intestinal villi when treated with various solutions. Peptone, dextrose, weak alkali carbonates, etc., call forth (1) lashing movements, and (2) alternating shortening and lengthening of the villi. Dilute hydrochloric acid checks the movements, and the villi return to the resting condition and become covered with mucus. Alcohol of 10% strength first stimulates, then depresses, and soon stops the movements entirely. The addition of water or salt solution restores activity again. The behaviour to various drugs has also been investigated. H. W. B.

**The Action of Univalent Alcohols on the Surviving Intestine of the Rabbit.** YAS KUNO (*Arch. expt. Path. Pharm.*, 1914, **77**, 206—217).—Portions of the rabbit's intestine have been suspended in isotonic Tyrode solution to which increasing quantities of methyl, ethyl, propyl, butyl and amyl alcohols have been added, and the effect on the intestinal movements graphically recorded. The chief effect is an inhibitory one, which becomes more pronounced as one passes from methyl up to the amyl alcohol.

With very small doses, the movements may first become slightly greater, but this effect soon passes off, and is replaced by inhibition. The action of the alcohols alters the extent of the movements of the tissue, the actual frequency remaining unchanged.

H. W. B.

**Carbon Dioxide Production from the Nerve Fibre in an Atmosphere of Hydrogen.** SHIRO TASHIRO and H. S. ADAMS (*Amer. J. Physiol.*, **34**, 405—413. Compare A., 1913, i, 313; ii, 725).—The author has measured by his new method (*loc. cit.*) the amounts of carbon dioxide evolved from the claw nerve of the spider crab when placed in air and in an oxygen-free atmosphere. In the absence of oxygen, the claw nerve gives off decidedly less carbon dioxide than in air, and the application of a weak induction current which, in air, stimulates the nerve and more than doubles its carbon dioxide output, fails, in the oxygen-free atmosphere, to bring about any acceleration in the production of this gas. These results indicate that oxygen is primarily concerned in nerve metabolism, and are in harmony with the view that the real basis of all protoplasmic irritability is a chemical one.

H. W. B.

**The Relation between the Electrolyte Concentration of Some Neutral Perfusion Liquids and the Frequency of Beat of the Frog's Heart.** MARY D. WALLER (*Proc. physiol. Soc.*, xlviii—1; *J. Physiol.*, 1914, **48**).—The replacement of part of Ringer's solution by a neutral isotonic solution of a non-electrolyte (carbamide or sucrose) in a perfusing fluid produces a definite diminution of the number of heart-beats, depending on the amount of the substitution.

S. B. S.

**Carbohydrate Metabolism of the Isolated Heart of Normal and Diabetic Animals.** O. LOEWI and O. WESELKO (*Pflüger's Archiv*, 1914, **158**, 155—188).—Glycogen in the rabbit's heart is not used up on perfusion with Locke's fluid, but it almost completely disappears if the dextrose is omitted from the perfusion fluid. Substitution of levulose for the dextrose, as well as other alterations in the composition of Locke's fluid, also lead to glycogenolysis. Similar results are obtained with hearts from rabbits previously injected with adrenaline (adrenaline-hearts).

Perfusion of normal and adrenaline-hearts from ill-nourished rabbits with Locke's fluid shows that the latter have to some extent lost their power of decomposing the dextrose. Reduction of the amount of potassium or calcium in the Locke's fluid increases the glycolytic action of the adrenaline-heart, a similar effect not being observed with the normal heart. If the perfusion fluid, containing 0.02% of potassium chloride, after leaving the heart, is shaken with oxygen or nitrogen at 38°, the dextrose disappears. This is due to the presence of formed elements from the heart, for, by centrifugalising, the perfusion fluid may be clarified, and has then no glycolytic power.

H. W. B.

**Degradation of Cholesterol in Animal Organs. VI. Cholesterol. Bile Acids.** I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1914, 91, 309—328. Compare A., 1913, i, 932).—The unsaponifiable portion of the fat of the liver consists partly of cholesterol and partly of the so-called "non-cholesterols." The latter are cholesterol derivatives, however, for on oxidation, the acetic acid-sulphuric acid reaction of oxycholesterol can be obtained. This reaction is also given (after oxidation) by the bile acids and by the bile itself.

R. V. S.

**Mobilisation of Sugar in the Surviving Liver of the Cold-blooded Animal.** A. FRÖHLICH and L. POLLAK (*Arch. exp. Path. Pharm.*, 1914, 77, 265—298).—The authors have endeavoured to ascertain whether the glycosuria resulting from the administration of various substances to the cold-blooded animal is due to a direct action on the liver cell, leading to the formation of sugar from stored glycogen, or is an indirect one operating through the nervous system.

Direct perfusion of the surviving liver of the frog with adrenaline leads to glycogenolysis, but this is prevented if ergotoxin, which paralyzes sympathetic nerve endings, is simultaneously present in the perfusion fluid. On the other hand, ergotoxin does not inhibit the glycogenolysis brought about by ether or pituitary extract, which, therefore, has a different point of attack in the liver, leading, however, to the same end-result.

The formation of dextrose following perfusion with pyruvic and other ketonic acids is due, not to their being transformed into dextrose, but to their stimulating action on glycogenolysis, because the effect is immediate, even at the low temperature and depressed metabolic activity associated with the tissues of the cold-blooded animal. Moreover, other ketonic acids, such as benzoylactic acid, from which dextrose could not readily be produced, bring about the same effect, and, further, their action is annulled if ergotoxin is also added to the perfusing solution exactly as is the action of adrenaline.

As to the cause of the increased glycogenolysis, it may be due to an easier passage of the diastase to the glycogen in the cell or to the new formation of, or activation of, preformed enzyme. Perfusion with a diastase solution does not hasten the change; neither does the addition of adrenaline hasten glycogenolysis in minced liver; but ether does. The conclusion so far is that different agents act in different ways.

H. W. B.

**The Importance of the Liver in the Formation of Urea from Amino-acids.** CYRUS H. FISKE and JAMES B. SUMNER (*J. Biol. Chem.*, 1914, 18, 285—295).—Experimental evidence is brought forward showing that the liver is not the only site of the formation of urea in the animal organism.

The influence of the liver, kidney, and other abdominal organs on the blood circulation in the cat has been removed by the ligation of the corresponding arteries and veins, and it has then

been found that the injection of solutions of amino-acids is followed by the formation of urea, just as when the liver is present. The increase in urea was observed in both blood and muscles, and was of about the same extent in "operated" as in "control" animals.

H. W. B.

**The Ferments of the Pancreas. IV. Steapsin.** JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1914, 48, 287—302).—The stability of steapsin in alkaline solution is similar to that of trypsin. Fresh pancreatic juice loses 10% in an hour at 40°, 50% at 50°, and at 60° the whole is destroyed within five minutes. Steapsin is stable in the presence of large quantities of the higher fatty acids, but is rapidly destroyed by minute amounts (0.02*N*-hydrochloric acid) of free mineral acids. It cannot exist in the presence of free trypsin, and is therefore rapidly destroyed when pancreatic juice is activated by enterokinase. Serum or egg-albumin protect the steapsin from destruction under these conditions, owing to their containing antitrypsin. The lipolytic activity is largely increased by bile and bile salts, but electrolytes have little influence. There is no evidence that pancreatic steapsin can be separated into an enzyme and co-enzyme. The destruction of steapsin by trypsin is absolute, and the ferment cannot be reactivated by the addition of serum or bile.

S. B. S.

**Physiology of the Thyroid. IV. Fate of Iodine in the Thyroid Gland.** F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1914, 91, 400—424. Compare this vol., ii, 670).—Most of the iodine of the thyroid gland is present in the form of a compound with protein, but a small portion exists in the form of compounds soluble in acetone; among these the presence of free alkali iodide can be demonstrated. Alkali iodide occurs in this way, even when it cannot have been contained in the food. The quantity of iodine found in the thyroid gland varies greatly; in the sheep 1—1.5 milligrams per gland is an average value; in the dog the quantity is less on the average, but varies more. When alkali iodide is administered, the amount of iodine in the thyroid increases, but it is present there in organic combination. The iodo-protein of the thyroid (thyreoglobulin) has not a constant iodine percentage; the percentage increases after administration of alkali iodide. Administration of alkali iodide after removal of one lobe of the gland causes an increase in the amount and iodine percentage of the thyreoglobulin in the remaining lobe. When iodine is no longer present in the food, it remains in the thyroid, and if it was present there in unusual amount before, the amount remains high afterwards.

R. V. S.

**Physiology of the Thyroid. V. Does Iodine Occur in Blood?** F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1914, 91, 450—464).—Iodine found in the blood can be considered of thyroid origin only if it is in organic combination, and this the authors have been unable to find in normal blood. Iodine in inorganic

combination when present in the blood has arisen from the food, and is a transient occurrence. Animals fed with iodine-free food have no inorganic iodine in their blood, although their thyroids contain much iodine.

After administration of alkali iodide "inorganic" iodine can be detected in the blood for a long time. In some pathological conditions (eclampsia, nephritis) "organic" iodine probably of thyroid origin can be found in some of the cases.

R. V. S.

**The Significance of the Thyroid Gland in Carbohydrate Metabolism.** GUNNAR BÖE (*Biochem. Zeitsch.*, 1914, 64, 450—470).—The experiments were carried out on rabbits, and the estimations of blood-sugar were made by Bang's microchemical method. The values of the blood-sugar are not altered either by hypo- or hyperthyroidism. The administration of thyroid gland does not alter the action of adrenaline on the blood-sugar. On the other hand, it inhibits the action of pituitrin on adrenaline hyperglycæmia. In hyperthyroidism the inhibitory action of pituitrin on the thyroid is weakened, whereas in athyroidism it is increased. Some months after thyroidectomy, an increase in the weight of the pituitary body can be observed; in the course of this time the diminished action of the thyroids on the pituitary body is compensated; anatomical investigations show that the compensation takes place contemporaneously with a hypertrophy of the glandular portion of the pituitary body; this organ appears, therefore, to act as a reserve to the thyroid action on the blood-sugar.

S. B. S.

**The Active Principle of the Pituitary Body.** M. GUGGENHEIM (*Biochem. Zeitsch.*, 1914, 65, 189—218).—In addition to the ordinary proteinogenous amines which occur in other organs, the pituitary body contains a specific substance, which can be distinguished by its characteristic actions on blood pressure and respiration, but, above all, by its production of increased tone in the rat's uterus. The substance in question is extremely sensitive to the action of alkali hydroxides, which destroy it, and is in this respect analogous to pilocarpine, to which it is also alike in certain pharmacological actions. The activity of the pituitary substance differs from this alkaloid in that its activity cannot be restored after it has once been destroyed by alkalis. It is, however, more nearly allied, both chemically and pharmacologically, to acetylcholine. It differs from this base in that the latter, after repeated injection into the same animal, still reproduces the same effects, whereas the animal fails to react to the rise in blood pressure after repeated doses of the pituitary substance. The author believes that the active substance is an ester-like derivative of an alkanolamine with an acetyl residue.

S. B. S.

**Chemistry of Lipoid Substances in the Suprarenal Capsules.** H. BEUMER (*Arch. exp. Path. Pharm.*, 1914, 77, 304—316).—Several phosphatides have been extracted from the suprarenal bodies of the sheep and ox, including two monoaminomonophospha-



tides, lecithin and cephalin, cuorin, sphingomyelin, jecorin, and two other phosphatides. Cholesterol was also found in the suprarenals of both animals, chiefly in the free state, with only a small proportion in the form of ester.

No relation could be established between the content of cholesterol ester in the blood serum and suprarenals respectively. The suprarenals have the power of storing up cholesterol esters and free fatty acids.

H. W. B.

**The Cephalin and Other Lipoids of the Cortex of the Suprarenals.** RICHARD WAGNER (*Biochem. Zeitsch.*, 1914, 64, 72—81).—The following lipid substances could be found in the cold alcoholic extract of suprarenals—a monoaminophosphatide (cephalin), which is insoluble in acetone and absolute alcohol, but soluble in ether; a substance insoluble in acetone, alcohol, or ether, but soluble in chloroform or benzene, which darkens in the air and contains nitrogen and phosphorus (corresponding with the sphingomyelin of other authors); a phosphatide of the character of lecithin, which is insoluble in acetone, but soluble in alcohol or ether, and various nitrogen-free fats. A substance of aminolipoid character was not obtained. The cephalin yields on hydrolysis a substance which is probably hydroxyethylamine.

S. B. S.

**The Amount of Carnosine in Mammalian Muscle.** OTTO VON FÜRTH and THEODOR HRYNTSCHAK (*Biochem. Zeitsch.*, 1914, 64, 172—193).—The so-called carnosine fraction of meat extract (that is, the part precipitated by silver salts and barium hydroxide after preliminary separation of the colloids by lead acetate) contains some nitrogenous substance other than carnosine. The true carnosine content in this fraction can, however, be estimated by two colorimetric methods. One of these depends on the colour yielded by the histidine complex in the molecule with diazobenzenesulphonic acid, and the other on the violet colour yielded by carnosine itself when boiled with cupric hydroxide. It is possible to obtain the copper salt, to which this colour is due, in a crystalline form, but, as a rule, not more than one-half to two-thirds of the carnosine present can be so isolated. The amount of carnosine in 1 kilo. of meat is estimated to be between 2 and 3 grams.

S. B. S.

[ **The Amino-acids of Horse-flesh Hydrolysed by Sulphuric Acid.** TULLIO GAYDA (*Biochem. Zeitsch.*, 1914, 64, 438—449).—Analyses of the distribution of nitrogen in the products of hydrolysis by van Slyke's method have been carried out. The comparison of the numbers obtained by other authors for other varieties of muscular tissue is made, and the evidence indicates that these proteins have different constitutions.

S. B. S.

**The Influence of Ultra-violet Rays on the Colour of the Hair of Rabbits and Guinea-pigs.** S. SECEROV (*Compt. rend.*, 1914, 158, 1826—1828).—Exposure of white-haired guinea-pigs or rabbits to the action of ultraviolet rays at a distance of 9—10 cm.

from the lamp for a considerable time produces a coloration of the hair. In the case of the guinea-pig the white hairs become yellow after thirty-five to forty hours, and in the case of the rabbit after eighty hours, the colour finally becoming reddish-yellow. The coloration only occurs at those parts directly exposed to the rays. In the case of animals partly black- and white-haired the coloration of the white hairs takes place more rapidly than with a pure white animal. The coloration is produced in the hair when detached from the animal, but less rapidly than when growing. Heat produces a yellow coloration, but a temperature of  $150^{\circ}$  is necessary.

W. G.

**The Purine Enzymes of the Orang-utan (*Simia Satyrus*) and Chimpanzee (*Anthropopithecus Troglodytes*).** H. GIDEON WELLS and GEORGE T. CALDWELL (*J. Biol. Chem.*, 1914, 18, 157—165).—No enzymes capable of decomposing uric acid were found by the authors in the tissues of an orang-utan and of a chimpanzee. These results are in accord with Wiechowski's observation that the chimpanzee excretes uric acid and no allantoin in the urine. The anthropoid apes resemble man, therefore, in this respect, wherein they constitute a marked exception to all other mammals, including the monkey. The anthropoids, like adult man, also contain little, if any, adenase, but guanase is present in nearly all their tissues. Xanthine-oxydase was present in the liver of the chimpanzee, but not in any tissues of the orang-utan.

H. W. B.

**Some Extractives from the Crayfish. Formation of Creatine in Animals.** FR. KUTSCHER (*Zeitsch. Biol.*, 1914, 64, 240—246).—The muscle of the crayfish (*Astacus fluviatilis*) contains the same extractives as that of the shrimp (compare Ackermann and Kutscher, A., 1907, ii, 283, 491; 1908, ii, 53), namely, leucine, tyrosine, purine bases, *D*-arginine, betaine, and neosine. The presence of arginine instead of creatine in these cold-blooded animals, with depressed oxidative processes, confirms the view that arginine is the precursor of creatine in muscle.

H. W. B.

**The Secretions of Fishes' Skins. Part I. The Chemistry of Eel-slime.** JOHANNES MÜLLER and HANS REINBACH (*Zeitsch. physiol. Chem.*, 1914, 92, 56—74).—Eel-slime contains about 12% dry substance, 75% of which consists of a protein resembling the nucleo-albumin of snail's liver. The remainder is made up chiefly of lipoids, namely, esters of cholesterol, a crystalline diaminomono-phosphatide,  $C_{51}H_{106}O_{12}N_2P$ , which commences to liquefy at  $120^{\circ}$  and melts finally at  $177$ — $179^{\circ}$ ; a diaminomono-phosphatide,  $C_{52}H_{96}O_{14}N_2P$ , which is possibly an oxidation product of the crystalline phosphatide; a phosphatide of the lecithin type; and a basic substance of betaine nature. No true mucin was detected.

H. W. B.

**Reactions of Earth-worms to Hydroxyl Ions.** A. T. SHOHL (*Amer. J. Physiol.*, 1914, 34, 384—404).—The author has placed

earthworms (*Allolobophora foetida*) in contact with alkali solutions of various concentrations, and has measured the times which have elapsed before the worms have withdrawn themselves from the solutions (reaction time). The reaction time has been found to be proportional to the number of hydroxyl ions in the solution, and to be independent of the anion. Temperature is an important factor; the higher the temperature the quicker the reaction.

H. W. B.

**Estimation and Significance of the Ammonia Content of Milk.** J. TILLMANN, A. SPLITTGERBER, and H. RIFFART (*Zeitsch. Nahr. Genussm.*, 1914, 27, 801).—In connexion with their recent paper on this subject (this vol., i, 454), the authors wish to make mention of a previous investigation by Rullmann (A., 1911, ii, 667). The latter found larger quantities of ammonia in fresh milk than did the authors in their experiments, the difference probably being due to the fact that Rullmann distilled the milk with the addition of calcium hydroxide.

W. P. S.

**Source of the Thiosulphate in Rabbit's Urine.** E. SAL-KOWSKI (*Zeitsch. physiol. Chem.*, 1914, 92, 89—103).—The substance which causes the appearance of thiosulphate in rabbit's urine is contained in an aqueous extract of cabbage. It is not thiosulphate, but is destroyed by warming with hydrochloric acid. The administration of thiosulphate, sodium sulphite, and sodium sulphate is, in each case, followed by the elimination of a small amount of thiosulphate in the urine.

White cabbage contains about five times as much organic sulphur as carrots, and after feeding rabbits with these materials the urine contains corresponding quantities of organic sulphur. H. W. B.

**Alteration in the Oxidation of Methyl Alcohol by Other Alcohols.** ERNST ASSER (*Chem. Zentr.*, 1914, i, 1359; from *Zeitsch. expt. Path. Ther.*, 15, 322—334).—It has been shown by Król (*Arch. expt. Path. Pharm.*, 1913, 72, 444) that formic acid is an intermediate product in the oxidation of methyl alcohol. Determinations of formic acid in the urine (compare Fincke, A., 1913, ii, 636) show a decrease in the amount of acid after administration of alcohol, amyl alcohol, or acetone. If this effect is due to a limitation of the oxidation, an increase in the amount of exhaled methyl alcohol might be expected; an experimental investigation by the method of Völtz and Dietrich (A., 1912, ii, 575) shows that this is not the case. The diminished elimination of formic acid must therefore be attributed to an increased oxidation of the latter. If these results, obtained with formate and ethyl alcohol, are applied to experiments with methyl and ethyl alcohols (in which the former may be regarded as a source of formic acid), the conclusion may be drawn that the administration of ethyl alcohol increases the power of oxidation of formate in the body.

H. W.

**Creatinine and Indican in the Urine of Domestic Animals.** HUGO MÜNZER (*Pflüger's Archiv*, 1914, 158, 41—83).—The amounts

of creatinine and indican in a large number of animal urines have been determined by means of the Autenrieth-Königsberger colorimeter. The average quantities in grams per litre of urine were, as regards creatinine, horse 1.94, pig 1.49, sheep 1.44, ox 1.12, goat 0.38, and indican, horse 0.039, sheep 0.037, ass 0.024, ox 0.020, pig 0.01, goat 0.005. Calves on milk diet passed more creatinine than full-grown animals.

H. W. B.

**The Contribution of Bacteria to the Fæces after Feeding Diets free from Indigestible Components.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1914, 18, 177—182).—The amount of bacteria in the fæces of rats fed on various artificial diets has been determined by extracting the dried fæces successively with ether, alcohol, 80% alcohol, 0.2% hydrochloric acid, and alcohol containing 0.2% hydrochloric acid. The dry residue was assumed to be composed almost entirely of bacteria on the grounds that a stained specimen had the characteristic appearance of bacteria similarly treated, and that it contained about the same percentage of nitrogen (10.7 to 12.2) as most bacterial cellular substances. The actual amount of bacteria thus determined varied from 30 to 40% of the dry fæces.

H. W. B.

**The Bone Disorders Produced by Diet Poor in Phosphorus.** III. M. MASSLOV (*Biochem. Zeitsch.*, 1914, 64, 106—110. Compare A., 1913, i, 1264, 1265).—The author gives a description of the histological appearance of the bones of animals which have been fed on a diet poor in phosphorus. The general characters are somewhat similar to those observed in Barlow's disease.

S. B. S.

**Gluconeogenesis.** IX. **The Formation of Dextrose from Dihydroxyacetone in the Diabetic Organism.** A. I. RINGER and E. M. FRANKEL (*J. Biol. Chem.*, 1914, 18, 233—236. Compare this vol., i, 903).—The subcutaneous administration of dihydroxyacetone to phloridzinised dogs is followed by a rise in the amount of dextrose eliminated in the urine. In one experiment the dihydroxyacetone appeared to be quantitatively transformed into dextrose. The injection of dihydroxyacetone inhibited the acidosis in three out of the four experiments.

H. W. B.

**The Excretion of Creatine in Severe and Mild Cases of Diabetes Mellitus.** R. A. KRAUSE (*Proc. physiol. Soc.*, xliii—xliv; *J. Physiol.*, 1914, 48).—Even in a mild case of diabetes mellitus, with no appreciable amount of acidosis, creatine could be detected in the urine.

S. B. S.

**Creatine and Creatinine Metabolism.** III. **The Origin of Urinary Creatine.** STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1914, 18, 195—214).—The authors have studied the effects of a creatine-free protein diet on the elimination of creatine and creatinine in dogs completely under the influence of phlorid-

zin. The amount of creatinine in the urine slowly diminishes, no matter whether the animal is in a fasting state or fed on protein. The amount of creatine varies considerably, and is wholly independent of the amount of body tissue destroyed. Analysis of the muscular tissue of the animals at the end of the experimental periods showed the presence of amounts of creatine rather above the normal, so that the creatine eliminated in the urine did not have its origin in preformed creatine of the muscles. The view expressed is that creatine is probably being formed in the animal organism in relatively large amounts, and is normally either utilised or destroyed, the power to metabolise creatine being directly related to that of metabolising carbohydrate.

The relation of urinary creatinine to muscle creatine has not yet been established.

H. W. B.

Gout. III. H. BECHHOLD and J. ZIEGLER (*Biochem. Zeitsch.*, 1914, 64, 471—489).—Measurements of the solubilities of uric acid and sodium urate in water, salt-free sera, normal sera, and sera with and without the globulin fraction, are given. The measurements were made either by cooling supersaturated solutions or by shaking the fluid with excess of solids. In using the first method an important factor must be taken into account, namely, the time, for whereas in the case of aqueous solutions the separation of the excess of solute takes but a short time, a prolonged period elapses in the presence of serum before the solution reaches a constant composition. Attention is called to the importance of this factor in the study of gout. Experiments carried out by the ultra-filtration method tend to show that sodium urate can exist in colloidal solution.

S. B. S.

The Mechanism of Certain Forms of Hyperglycæmia produced Experimentally in Rabbits. II. and III. IVAR BANG (*Biochem. Zeitsch.*, 1914, 65, 283—295, 296—310. Compare this vol., i, 230).—II. The author finds that diuretin in many cases does not lead to hyperglycæmia, and that the results with this drug are by no means uniform. Generally, the combined action of diuretin and larger amounts of urethane leads to hyperglycæmia, but the want of uniformity in the results compels him to abandon the hypothesis he has previously put forward, as to the psychic action of the diuretin, although he believes that small amounts of narcotics can partly or wholly suppress various forms of hyperglycæmia (compare this vol., i, 230). Hyperglycæmia due to the combined administration of urethane and diuretin is due to the former.

III. The author draws the conclusion that hyperglycæmia due to urethane is not a form of adrenaline hyperglycæmia. It is produced with certainty only by relatively large doses of the drug (1·7 grams per kilo. of body weight or over); it is more readily produced in animals in low condition (after treatment previously with the drug, or other drugs which have affected its general condition, or in fasting animals); it is independent of the store of

glycogen in the liver, and it is not inhibited by pituitrin. The author believes that the urethane affects the lipoids of the organs of the body generally, and especially those of the pancreas, and the glycosuria and hyperglycæmia produced are analogous in many respects to those in pancreatic diabetes. The hyperglycæmia is of about the same intensity in both cases; glycosuria sets in with a relatively low degree of hyperglycæmia, and is, furthermore, in both cases accompanied by acetonuria. In the two last instances it differs from adrenaline glycosuria. It is not improbable that glycosuria due to narcotics is the effect of the stoppage of the secretion of the pancreatic hormone.

S. B. S.

**The Excretion of Potassium during Malaria.** ALADAR ELFER and BÉLA VON PURJESZ (*Biochem. Zeitsch.*, 1914, 64, 63—71).—In malaria infection it was found, in the case of the patient under investigation, that the increased output of nitrogen was accompanied by an increased output of potassium. This potassium loss is still evident when the utilisation of sodium and chlorine is normal. The potassium metabolism is similar in this respect to the nitrogen metabolism, but the deficit in the latter element, in contrast to potassium, is most marked in the period of high temperature.

S. B. S.

**A Case of Pentosuria. II.** P. A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1914, 18, 319—327. Compare A., 1913, i, 1274).—The osazone and *p*-bromophenylhydrazone of the urinary pentose have been prepared and contrasted with similar compounds obtained from *d*- and *l*-xylose, *d*- and *l*-arabinose, and *d*-lyxose, with none of which, however, have they been found to be identical. The osazone has m. p. 160°, with effervescence at 163°, and  $\alpha_D + 0.15^\circ$  (in pyridine alcohol), rising to  $+0.57^\circ$  in eighteen hours. The pentose-*p*-bromophenylhydrazone ( $C_{11}H_{15}O_4N_2Br$ ) has m. p. 130—131° (corr.), and decomposes at 154°. The rotation in alcohol increased from  $[\alpha]_D - 1.00^\circ$  to  $+1.12^\circ$  in eighteen hours. *l*-Xylose-*p*-bromophenylhydrazone had  $[\alpha]_D - 0.06^\circ$  in alcohol, rising to  $+0.06^\circ$  in eighteen hours. *d*-Lyxose-*p*-bromophenylhydrazone had m. p. 161.5° (corr.) and  $[\alpha]_D + 1.06^\circ$  in pyridine, changing to  $+0.26^\circ$  in twenty-four hours. *d*-Lyxose-*p*-nitrophenylhydrazone melted at 172° (corr.).

Hydrolysis of the urinary pentose-*p*-bromophenylhydrazone was carried out with benzaldehyde, but the free sugar was not obtained in crystalline form, nor did it furnish a crystalline oxidation product. The conclusion is drawn that the pentose is a keto-pentose corresponding with *l*-lyxose or *d*-xylose.

H. W. B.

**The Curative Action of Autolysed Yeast against Avian Polyneuritis.** EVELYN ASHLEY COOPER (*Biochem. J.*, 1914, 8, 250—252).—Small doses of autolysed brewer's yeast readily cure avian polyneuritis. The liquid retains its curative properties for at least eight weeks, and, when given to birds in doses ten times as great as the minimum curing dose, has no toxic action. Air-

dried yeast retains its curative power for two years. The use of autolysed yeast as suitable material for the preparation of anti-beriberi vitamine is recommended.

H. W. B.

**Metabolism in Bence-Jones Proteinuria.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1914, 18, 277—283. Compare Hopkins and Savory, A., 1911, ii, 417).—A case of multiple myeloma of the ribs is described, in which a few observations were made of the effect of diet on the excretion of the Bence-Jones protein. For the determination of the amount of Bence-Jones protein, 10 c.c. of the urine and 1 c.c. of 5% acetic acid were heated in a weighed centrifuge tube for some hours at 60°, then centrifuged, and the deposited protein washed with alcohol and dried at 100°. During the first period the patient, on a low protein diet, excreted about 2 grams per day of the Bence-Jones protein, which during the following period, on a high protein diet, increased to 6.5 grams, the total nitrogen also rising from about 6 to 16 grams per day. Much creatine was also eliminated during the latter period. After a short interval the patient fasted for two days, when 5 grams of Bence-Jones protein and 8.4 grams of non-protein nitrogen were daily eliminated. Equal amounts of Bence-Jones protein were excreted during twelve-hour day and night periods.

The conclusions reached are that the formation of the Bence-Jones protein is independent of the total protein metabolism, and is probably due to an internal autolytic digestion.

H. W. B.

**The Occurrence of a Crystallisable, Non-coagulable [Bence-Jones] Protein in the Urine of a Patient with Cancer of the Stomach.** O. SCHUMM and A. KIMMERLE (*Zeitsch. physiol. Chem.*, 1914, 92, 1—12).—A specimen of the urine was treated with sodium chloride and a trace of acetic acid, boiled, and filtered to remove coagulable protein. Alcohol was added to the filtrate, and the resulting precipitate redissolved in warm acetic acid. On keeping, crystalline needles of a substance settled out, which proved to be of protein nature. All subsequent attempts to again obtain the protein from the urine in crystalline form were unsuccessful.

The needle-shaped crystals contained nitrogen and sulphur, gave positive Millon's, Molisch, Ehrlich, biuret and xanthoproteic reactions, dissolved in dilute acids and alkalis, and in their general behaviour closely resembled the crystals of "Bence-Jones" protein described by Grutterink and de Graaff (A., 1906, i, 326). Post-mortem examination showed that the pathological changes in the bone marrow usually associated with the "Bence-Jones" albuminuria were absent.

H. W. B.

**The Iodine Content of Tuberculous Tissues.** PAUL A. LEWIS and ROBERT B. KRAUSS (*J. Biol. Chem.*, 1914, 18, 313—317).—Tuberculous tissue derived from animals to which no iodine preparation has been knowingly administered may contain amounts of iodine very appreciably higher than normal control tissue of the same animal. The statement that tuberculous tissue in animals

treated with iodine products may store up iodine must therefore be accepted with reserve.

H. W. B.

**Retention of Nitrogen by Administration of Ammonium Salts or Urea, investigated by Permanent Intravenous Injection Experiments.** V. HENRIQUES and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1914, **92**, 21—45. Compare Grafe, 1913, *A*, i, 125, 547, 1128).—The experiments were carried out on goats and turkeys with cannulæ permanently inserted into peripheral veins, by means of which sugar, sodium acetate, sodium citrate, and simple nitrogenous substances, such as urea and ammonium acetate, were administered to the animals day by day. In this way, the possibility of synthetic action through the agency of bacteria in the intestine was avoided. The results showed that a permanent retention of nitrogen in the body was in no case achieved, and the conclusion drawn is that the nitrogen retention on feeding with urea and ammonium salts, observed by Grafe and others, was due to the action of bacteria in the alimentary canal or to a simple retention of these substances in an unaltered form in the body.

H. W. B.

**Reversible Paralysis of Peripheral Nerves by Acids and Salts.** FRIEDRICH HACKER (*Zeitsch. Biol.*, 1914, **64**, 224—239).—Injection of dilute inorganic or organic acids temporarily paralyses the neighbouring peripheral nerves, as evidenced in man by the local anæsthesia produced, and in frogs by the increase of the threshold stimulus of the sciatic nerve. The extent of the paralysis is largely dependent on the concentration of hydrogen ions. When bases are injected, hyperalgesia results as a secondary effect of the contemporary hyperæmia. Salts which are partly hydrolysed in solution exert on injection the same action as the stronger ion. The weak local anæsthetic action of morphine hydrochloride is not due to the morphine, because when coupled with a weaker acid no anæsthesia is produced. The analgesic action of potassium sulphate is due to the potassium ion. In practice, the use of magnesium sulphate, or, better, chloride, is preferred, because these salts on injection produce less injury to the tissues and no pain.

H. W. B.

**The Pharmacological Action of Acids which Precipitate Calcium and of Magnesium Salts.** E. STARKENSTEIN (*Arch. exp. Path. Pharm.*, 1914, **77**, 45—82).—Similar toxic effects are produced by the administration to rabbits of any of the following substances, which form precipitates with calcium ions: oxalic acid, sodium salts of ortho-, pyro-, and meta-phosphoric acids, sodium inositol-phosphate (phytate), and sodium fluoride. Animals showing intense toxic symptoms as the result of lethal doses of these substances may nevertheless recover if calcium chloride is injected. Conversely, a preliminary injection of calcium chloride renders these substances innocuous. The toxic symptoms are lowering of



blood pressure, rise of temperature, and slowing of the heart, with eventual arrest in diastole.

Phosphates and phytates inhibit blood clotting in a similar manner to oxalates and fluorides. Addition of magnesium salts restores the clotting property of the blood. Mixtures of salts of calcium-precipitating acids and magnesium salts, and the soluble magnesium salts of oxalic and metaphosphoric acids, do not exert any toxic action. As these salts and salt mixtures precipitate the calcium ion, it follows that the magnesium ion can replace the calcium ion in certain of its functions in the body, and the toxic action of acids which precipitate calcium is due to the withdrawal of calcium ions, and not to the respective anions. H. W. B.

**The Action of Iodine in the Animal Body.** LEO ADLER and LUDWIG CZAPSKI (*Biochem. Zeitsch.*, 1914, 65, 117—128).—It has been shown by Adler that the injection of iodine in potassium iodate (Lugol's solution) can lead to an injury to the testicles, resulting, with the correct dose, in a complete destruction of the parenchyma. The same result cannot be produced by potassium iodide alone. Experiments were carried out on rabbits with the object of throwing light on this action. The iodine in various tissues was estimated after injection both of the iodine alone and of the iodate containing free iodine. After both injections, however, the iodine was found in inorganic form in testicles and other organs, and not combined with any organic substance. In no case could any iodine derivative of a protein be detected. So far, the results offer no explanation of the characteristic action of solutions containing free iodine. S. B. S.

**The Synthesis of Hippuric Acid in the Animal Organism.**  
II. **The Synthesis and Rate of Elimination of Hippuric Acid after Benzoate Ingestion in Man.** HOWARD B. LEWIS (*J. Biol. Chem.*, 1914, 18, 225—231. Compare this vol., i, 774).—In man, after the administration of from 6 to 10 grams of sodium benzoate, elimination as hippuric acid takes place very rapidly, 85 to 90% of the ingested benzoate being excreted in from five to six hours. The rate of elimination of hippuric acid after the administration of sodium benzoate is only slightly less rapid than after the administration of hippuric acid. After benzoate ingestion, the urine collected during the first six hours, the period during which the greater part of the hippuric acid is being excreted, has a lower urea + ammonia content than in a normal control period, indicating that hippuric acid nitrogen is derived at the expense of the nitrogen normally eliminated as urea. H. W. B.

**The Action of Caffeine on Striped Muscle.** KNUD J. A. SECHER (*Arch. exptl. Path. Pharm.*, 1914, 77, 83—121).—Perfusion with 1:30,000 caffeine solution produces histological changes in the voluntary muscle fibres of the frog similar to those brought about by xanthine, theobromine, and theophylline. Similar results are obtained with birds and mammals, but only with solutions of

much greater concentration (up to 2%). Caffeine in low concentration increases contractility of the muscle, but the work done is increased only when the muscle is unsupported. H. W. B.

**The Behaviour of Sodium Formaldehydesulphite (Hydroxymethanesulphonate) in the Organism; its Applications to Therapeutics.** FRIEDRICH SIMON (*Biochem. Zeitsch.*, 1914, 65, 71—106).—This substance can be tolerated in relatively large doses. Thus, a man can take 9 grams within fourteen hours, and a dog 30 grams within three days, and rabbits doses equivalent to 1 gram per kilo. of body-weight, without ill-effects. The scission of the compound takes place very rapidly in the blood stream, and formaldehyde can only be detected in the blood in the first few minutes after intravenous injection. Neither the unchanged drug nor formaldehyde could be detected in the urine. There is no evidence that the drug possesses any value either as solvent for uric acid or as a urinary disinfectant. As an antidote to phenol (in experiments on rabbits) it is unable to counteract the final action of a lethal dose, but with smaller doses it can counteract or lessen the duration of the convulsions. It can increase the power of the organism to reduce methylene-blue. S. B. S.

**Some Physiological Properties of Galegine Sulphate.** GEORGES TANRET (*Compt. rend.*, 1914, 159, 108—111. Compare this vol., i, 721, 859).—Galegine in the form of its sulphate has a toxic effect both on cold- and warm-blooded animals. In the case of the frog, 0.02 to 0.03 gram injected into the peritoneum produces total paralysis in ten to fifteen minutes, with abolition of the reflexes. The respiration ceases at the end of one hour, whilst the heart only ceases to beat after several hours. With the guinea-pig, death ensues fifteen minutes after hypodermic or intraperitoneal injection of 0.23 to 0.26 gram per kilogram of live-weight, fifty-five minutes after 0.1 gram, and 105 to 130 minutes after 0.03 to 0.05 gram. A guinea-pig resists an injection of 0.01 to 0.02 gram of the sulphate per kilogram of live-weight. The rabbit is slightly more resistant than the guinea-pig, whilst the dog comes between them. In all cases the first effect is to produce paralysis of the medulla and nerve centres, followed by asphyxia, the cardiac muscle in all cases surviving the cessation of respiration. Galegine sulphate has no hæmolytic action, but in feeble dose the injection is followed by a short, rapid lowering of the blood pressure, and then a gradual and continuous rise, reaching 4—5 cm. of mercury in five to six minutes, returning to its original value after twenty minutes. With toxic doses, the pressure diminishes at the end of a very short time, falling more or less rapidly, and does not reascend. W. G.

**Action of Hydroxyquinoline and Certain of its Derivatives on Purine Metabolism.** FELIX BOENHEIM (*Chem. Zentr.*, 1914, i, 1685; from *Zeitsch. expt. Path. Ther.*, 15, 379—384).—The effect of 8-hydroxyquinoline-*o*-acetoxybenzoate, "8-hydroxyquinoline-

glycerol ether, and hydroxyquinoline hydrochloride on the elimination of uric acid and allantoin in dogs has been investigated. Small doses of 8-hydroxyquinoline-*o*-acetoxybenzoate have no effect, whilst the quantity of uric acid is slightly diminished and that of allantoin increased after medium doses; quantities of 5 grams have a similar effect, whilst, after 10 grams, an appreciable diminution of allantoin occurs on the first day. A toxic action is not observed. "8-Hydroxyquinoline glycerol ether" causes an increase in the uric acid, a diminution in the allantoin elimination. Ethyl phenylcinchonate brings about a slight diminution in the uric acid and increase in allantoin, whilst hydroxyquinoline causes a decrease in uric acid and in allantoin. H. W.

**Chemical Study of Certain Causes of Poisoning by Carbon Monoxide.** E. KOHN-ABREST (*Ann. Falsif.*, 1914, 7, 292—304).—Carbon monoxide may be introduced into the atmosphere from sources such as charcoal furnaces, internal-combustion engines, gas stoves, etc., and analyses are recorded showing the composition of the gases produced in these cases. The gases from a charcoal fire may contain up to 1.8% of carbon monoxide, those from a petrol engine 7.32% (in these gases the quantity of carbon monoxide exceeds that of the carbon dioxide), whilst the combustion products from gas heaters contain from 1 part in 15,000 to 0.3% of carbon monoxide, according to the supply of air to the burner. The cumulative action of carbon monoxide on the animal system emphasises the necessity of thorough ventilation when any of the above-mentioned sources of heat are employed. W. P. S.

**The Bases of Gas-works Coal-tar which are believed to be the Predisposing Cause of Pitch Cancer, with Special Reference to their Action on Lymphocytes, together with a Method for their Inactivation. I. Auxetic Action.** DOROTHY NORRIS (*Biochem. J.*, 1914, 8, 253—259).—Coal-tar from gas-works contains certain bases which excite division of blood lymphocytes and other living cells (auxetic action), leading to ulcers and epithelioma among the workmen employed. The auxetic bases have been extracted with 5% hydrochloric acid, and isolated in the form of their crystalline picrates. Picrate A has m. p. 199—201° and empirical formula  $C_{22}H_{14}O_5N_6$ , and is less soluble in alcohol than picrate B, m. p. 161—162°. Hydrolysis of picrate A yielded a small quantity of active auxetic base. A practical method, applicable on the large scale, of inactivating these bases in the tar is described, depending on the rapid loss of auxetic power on oxidation by air. H. W. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Comparative Investigations on the Action of Chemiotherapeutic Preparations and Other Antiseptics on Bacteria.** O. SCHIEMANN and T. ISHIWARA (*Chem. Zentr.*, 1914, i, 1449—1450; from *Zeitsch. Hyg. Infekt.-Krankh.*, 1914, **77**, 49—100).—The drugs salvarsan and ethylhydrocupreine are powerful antiseptics *in vitro*; experiments in bouillon show that their power of checking development, like that of mercuric chloride, extends to a dilution of 1 in 500,000 to 1 in 1,000,000. The bactericidal action of salvarsan is noticeable at about the same dilution. In comparison with other antiseptics, the action of these substances is highly selective. At the given dilution, salvarsan is only active towards the bacilli of dysentery, splenalgia, and glanders, ethylhydrocupreine towards pneumococci; the action towards other bacilli is one hundred to one thousand times weaker and slower. In all cases investigated, the action *in vivo* corresponds with that *in vitro*. The selective action of the chemiotherapeutic preparations on the above bacteria is approximately as powerful *in vitro* in serum as in bouillon, and actually better in active than in inactive serum. Sublimate behaves in the opposite manner. Phenol is much less weakened by serum than is sublimate. The action of salvarsan is not identical in all sera; thus, it is noticeably weaker in ox serum than in rabbit serum. The opposed behaviour in active serum of salvarsan and ethylhydrocupreine on the one hand, and sublimate on the other, points to an action of the labile components of serum, such as lipoids and lipid albuminoids, during disinfection *in vivo*. A considerable weakening of the antiseptic action of salvarsan, sublimate, and phenol in bouillon is caused by the addition of lecithin or cholesterol in considerable concentration (1:100). With regard to the quantitative relationship between the amounts of bacteria and antiseptic, the latter is found to increase disproportionately with the former. With similar concentrations of disinfectant and similar seeding, larger volumes of sublimate or salvarsan solutions showed somewhat more powerful actions, both bactericidally and in the prevention of development. In respect of these quantitative relationships, no distinct difference could be perceived between salvarsan, sublimate, and phenol. H. W.

**Behaviour of Bacteria, Yeasts, and Moulds towards Iodine Compounds.** ALEXANDER KOSSOWICZ and WALTER LOEW (*Bied. Zentr.*, 1914, **43**, 359; from *Zeitsch. Gärungsphysiol.*, 1913, **2**, Heft 3).—With different varieties of pure yeasts grown in sugar solutions containing potassium iodide, no separation of iodine occurred. Similar results were obtained with most of the moulds employed. On the other hand, there was a considerable separation of iodine in cultures of *Penicillium glaucum* and *Aspergillus niger*, and also, in more prolonged experiments, with *Cladosporium herbarum*.

The positive results obtained with yeasts by Bokorny (A., 1912, ii, 1201) are attributed to the presence of bacteria.

N. H. J. M.

**Decomposition of Formates by *Bacillus coli communis*.** EGERTON CHARLES GREY (*Proc. Roy. Soc.*, 1914, [B], 87, 461—471).—The power of *B. coli communis* to decompose formic acid varies considerably when the organism has been kept on artificial media. A very small excess of acid or alkali inhibits the decomposition of formates, and addition of dextrose greatly increases the decomposition, owing to the neutralisation of the alkali of the formate by the acid produced from the sugar.

Formates may be conveniently employed as neutralising agents; the activity of gas-forming organisms is considerably increased.

A method is described, with sketch, by which the decomposition of various substances by micro-organisms, in 50—100 c.c. of solution, may be followed quantitatively.

N. H. J. M.

**Enzymes which are Concerned in the Decomposition of Dextrose and Mannitol by *Bacillus coli communis*.** EGERTON CHARLES GREY (*Proc. Roy. Soc.*, 1914, B, 87, 472—484).—Whilst artificially selected strains of *B. coli communis* did not lose the enzymes which cause the final reaction in the production of alcohol and acetic acid, there was an absence or diminution of the reducing mechanism of the cell, so that some intermediate substance, from which formic acid and the precursor of alcohol and acetic acid are derived, cannot be readily decomposed.

N. H. J. M.

**Influence of Organic Substances on Nitrification and Denitrification in Soils.** CHR. BARTHEL (*Bied [Zentr.]*, 1914, 43, 372—373; from *Medd. Centralanst. försöksväs. Jordbr.*, 1913).—The results of experiments in which ammonium sulphate and various organic substances were added showed that the extent to which nitrification was hindered by the different substances diminished in the following order: peptone, asparagine, acetamide, ammonium acetate, carbamide. So that, in accordance with the previous results of Winogradski and Omelianski, the inhibiting action on nitrification disappears more or less quickly, according to the rate of decomposition of the organic substance employed.

Dextrose and other readily soluble non-nitrogenous substances have a distinctly retarding effect on nitrification, even when only small amounts are present.

Whilst soils rarely contain sufficient soluble organic matter to retard nitrification, the activity of nitrifying organisms is almost completely checked in manure heaps.

N. H. J. M.

**The Formation of Acetaldehyde in Alcoholic Fermentation.** S. KOSYTSHEV (*Biochem. Zeitsch.*, 1914, 64, 237—250).—The author replies to a criticism of Neuberg and Kerb (this vol., i, 118) of their work (A., 1912, i, 323) on the increased production of acetaldehyde by fermentation with yeast in the presence of zinc

chloride. He incidentally shows that alcohol can be estimated by Nicloux's method when aldehyde is present if the mixture is distilled in a vacuum (at 30—35°) over sodium hydrogen sulphite, to separate the aldehyde. S. B. S.

**The Part Played by Acetaldehyde in Alcoholic Fermentation.** C. NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1914, **64**, 251—256).—A detailed reply to Kostytshev (see preceding abstract). S. B. S.

**Can the Phenomenon of Thermo-regeneration be Extended to the Different Diastases of Yeast.** GABRIEL BERTRAND and M. ROSENBLATT (*Compt. rend.*, 1914, **158**, 1823—1826).—Maltase and catalase obtained from slightly autolysed bottom yeast do not undergo thermoregeneration in the same way as invertase (compare this vol., i, 909). The activity of both of these enzymes is destroyed by heating their solution to 70°, and is not restored by heating for one minute at either 80°, 90°, or 100°. W. G.

**The Enzymes of Washed Zymin and Dried Yeast (Lebedev). III. Peroxydase, Catalase, Invertase, and Maltase.** ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1914, **8**, 217—226).—Fresh English yeast gives the peroxydase coloration with hydrogen peroxide and *p*-phenylenediamine. After drying at 38°, the yeast, on suspending in water, no longer gives a positive reaction for peroxydase, owing to the presence of an inhibiting agent produced during the drying process. By repeatedly washing the dried yeast, the inhibiting agent is removed and the apparent peroxydase content restored.

Washing does not affect the activity of the catalase of dried yeast. Invertase and maltase are not readily removed from dried yeast by washing, the power of hydrolysing sucrose being reduced after six washings by a third, whilst that of hydrolysing maltose is scarcely affected. H. W. B.

**Assimilation of Elementary Nitrogen by Yeasts and Moulds.** ALEXANDER KOSSOWICZ (*Biochem. Zeitsch.*, 1914, **64**, 82—85).—From experiments on the growth of various moulds and yeasts in nitrogen-free media, the conclusion was drawn that these organisms cannot assimilate elementary nitrogen. A minute amount of nitrogen could be detected in the cultures when in contact with air from which nitrogen compounds had not been removed. No such increase could be found, however, when the air in contact with the cultures had been purified in such a way as to exclude the small amount of nitrogen compounds it is apt to contain. S. B. S.

**Synthesis of Nitrogenous Substances in Yeast Juice Obtained by Maceration.** S. KOSTYTSHEV and W. BRILLIANT (*Zeitsch. physiol. Chem.*, 1914, **91**, 372—391).—The juice always contains a considerable quantity of proteins and endotryptase. Autolysis proceeds readily at 34°, and the hydrolysable proteins are all

decomposed in two days, but a small, constant amount of protein remains unattacked even after nine days. After hydrolysis of the proteins, synthetic processes may occur, the necessary conditions being a sufficient amount of decomposed protein and a high concentration of sugar. Subsequently, the nitrogenous products precipitable by Stutzer's method with copper hydroxide is found to be increased. The increase may amount to 16% of the quantity present before autolysis. Precipitation of these nitrogenous substances with basic lead acetate gives considerably lower values.

R. V. S.

**Formation of Chemical Compounds during the Destruction of Yeast Organisms by Different Chemical Agents.** With-  
drawal of the Agents from Solution. TH. BOKORNY (*Chem. Zentr.*, 1914, i, 1363—1364; from *Allg. Brauer-u. Hopfenzeit.*, 54, 541—544, 567—569, 583—585, 592—594).—A chemical compound between the poison and the yeast cell is formed when the latter is killed by chemical agents. The concentration of poison in the solution is in most cases considerably diminished by the introduction of living yeast. The death of the cell appears to occur before the union of poison and protoplasm ceases. A table is given showing the quantities of the following substances which in *N*-, *N*/10-, and *N*/100-solution combine with 20 grams of living yeast in twenty-four hours, namely, ammonia, sodium hydroxide, sulphuric acid, formic acid, hydrofluoric acid, hydrazine hydrate, iodine, sulphurous acid, oxalic acid, and acetic acid. Combination is observed in all cases except with formic acid, which appears to function as a contact poison. Further, magenta, iodine-violet, methyl-green, malachite-green, tropäoline, eosin, chrysoidine, Victoria-blue, and dianyl-black are found to combine with yeast. Aniline dyes, particularly those which possess a great capacity for dyeing, are found to have a poisonous action even at a dilution of 1 in 100,000, that is, at a dilution at which the most powerful poisons are ineffective.

H. W.

**The Oxidation and Reduction Processes Taking Place at the Expense of the Water Produced by Killed Yeast.** W. PALLADIN and E. LOVTSCHINOVSKAJA (*Biochem. Zeitsch.*, 1914, 65, 129—139\*).—The experiments were carried out with the object of testing further the views of Palladin as to the part played by water in biological oxidation and reduction processes in the presence of a hydrogen acceptor. In confirmation of the results of Neuberg and of von Lebedev, it was found that the killed yeast can destroy potassium gluconate. The presence of methylene-blue largely increases the amount of carbon dioxide evolved in the reaction. This fact leads to the assumption that yeast contains a reduction ferment which is able, in the presence of a hydrogen acceptor, to decompose organic acids, with evolution of carbon chloride. The same result was observed in the case of lactic acid. Potassium glycuronate is also decomposed by the yeast, but in this

\* and *Bull. Acad. Sci. St. Petersbourg*, 1914, [ii], 8, i, 749.

case methylene-blue inhibits the reaction. Saccharic acid is also decomposed, but in this instance the process is not stimulated by the dye. The decomposition of the gluconic and lactic acids in the presence of methylene-blue is the first instance of the artificial conversion of a fermentation into a respiration process.

S. B. S.

**The Protein Substances of *Aspergillus niger*.** PIERRE THOMAS and ROBERT C. MORAN (*Compt. rend.*, 1914, 159, 125—127).—Using the method employed for the examination of yeast (compare A., 1913, i, 942), the authors have isolated from *Aspergillus niger* two protein substances corresponding with those obtained from yeast. The one is easy to isolate, being insoluble in water, sparingly soluble in 10% sodium chloride solution, soluble in aqueous sodium hydroxide, ammonia, alkali carbonates, or lime-water, and from these solutions is precipitated by mineral acids. It contains 12·3—12·9% nitrogen, 0·7% phosphorus, and 0·5—0·6% sulphur. It gives the xanthoprotein reaction, the biuret reaction, Hopkins' glyoxylic reaction, and reacts with Millon's, Molisch's, and the Ehrlich-Pröscher reagents, the latter showing the presence of glucosamine. With hydrochloric acid in the cold it gives a green coloration, which slowly passes to the ordinary Liebermann violet colour. On careful warming with orcinol hydrochloride it gives a purple precipitate and a green liquid, and with phloroglucinol hydrochloride an abundant, deep red precipitate. It gives no coloration on boiling with an alkaline solution of lead oxide. Using the modified Hausmann's method of hydrolysis (compare A., 1913, i, 1026) for determining the division of the nitrogen, the substance is found to contain less diamino- and more monoamino-nitrogen than the corresponding compound obtained from yeast. From its properties and analysis, it appears to be closely allied to casein, and to be derived from a nucleoprotein existing in the cells of the mould.

The second compound is a coagulable albumin, but occurs in too small a quantity to allow of it being characterised at present.

W. G.

**Organic Antiseptics which are Attacked by Micro-organisms.** S. CONDELLI (*Chem. Zentr.*, 1914, i, 1208; from *Staz. sperim. agrar. ital.*, 1913, 47, 85—94).—A culture solution containing mandelic acid was seeded with *Penicillium glaucum*, but a resolution of the acid could not be observed, although the organism developed readily; parallel experiments with *Aspergillus niger* showed a slight resolution. In a further series of experiments the mandelic acid was replaced by sodium benzoate, phenylacetic acid, and amygdalin respectively. After seeding with *Aspergillus niger*, a copious growth was observed after a few days in the solution containing the benzoate, followed in point of time by the solution containing amygdalin, and finally by that containing phenylacetic acid. Finally, it was shown that the percentages of benzoic acid, phenylacetic acid, mandelic acid, and amygdalin decomposed were 5·62, 6·26, 7, and 23·53 respectively.

H. W.



**The Soluble Polysaccharides of Lower Fungi. I. Mycodextran, a New Polysaccharide in *Penicillium Expansum*.** ARTHUR W. DOX and RAY E. NEIDIG (*J. Biol. Chem.*, 1914, **18**, 167—175).—Mycodextran has been prepared by extracting large quantities of this mould (which occurs characteristically on decaying apples) with boiling water. On cooling, the clear extract deposited the new polysaccharide in an impure form, and by repeated reprecipitation by alcohol from its aqueous solution, and finally drying in a vacuum, it was obtained as a fine powder containing 0.09% ash, and giving no colour reaction with iodine. The dry powder swells in cold water, and on warming dissolves to a clear solution. If 1% of the substance is present, a stiff, white paste results on cooling. It is soluble in cold sodium hydroxide and in hydrochloric acid, insoluble in ammonia, acetic acid, and sodium carbonate. It has  $[\alpha]_D^{20} + 251^\circ$ , and  $n_D$  0.00131. The empirical formula is  $C_6H_{10}O_5$ , and on hydrolysis it gave only dextrose, which was recognised by the polarimeter, Fehling's solution, and the preparation of glucosazone.

The ordinary amylolytic enzymes were without action on mycodextran.  
H. W. B.

**The Toxin of *Rhizopus Nigricans*.** ROSS AIKEN GORTNER and A. F. BLAKESLEE (*Amer. J. Physiol.*, 1914, **34**, 353—367).—The toxic substance of *Rhizopus Nigricans* has been obtained in an impure state by precipitation of an aqueous extract of the mould with alcohol. The product gives the reactions for protein and carbohydrate. It is slowly destroyed by boiling its aqueous solution, and more rapidly by boiling with *N*/10-hydrochloric acid. Peptic digestion for three hours is without effect on the toxicity.

In intravenous injections into rabbits, the lethal dose is about 1:250,000 parts of body-weight; but large doses may be given by the mouth without any harmful effect being observed.

H. W. B.

**Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds.** FRANKLIN KIDD (*Proc. Roy. Soc.*, 1914, *B*, **87**, 408—421, 609—625).—The results of experiments with various seeds showed that germination is retarded or inhibited by high partial pressure of carbon dioxide. Whilst some seeds, such as beans, cabbage, barley, and peas germinate at once when the carbon dioxide is removed, other seeds fail to germinate until they have been completely dried and re-wetted, or the germinating power may be restored by removing the testa. In this class of seeds it seems that the permeability of the testa is diminished under the influence of carbon dioxide, and this would result in a reduced amount of oxygen reaching the embryo, and in a relative rise in the carbon dioxide pressure in the embryo tissues.

An experiment was made in which a layer of fresh grass (7.5 cm.) was covered with 45 cm. of soil, in which a week later seeds were buried at depths of 7.5, 15, and 22.5 cm. After seven

days it was found that only three out of twenty-five of the seeds 7.5 cm. deep had sprouted, and that all the seeds at the lower depths failed to germinate. In a control experiment, without grass, all the seeds germinated. Two weeks after the pit containing grass was made, it was found that the air from 15 and from 30 cm. below the surface contained, respectively, 16.5 and 20.0% of carbon dioxide.

The inhibitory value of given carbon dioxide pressures is increased by low temperatures and by a low supply of oxygen, and diminished by a rise of temperature and an increased supply of oxygen.

In the case of seeds such as *Hevea Brasiliensis*, which rapidly deteriorate, the carbon dioxide produced by respiration in a closed flask rose to 40%; seeds kept in this manner showed a marked increase in vitality.

Both the arrested development of moist maturing seeds on the plant, and the retarded germination of moist resting seeds under apparently suitable conditions of temperature, moisture, and supply of oxygen, are connected with an inhibitory partial pressure of carbon dioxide in the tissues of the embryo. N. H. J. M.

**Action of Carbon Tetrachloride and Carbon Disulphide Vapours on the Germinating Power of Seeds.** RIEHM (*Bied. Zentr.*, 1914, 43, 358; from *Mitt. K. Biol. Anst. Land-u. Forstwirts.*, 1913, 14, 25).—Whilst hemp and barley were found to be greatly injured, rape is more resistant. The effect on maize varied considerably with different varieties. Carbon disulphide acts more quickly than carbon tetrachloride. N. H. J. M.

**Absorption of Ions by Plants.** F. PLATE (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 839—844).—The paper describes a series of quantitative experiments with *Triticum sativum* and *Hyacinthus orientalis* grown in solutions containing one of the following salts: manganese chloride, manganese bromide, manganese nitrate, and manganese sulphate. Anion and cation are absorbed in the same proportion as that in which they exist in the solution; the anion chiefly reaches the shoot, whilst the cation is found especially in the root. R. V. S.

**Influence of the Continuous Electric Current on the Absorption of Nutritive Substances by Plants.** D. CHOUGHAK (*Compt. rend.*, 1914, 158, 1907—1910).—In order to investigate the causes producing the variation of absorption of a nutritive substance by roots of a plant with changes in the medium in which the roots are immersed (compare A., 1913, i, 801), the author has examined the influence of an electric current. A number of young wheat plants were threaded on a fine platinum wire and plunged into the nutritive solution. A second wire was immersed in the solution, and the two connected to the poles of a battery giving a current intensity of 0.5 to 250 millionths of an ampere. At the end of the experiment the amount of the nutritive elements

absorbed were determined. Similar experiments were performed to measure the adsorption by the roots of plants, killed by immersion in boiling water for ten minutes. The current, according to its intensity and direction, produces a variation in the velocity of absorption of cations and anions. In the case of the cations, the velocity is constant when the plants are connected to the positive pole, but increases at first very rapidly with the current intensity to a certain point, after which it is almost constant, when the plants are connected with the negative pole. The inverse is true for anions. This variation is not due to electrolysis, since the increase in absorption is greater than can be accounted for by the increased number of ions liberated, due to the increased current. The velocity of adsorption by roots of dead plants is influenced in the same sense by the electric current.

W. G.

**The Study of Plant Enzymes, particularly with Relation to Oxidation.** A. D. HALL, E. F. ARMSTRONG, H. E. ARMSTRONG, F. KEEBLE, and E. J. RUSSELL (*Rep. Brit. Assoc.*, 1913, 143—145).—A short report of work published during 1913. C. H. D.

**The Velocity of Hydrolysis and Displacement by Water of the Nitrogenous and Mineral Substances Contained in Leaves.** G. ANDRÉ (*Compt. rend.*, 1914, 158, 1812—1815. Compare A., 1913, i, 233, 431).—The author has determined the amounts of nitrogenous matter, expressed as nitrogen, phosphorus expressed as  $H_3PO_4$ , and potassium expressed as  $K_2O$ , passing by exosmosis from the leaves of chestnut trees immersed in water for one, two, and six months, the leaves being taken: (a) when quite young; (b) at the period of flowering; (c) at the time of maturity of the fruit. The exosmosis of nitrogen is small even at the end of six months, varying from 6.32% of the total nitrogen in young leaves down to 2.0% in the oldest leaves. The amount of nitrogen passing out from the leaf after the first month is almost a constant percentage of the total passing out, independent of the age of the leaf. The exosmosis of phosphorus is greater, corresponding with rather more than 50% of the total amount in the leaf, and does not appear to vary with the age of the leaf. The amount of phosphorus passing out in the first month's immersion, expressed as a percentage of the total passing out in six months, decreases regularly with the age of the leaf. Potassium is the element which passes out to the greatest extent, varying from 97.85% of the total in the young leaves to 87.2% of the total in the oldest leaves. As in the case of phosphorus, the loss during the first month diminishes with the age of the leaf.

W. G.

**Absorption of Certain Radicles by Leaves in Varying Stages of Decay, and the Effect of Leaves on the Absorption of these Radicles by a Soil.** H. A. NOYES (*J. Ind. Eng. Chem.*, 1914, 6, 574—576).—Leaves, undecayed and in varying stages of decay, show absorption for certain radicles, particularly ammonium,

potassium, and calcium, and phosphoric and sulphuric acids, but not for chlorine, bromine, iodine, nitric acid, or magnesium. The addition of soil to the leaves does not inhibit the absorption, but in the case of mixtures of leaves and soil the absorption does not proceed on the same basis as with the constituents separately.

W. P. S.

**The Nitrogenous Constituents of Plant Galls.** I. M. NIERENSTEIN (*Zeitsch. physiol. Chem.*, 1914, 92, 53—55).—Galls from *Quercus Aegilops*, L., were extracted with benzene or carbon tetrachloride, and, after distilling off the solvents, the residues deposited, in the course of two and a-half years, 9 grams of crystalline material, which, on recrystallisation from alcohol, had m. p. 234—238° (decomp.). The substance is probably 1-galloyl-leucine,  $C_{13}H_{17}O_6N$ , and has  $[\alpha]_D^{16} - 57.35^\circ$ . The structural formula is probably  $CHMe_2 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot C_6H_2(OH)_3$ .

On hydrolysis, gallic acid and *dl*-leucine were obtained and identified.

H. W. B.

[The Araliaceæ Family, with Special Reference to the Glucosides and Oxydases of the Leaves of *Polyscias nodosa*, Forst, and *Hedera Helix*. L...] JOS. HALBERKANN (*Arch. Pharm.*, 1914, 252, 187—190).—In reply to van der Haar (this vol., i, 122), the author states that several observers have recorded the production of arabinose from saponins, and also that neither he nor van der Haar has sufficiently characterised as sesquiterpenes the hydrocarbons obtained by the dry distillation of saponins.

C. S.

**The Enzyme of Chelidonium Seeds.** II. KONRAD BOURNOT (*Biochem. Zeitsch.*, 1914, 65, 140—157).—Further details of the preparation and properties already described (A., 1913, i, 920) of the chelidonium lipase are given. When free from oils, the dry powder loses part of its lipolytic activity by grinding. A very active powder can be obtained when the oil-containing seeds are allowed to remain with light petroleum; this separates in a fine state, and can be readily separated from the coarser particles. The oil obtained in this process, when the petroleum is distilled off at 20°, also has lipolytic properties, which it readily loses on warming to 30°. The ester-forming action on mixtures of monohydroxy-alcohols and fatty acids was studied, and when equivalent amounts of acid and alcohol were used, synthesis amounted to as much as 83.5%, which was not largely increased by excess of alcohol. With glycerol, on the other hand, the synthesis was furthered when excess of the alcohol was present and a little water was added; 78% of the acid could then be esterified. A comparison was made of the esterification of oleic acid by various alcohols; most of the primary monohydroxy-alcohols form esters readily (37 to 91%); the secondary and tertiary alcohols form esters with greater difficulty or not at all (for example, tertiary amyl alcohol). The polyhydroxy-alcohols do not esterify so readily, the maximum lying between 42 and 59%. The esterification of a large number of acids

by isobutyl alcohol was also studied. The author describes the preparation of  $\beta$ -mono-olein,  $C_3H_5O(OH)_2 \cdot C_{18}H_{33}O$ , m. p.  $26^\circ$ , and of isobutyl heptoate, b. p.  $209^\circ$ ,  $D^{20} 0.8593$ , by means of the enzyme. S. B. S.

**Plant Ferments. I. The Oxydases of the Maize Cobb.** G. DOBY (*Biochem. Zeitsch.*, 1914, 64, 111—124).—The style of the cobb owes its coloration to the presence of a peroxydase and oxygenase; a tyrosinase is absent. The peroxydase has a heat-stable zymogen; it is not a protein, but a non-reducing polysaccharide, which is soluble in water. The preparations contained 5 or more % of ash, in which manganese could not be detected. The peroxydase is readily injured by higher concentrations of hydrogen peroxide, and its action is impeded by the presence of sugars and carbohydrates. The oxygenase is always present in the styles, but is absent in the grains and axes, which contain, however, a peroxydase. Furthermore, the peroxydase continually increases in quantity in the styles, whilst no marked change in amount is observed in the grain and axes. The physiological significance of these facts is discussed by the author. The oxygenase also increases in quantity in the styles, but not so rapidly in proportion as the peroxydases. S. B. S.

**Morphology and Microchemistry of Podophyllum peltatum.** O. TUNMANN (*Pharm. Zentr.-h.*, 1914, 55, 619—623).—Podophyllotoxin occurs fairly regularly in all the parenchymatous cells of the rhizome, whilst the resinous portions of the podophyllin are found in the adjacent, excretory cells. The presence of quercetin can be detected, by sublimation, in as little as 0.1 to 0.2 gram of podophyllum (drug). The first sublimate consists of fatty drops with crystals of fatty acids and phytosterols; this is followed by tarry substances, and finally by quercetin. Quercetin is not specially localised in the cork and bark, but seems to accompany the podophyllotoxin. N. H. J. M.

**Dependence of the Relation of Lime and Magnesia on the Concentration.** P. L. GILLE (*Porto Rico Exper. Stat. Bull.*, 12, 1913).—Water-culture experiments with rice in which calcium and magnesium were supplied in various relations to each other and to the other nutrients. In the presence of small amounts of all other foods, solutions of equal percentage amounts of calcium and magnesium chlorides seem to have the same toxic effect. In concentrated solutions of calcium chloride, containing small amounts of the other nutrients, the growth of rice is considerably increased by a slight increase in the amount of magnesium chloride.

In solutions of 172 to 109 per 100,000 of calcium and magnesium chlorides, with minor amounts of all other nutrients, growth was distinctly better when the bases lime and magnesia were present in the ratio 1:1 than in the ratio of 10:1, 5:1, 1:5, or 1:10. In solutions of 62 to 23 per 100,000 of the combined chlorides, the growth of rice seemed to be unaffected by the ratio of lime to magnesia between ratios of 10:1 and 1:10.

The results show that rice differs from many plants in being

relatively less sensitive to magnesium chloride. Whilst the ratio has an effect at comparatively high concentrations, it does not, within the limits of the experiments, at low concentrations.

The conclusion is drawn that the toxicity of an excess of lime or magnesia is not due simply to an unfavourable proportion between the two salts alone, but to an unfavourable proportion between the salt which is in excess and all the other salts present. In ordinary soils the ratio of available lime and magnesia may be expected to be without effect. In alkali soils the ratio may be of the greatest importance.

N. H. J. M.

**Solubility of Soil Constituents.** HER. FISCHER (*Bied. Zentr.*, 1914, 43, 292—294; from *Intern. Mitt. Bodenk.*, 1913, 3, 331).—Indications were obtained of a suitable method for obtaining available potassium from sparingly soluble rocks, in which phonolite is fused with calcium carbonate and sodium chloride, the product ground, and extracted with water.

Experiments are described in which the amounts of potassium dissolved by water, saturated with carbon dioxide, from biotite and phonolite were estimated. The solubility of biotite was found to be less than that of phonolite. On the other hand, Pfeiffer and Blanck found in experiments with oats that the potassium of phonolite is less available than that of biotite.

N. H. J. M.

**Decomposition of Silicates by Soil Bacteria.** K. BASSALIK (*Bied. Zentr.*, 1914, 43, 502; from *Zeitsch. Gärungsphysiol.*, 1913, 3, 15—42).—In experiments with a number of finely powdered minerals it was found that nepheline, magnesia, talc, and augite were the most readily attacked by *Bacillus extorquens*, which dissolved from 4 to 6% of the minerals. Butyric acid bacteria acted similarly, except that they decomposed apatite more readily. Nitrite bacteria acted comparatively vigorously, notwithstanding the slight production of acid.

N. H. J. M.

**Plastic and Adhesive Constituents of Clays.** A. ATTERBERG (*Bied. Zentr.*, 1914, 43, 295—301; from *Intern. Mitt. Bodenk.*, 1913, 3, 291).—From the results of experiments with a number of minerals, the conclusion is drawn that it is the particles which form scales which impart plasticity. In the case of the clays of northern Europe, biotite is the predominant plastic constituent, whilst in the case of the red soils in southern latitudes plasticity is chiefly due to hematite and limonite.

N. H. J. M.

**Microscopic Estimation of Soil-forming Minerals.** W. J. McCaughey and William H. Fry (*Bied. Zentr.*, 1914, 43, 368—371; from *U.S. Dept. Agric. Bur. Soils. Bull.*, 91, 1913).—The minerals found most frequently and in greatest amounts are feldspars, albite and oligoclase being fairly well preserved, whilst the basic members of the group are more readily altered, and can frequently not be identified except in soils of the arid regions. Hornblende and epidote are the predominating minerals, and most of the soils contained tourmaline, rutile, and zircon. Apatite (fluorine apatite) was found in half of the soils, and garnet in ten.

Quartz frequently contains apatite, rutile, zircon, and gas, and sometimes liquids.

Soils derived from sandstone and slate formations vary very distinctly according to climatic conditions. In rainy districts quartz predominates, the other minerals being largely decomposed, whilst in arid regions the reverse is found.

The methods employed are described, and a detailed description of the minerals is given in the original paper. N. H. J. M.

**Distribution of Certain Constituents in the Separates of Loam Soils.** L. A. STEINKOENIG (*J. Ind. Eng. Chem.*, 1914, 6, 576—577).—Analyses of separates of varying coarseness, obtained by submitting the soils to sedimentation and centrifugal action, showed that the percentage of silica is greater, in all cases, than that of any other oxide; alumina is usually second in quantity, followed by iron. The proportion of silica diminishes from the coarser to the finer particles, and zirconia shows the same variation. Iron oxide, alumina, titanium, potash, and phosphoric acid increase in quantity in the finer particles. The distribution of soda, lime, and magnesia appears to follow no general rule.

W. P. S.

**Effect of Heat on Hawaiian Soils.** W. P. KELLEY and WILLIAM MCGEORGE (*Hawaii Agric. Exper. Stat. Bull.*, 30, 1913, 38 pp.)—Experiments on the effects of heating at 100° and 250°, and of ignition, on twelve different soils. Whilst the results varied a good deal, it was found that, on the whole, heating at 100° increases the amounts of manganese, calcium, magnesium, phosphoric acid, sulphates and hydrogen carbonates, and, in most cases, iron, soluble in water; in about half the soils the solubility of the potassium, aluminium, and silica was also increased.

The results obtained at the higher temperatures (250° and ignition) were similar, the increase in solubility being sometimes greater and sometimes less than that obtained at 100°.

The solubility in *N*/5-nitric acid was not altered much by heating at 100°. Heating at 250° sometimes considerably increased the solubility of aluminium, manganese, potassium, and phosphoric acid, and diminished the solubility of the calcium and magnesium.

The changes involved in heating soils are very complex and include, among others, flocculation, deoxidation of manganese dioxide, oxidation, particularly of iron, double decomposition, dehydration, and physical alterations of soil films.

The nitrates present in soils are practically all destroyed at 200—250°; whilst a decrease occurred at 100°.

Heating at 200° resulted in a loss of about 25% of the total nitrogen and in the production of abnormally large amounts of ammonia. The burning of brush in the field was found to cause a stimulation of ammonification, whilst nitrification was not restored in two months.

N. H. J. M.

## Organic Chemistry.

**Observations on the Acetylene Dichlorides.** G. CHAVANNE (*Bull. Soc. chim. Belg.*, 1914, 28, 234—240).—The formulæ assigned to the isomeric acetylene dichlorides [*s*-dichloroethylenes] in a previous paper (A., 1912, i, 330) on the basis of the rate at which they react with alcoholic potassium hydroxide, are found to require transposition. The isomeride boiling at 60·25° is the *cis*-form, whilst the more reactive isomeride boiling at 48·35° is the *trans*-form. The equilibrium mixture contains 80% of the former and 20% of the latter.

If the *s*-dichlorodibromoethane, which is obtained from either of the isomerides on the addition of bromine, is acted on by zinc in presence of alcohol, the bromine is removed and an equilibrium mixture of the two acetylene dichlorides is obtained. If the dichlorodibromoethane is added slowly to the mixture of zinc and alcohol, the equilibrium mixture is obtained in almost theoretical yield. An explanation of the formation of the two isomerides in this ratio has not yet been found.

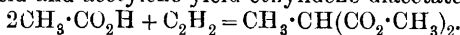
Experiments have also been made to determine the rate of addition of bromine by the two isomeric forms. Small quantities of bromine were dissolved in the pure liquids, and the rate of disappearance of the bromine on exposure to the light from a Nernst lamp was measured at about 12°. The reaction proceeds in accordance with the equation for a unimolecular change, although the coefficient increases somewhat during the initial stages of the reaction. The results show that the reaction velocity is about twice as great for the *trans*-form as for the *cis*-form of the dichloride. Experiments with the equilibrium mixture gave an intermediate value for the velocity coefficient. H. M. D.

**The Presence of an Alcohol and an Acid, each having C<sub>32</sub>, in the Wax from Tachardia lacca.** ALBERT GASCARD (*Compt. rend.*, 1914, 159, 258—260).—Lac gum on extraction with boiling alcohol loses all its resin and the greater part of its wax. The residue consists of fragments of wood and insect remains, and on extraction with boiling benzene yields a further small amount of wax, which on purification is shown to be an *ester*, m. p. 94°. This on saponification with boiling potassium hydroxide yields an alcohol and an acid, the latter being separated by means of its calcium salt. The alcohol crystallises in lozenge-shaped plates, m. p. 88°, and is shown to be *dotriacontanol* (*laccerol*), C<sub>32</sub>H<sub>65</sub>·OH. It yields the corresponding *dotriacontanyl iodide*, C<sub>32</sub>H<sub>65</sub>I, m. p. 71°, and on reduction *dotriacontane*, m. p. 70·5°. The acid obtained by the saponification is *dotriacontanoic* (*lacceroic*) *acid*, m. p. 95—96°, giving an *ethyl ester*, m. p. 76°, which on reduction yields *dotriacontanol*. W. G.

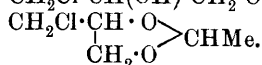
**Preparation of Esters and Ethers of Ethylidene Glycol and Vinyl Alcohol.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 271381).—In presence of mercuric salts such as the sulphate or phosphate,



compounds containing hydroxyl or carboxyl groups absorb acetylene with great rapidity, the reaction being often facilitated by the addition of small proportions of catalysts such as mineral acids, acid salts, &c. Thus, acetic acid and acetylene yield ethylidene diacetate,



In other instances 1 mol. of the carboxylic or hydroxylic compound reacts with 1 mol. of acetylene; for instance,  $\text{CCl}_3\cdot\text{CO}_2\text{H} + \text{C}_2\text{H}_2 = \text{CCl}_3\cdot\text{CO}_2\cdot\text{CH}:\text{CH}_2$  and  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH} + \text{C}_2\text{H}_2 =$



T. H. P.

**Phytochemical Formation of Ethyl Mercaptan.** C. NEUBERG and F. F. NORD (*Ber.*, 1914, **47**, 2264—2271).—It is suggested that the thiocarbimides and organic sulphides found in plants have their origin in the mercaptans. The last-named substances are not easily formed from the corresponding alcohols, but as the latter are possibly produced through the aldehydes in fermentation processes, the possibility of the aldehydes as an important stage in the formation of mercaptans has been considered. The accompanying experimental evidence is in favour of this view.

As the unstable unimolecular thioaldehydes and the very sparingly soluble trimolecular compounds were unsuited to examination, thialdine,  $\text{CHMe} \begin{smallmatrix} \text{S}\cdot\text{CHMe} \\ \text{S}\cdot\text{CHMe} \end{smallmatrix} \text{NH}$ , which should be able to undergo fission into ethyl mercaptan and aldehyde-ammonia, was used. If an alcoholic solution of this substance is added to a solution of sucrose which is in a state of fermentation, the odour of mercaptan is soon evident. The mercaptan was separated from the accompanying carbon dioxide by bubbling the evolved gas through a series of flasks containing a solution of mercuric cyanide; by treating the precipitate of mercuric mercaptide with hydrochloric acid and warming, the mercaptan was obtained in a purer condition and was immediately converted into the lead salt in which form its identity was established. From 20 grams of thialdine, 1.3 of the lead salt was finally obtained.

Only living yeast is able to reduce thialdine in this way in the presence of sugar, and the process presumably is analogous to the production of alcohol from an aldehyde.

D. F. T.

**Preparation of Acetic Anhydride.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 273101).—The preparation of acetic anhydride by passing chlorine into a mixture of an acetate with sulphur necessitates the use of very low temperatures obtainable only with the help of a refrigerating machine. This disadvantage is obviated by replacing the sulphur by sulphur mono- or di-chloride or a mixture of the two, the reactions, which take place at about 20% and give good yields of the anhydride, being represented by the equations:  $16\text{CH}_3\cdot\text{CO}_2\text{Na} + \text{S}_2\text{Cl}_2 + 5\text{Cl}_2 = 12\text{NaCl} + 2\text{Na}_2\text{SO}_4 + 8\text{Ac}_2\text{O}$  and  $8\text{CH}_3\cdot\text{CO}_2\text{Na} + \text{SCl}_2 + 2\text{Cl}_2 = 6\text{NaCl} + \text{Na}_2\text{SO}_4 + 4\text{Ac}_2\text{O}$ .

T. H. P.

**Preparation of Cellulose Esters of Fatty Acids.** CHEMISCHE FABRIK VON HEYDEN A.-G. (D.R.-P. 273029).—Aliphatic esters of cellu-

lose or its transformation products are obtained by treatment of the dried cellulosic material with anhydrides of fatty acids in presence of chlorides of sulphuric acid without heating or at the ordinary temperature.

T. H. P.

Phosphates of  $\alpha\beta$ -Distearin. R. R. RENSCHAW and R. R. STEVENS (*J. Amer. Chem. Soc.*, 1914, 36, 1770—1772).—Grün and Kade (A., 1913, i, 158) have described certain distearin phosphates obtained by the action of phosphoric oxide on distearin. Similar experiments have been carried out by the authors, who have confirmed the work on the primary orthophosphate, and have isolated a sodium salt of stearin pyrophosphate, 
$$\text{C}_{17}\text{H}_{35}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\underset{\text{CH}_2\cdot\text{O}\cdot\text{PO}_2\text{Na}}{\overset{\text{CH}\cdot\text{O}\cdot\text{PO}_2\text{Na}}{\text{C}}}\cdot\text{O}>\text{O};$$
 the corresponding silver, barium, and calcium salts were prepared.

E. G.

Catalytic Reduction of Oleic Acid and Cottonseed Oil by means of Hydrogen in Presence of Finely Divided Nickel. T. W. A. SHAW (*J. Soc. Chem. Ind.*, 1914, 33, 771—774).—The first series of experiments deals with the reduction of oleic acid vapour. An apparatus is described in which the vapour of oleic acid is carried by a current of purified hydrogen under diminished pressure into a cylinder, heated at about  $300^\circ$ , containing broken pumice impregnated with about 13—14% of nickel (reduced from the oxide by hydrogen at about  $300^\circ$ ). The extent of the reduction is determined by estimating the iodine number of the product by the Wys-Hübl method. Under 100, 150, and 200 mm. pressure, 5, 15, and 20% respectively of the oleic acid vapour is reduced; these values are practically unchanged when the products are again passed through the apparatus.

The results indicate a state of equilibrium in the gaseous phase between hydrogen, oleic acid, and stearic acid; however, when stearic acid vapour and hydrogen are passed through the apparatus, the iodine number of the product is zero.

In a second series of experiments in the same apparatus, liquid oleic acid is kept in contact with the catalyst at about  $275^\circ$  for different periods of time, the pressure of the hydrogen being maintained at 1 atmos.; about 45% of the acid is reduced after nine hours.

A third series of experiments deals with the reduction of liquid oleic acid under very great pressures. An apparatus is described in which oleic acid is sprayed, by means of a specially designed feed-valve and glass sprinkler (not a soldered brass rose, because the acid dissolves from this some constituent which poisons the catalyst), over the catalyst in an atmosphere of hydrogen at a definite temperature and pressure, the rate of flow being about 40 c.c. per hour. At a temperature of  $250^\circ$ , the amount of oleic acid reduced is 4, 20, and 35% under pressures 5, 25, and 50 atmos. respectively.

A few experiments performed with cottonseed oil show that at  $200^\circ$ , and under pressures of 25 and 50 atmos., more than 50% of the glyceride is reduced and a hard product, m. p. about  $50^\circ$ , is obtained.

C. S.

**Preparation of Glycerol Halogenhydrins and Esters of Polyhydroxyaliphatic Acids.** ADOLF GRÜN (D.R.-P. 272337).—When castor oil or oxidised linseed oil, etc., is treated directly or in solution under pressure with the calculated proportion or an excess of hydrogen haloid, either as gas or dissolved in alcohol, the principal reactions taking place are as follows: (1) the triglyceride is converted by the hydrogen haloid into ricinoleic acid and its chlorohydrin ester, the latter then undergoing decomposition into chlorohydrin and free acid; (2)  $2\text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H} - \text{H}_2\text{O} = \text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H}$  and  $3\text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H} - 2\text{H}_2\text{O} = \text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H}$ ; (3) the di- and tri-ricinoleic acids undergo esterification by the alcohol present. The principal constituents of the resultant product are the mono- and di-chlorohydrins of glycerol and esters of polyricinoleic acids, but small proportions of glycerol and free di- and tri-ricinoleic acids are also present.

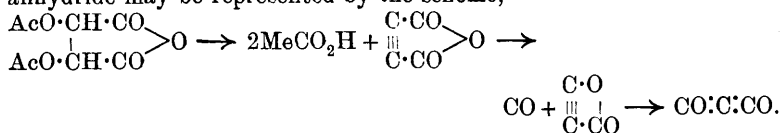
T. H. P.

**Optical Decomposition of the Iridotrioxalates.** M. DELÉPINE (*Compt. rend.*, 1914, 159, 239—241).—The author has prepared optically active iridotrioxalates of the type  $\text{M}_3\text{Ir}(\text{C}_2\text{O}_4)_3$ , by preparing the strychnine salts from the racemic potassium salt, and separating these into the dextro- and lævo-components by fractional precipitation. The potassium salt was prepared by the action of a solution of potassium oxalate on potassium iridi- or irido-chlorides or potassium iridodichlorodioxalate in an autoclave at  $130^\circ$  for eight hours. This salt after crystallisation was fractionally precipitated by strychnine sulphate, giving the two crystalline strychnine salts, differently hydrated, which in the anhydrous state,  $(\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2)_3$ ,  $\text{H}_3\text{Ir}(\text{C}_2\text{O}_4)_3$ , had  $[\alpha]_D + 11.8^\circ$  and  $-56.4^\circ$  respectively. These on decomposition with potassium hydroxide in aqueous solution gave the *d*- and *l*-potassium salts,  $\text{K}_3\text{Ir}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ ,  $[\alpha]_D \pm 82^\circ$ , and with barium hydroxide the *d*- and *l*-barium salts,  $\text{Ba}_3[\text{Ir}(\text{C}_2\text{O}_4)_3]_2 \cdot 15\text{H}_2\text{O}$ ,  $[\alpha]_D \pm 62.5^\circ$ . The silver salts prepared from these active salts by double decomposition could only be obtained in the form of amorphous, granular masses. The active salts in solution at  $100^\circ$  show a slow diminution of a few hundredths of a degree per hour in their optical activity. The *d*-potassium iridotrioxalate shows an anomalous rotatory dispersion and a circular dichroism. The maximum rotation is in the blue portion of the spectrum, and it disappears in the violet.

W. G.

**Pyrogenic Formation of Carbon Suboxide from  $\gamma$ -Lactones.** ERWIN OTT (*Ber.*, 1914, 47, 2388—2393).—When diacetyltartaric anhydride and acetoxymaleic anhydride are heated, they readily suffer decomposition into acetic acid and carbon suboxide. It is assumed that acetylenedicarboxylic anhydride is an intermediate product, for an appreciable quantity of carbon suboxide is only obtained from those acetylated 1:2-dicarboxylic anhydrides that, by losing acetic acid, can produce the acetylenic anhydride. Diacetoxymaleic anhydride, for example, yields acetic acid and keten, and only about 2% of carbon suboxide. Keten is also a product of the decomposition of triacetin, but not of all acetyl derivatives. The one feature common to these

compounds is the tendency to the elimination of acetic acid. The decomposition of acetylenedicarboxylic anhydride is accompanied by the production of carbon monoxide, which is often formed when 1:2-dicarboxylic acid derivatives, ethyl oxalate, for example, are heated. Assuming that the carbon suboxide is first set free in the form of  $\beta$ -oxypropiololactone, the decomposition of diacetyltartaric anhydride may be represented by the scheme,



Diacetyltartaric anhydride may be obtained in quantitative yield from acetic anhydride, tartaric acid and sulphuric acid (Wohl and Österlin, A., 1901, i, 365), and is a very suitable material for the preparation of carbon suboxide. For this purpose, it is quickly distilled under reduced pressure from a long-necked flask in a bath at 180—185°, over a glowing platinum spiral which is so adjusted that decomposition of the vapours is complete. In order to estimate the yields, the flask was connected with a receiver cooled to -80°, and a vessel containing aniline. The amount of acetic acid condensed represented a yield of 87%, and the malonanilide which collected in the second receiver corresponded with a 42.5% yield of carbon suboxide.

Acetoxymaleic anhydride (*ibid.*) sublimes in a vacuum at 65° and forms compact crusts, m. p. 91°. It decomposed at 140—150° and gave a 73% yield of acetic acid, 37% of malonanilide, 69.4% of carbon monoxide, and 31% of carbon dioxide. Diacetoxymaleic anhydride (Fenton, T., 1896, 69, 551) decomposed at 160—170°, and gave acetic acid 73%, carbon suboxide 2%, keten, weighed as acetanilide, 10%, carbon monoxide 91.5%, and carbon dioxide 70%. Triacetin was similarly treated at 155°, and gave acetic acid, acraldehyde and keten (26%).

J. C. W.

**Preparation of Cupric Cholate.** KNOLL & Co. (D.R.-P. 273317).—The interaction of solutions of a cupric salt and of sodium cholate in presence of methyl or ethyl alcohol yield *cupric cholats*,  $\text{Cu}(\text{C}_{24}\text{H}_{39}\text{O}_5)_2$ , which exerts a bactericidal action; it dissolves in 100 parts of castor oil.

T. H. P.

**Tetra-acetylmucyl Chloride and Azoimide.** Decomposition of the Latter by Heat. OTTO DIELS and FRITZ LÖFLUND (*Ber.*, 1914, 47, 2351—2355).—The authors have attempted the ring condensation of tetra-acetylmucic acid derivatives, but without success. The elimination of chlorine from the acid chloride was without result, and the action of heat on the azoimide seemed to follow an unusual course, for the nitrogen compound which was obtained was very stable.

Tetra-acetylmucic acid was shaken with phosphorus pentachloride and acetyl chloride for an hour or so, when the *chloride*,  $\text{C}_{14}\text{H}_{16}\text{O}_{10}\text{Cl}_2$ , separated quantitatively in small, silky needles, m. p. 179—180° (compare Jacoby, *Diss.*, Berlin, 1907). The *hydrazide*,  $\text{C}_{14}\text{H}_{22}\text{O}_{10}\text{N}_4$ , was prepared by adding the powdered chloride in small quantities to a 50%

solution of hydrazine hydrate, with vigorous stirring, and formed a very sparingly soluble, white powder. This was converted into *tetraacetylmucylazoimide*,  $C_{14}H_{16}O_{10}N_6$ , by the action of nitrous fumes. The bistriazo-compound was also prepared by mixing an acetone solution of the chloride with a solution of sodium azoimide in dilute acetone. It forms long prisms which decompose at above  $108^\circ$ , then re-solidify, and melt again at  $139^\circ$ . It was gradually heated to  $110^\circ$  in ethyl malonate, whereby two molecular proportions of nitrogen were evolved and a clear solution remained, from which, on cooling, the compound,  $C_{14}H_{16}O_{10}N_2$ , separated in large prisms, m. p.  $139^\circ$ .

J. C. W.

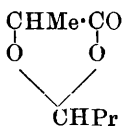
**Oxalocitrolactone and its Transformation into Tricarballic Acid.** H. GAULT (*Compt. rend.*, 1914, 159, 256—258. Compare this vol., i, 384, 484).—Oxalocitrolactone on heating with water or hydrochloric acid in sealed tubes at  $180^\circ$ , yields tricarballic acid and a large amount of resinous substances. On heating with alcohol in an autoclave at  $180$ — $200^\circ$ , it yields ethyl oxalate (3%), ethyl tricarballic acid (30%), and ethyl propanetetracarboxylate (60%). The two latter esters on hydrolysis with acid give a quantitative yield of tricarballic acid. Under the influence of hydrolysing agents the ketolactonic ring of oxalocitrolactone is opened or not, according as the hydrolysis is effected at a high ( $180$ — $200^\circ$ ) or a medium temperature ( $100$ — $120^\circ$ ).

W. G.

**Preparation of Acraldehyde.** EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1914, 36, 1766—1770).—Wohl and Mylo (A., 1912, i, 677) have described a method for preparing acraldehyde from glycerol in which anhydrous magnesium sulphate is used as catalyst. This method is very satisfactory, but involves the use of special expensive apparatus. A modification is now described in which the apparatus is so simplified as to be capable of construction from ordinary stock materials. The modified method does not give quite such large yields of pure acraldehyde as were obtained by Wohl and Mylo, but it is much more readily available for ordinary use.

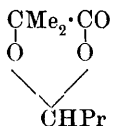
E. G.

**Syntheses by means of Organometallic Derivatives of Zinc: Aldehydes.** E. E. BLAISE (*Bull. Soc. chim.*, 1914, [iv], 15, 661—666).—Lactic acid and  $\alpha$ -hydroxyisobutyric acid when warmed with an excess of a mixture of formic acid and acetic anhydride yield the corresponding formic esters, which, like their acid chlorides, condense with zinc propyl iodide to give methylpropyl- and dimethylpropyl-cycloacetals, which on hydrolysis give butaldehyde. Lactic acid gives  $\alpha$ -formoxypropionic acid,  $CHO \cdot O \cdot CHMe \cdot CO_2H$ , m. p.  $78^\circ$ , b. p.  $120$ — $121^\circ/13$  mm., which yields an acid chloride, b. p.  $59^\circ/19$  mm., and an anilide, long needles, m. p.  $182^\circ$ . The acid chloride condenses with zinc propyl iodide to give 1-methyl-4-propyleycloacetal (annexed formula), b. p.  $82^\circ/17$  mm.



$\alpha$ -Hydroxyisobutyric acid yields  $\alpha$ -formoxyisobutyric acid,  $CHO \cdot O \cdot CMe_2 \cdot CO_2H$ , needles, m. p.  $64$ — $65^\circ$ , b. p.  $125$ — $126^\circ/15$  mm., giving an acid chloride, a dense liquid with a very disagreeable odour, b. p.  $53$ — $54^\circ/14$  mm.,

and an *anilide*, prismatic needles, m. p. 100—101°. The acid chloride with zinc propyl iodide yields 1:1-*dimethyl-4-propylcycloacetal* (annexed formula), b. p. 84°/20 mm.



Both these *cycloacetals* are readily hydrolysed on boiling with aqueous oxalic acid, giving butaldehyde, b. p. 73—74°, and the original hydroxy-acid. Both of the formoxy-acids are rapidly saponified on exposure to air.

W. G.

**Syntheses by means of Mixed Organometallic Derivatives of Zinc.  $\alpha$ -Monochloroketones.** E. E. BLAISE (*Bull. Soc. chim.* 1914, [iv], 15, 666—673. Compare preceding abstract).—By the following series of reactions the author has prepared a number of  $\alpha$ -chloro-ketones. An  $\alpha$ -chloro-acid chloride was condensed with a suitable  $\alpha$ -hydroxy-acid, either lactic acid or  $\alpha$ -hydroxyisobutyric acid, and the resulting ester acid converted into its acid chloride. This acid chloride was then treated with the necessary zinc alkyl iodide, giving a chloro-*cycloacetal*, which on hydrolysis gave the required  $\alpha$ -chloro-ketone.

The required  $\alpha$ -chloro-acid chlorides were prepared by chlorinating the corresponding alkylmalonic acids in solution in carbon tetrachloride by a current of dry chlorine, decomposing the chloroalkylmalonic acid by heat and treating the resulting  $\alpha$ -chloro-acid with thionyl chloride. Thus ethylmalonic acid yields  *$\alpha$ -chloroethylmalonic acid*, needles, m. p. 106—107°, which is decomposed on heating at 140°, yielding  *$\alpha$ -chlorobutyric acid*, b. p. 109·5°/24 mm., giving the corresponding *acid chloride*, b. p. 62—63°/70 mm. and 51—52°/41 mm.

On condensing lactic acid with  $\alpha$ -chlorobutyryl chloride in the presence of diethylaniline,  *$\alpha$ -chloroacetoxypropionic acid*,  $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , is obtained, m. p. 76°, b. p. 160—162°/15 mm., giving an *acid chloride*, b. p. 94°/11 mm., and an *anilide*, white needles, m. p. 95—96°.

Similarly prepared are  *$\alpha$ -chloroacetoxyisobutyric acid*,  $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , m. p. 75°, its *acid chloride*, a viscous liquid, b. p. 97°/12 mm., and its *anilide*, long needles, m. p. 127·5°;  *$\alpha$ -chlorobutyroxyisobutyric acid*,  $\text{CHEtCl} \cdot \text{CO} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , slender needles, m. p. 61—62°, its *acid chloride*, b. p. 106°/11 mm., and its *anilide*, m. p. 65—66°.

$\alpha$ -Chloroacetoxypropionyl chloride gives with zinc ethyl iodide the *cycloacetal*,  $\begin{array}{c} \text{CHMe} \cdot \text{O} \\ | \quad \diagup \\ \text{CO} \quad \text{O} \end{array} > \text{CEt} \cdot \text{CH}_2\text{Cl}$ , b. p. 106°/12 mm., which on hydrolysis yielded chloromethyl ethyl ketone, b. p. 67—68°.

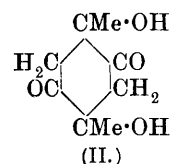
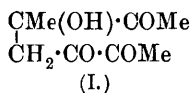
$\alpha$ -Chloroacetoxyisobutyryl chloride yields with zinc propyl iodide the *cycloacetal*,  $\begin{array}{c} \text{CMe}_2 \cdot \text{O} \\ | \quad \diagup \\ \text{CO} \quad \text{O} \end{array} > \text{CPr} \cdot \text{CH}_2\text{Cl}$ , b. p. 110·5°/10 mm., which gives *chloromethyl propyl ketone*, b. p. 154—156°/760 mm. or 58—59°/17 mm., yielding a *semicarbazone*, m. p. 157°. Together with the above *cycloacetal* a second *cycloacetal*,  $\begin{array}{c} \text{CMe}_2 \cdot \text{O} \\ | \quad \diagup \\ \text{CO} \quad \text{O} \end{array} > \text{CH} \cdot \text{CH}_2\text{Cl}$ , b. p. 91·5°/11 mm., is obtained, which on hydrolysis yields chloroacetaldehyde.

$\alpha$ -Chlorobutyroxyisobutyryl chloride yields with zinc ethyl iodide the cycloacetal,  $\begin{array}{c} \text{CMe}_2\cdot\text{O} \\ | \\ \text{CO}-\text{O} \end{array} \text{C} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CEt}\cdot\text{CHClEt}$ , b. p. 118.5°/12 mm., which on hydrolysis gives *ethyl  $\alpha$ -chloro-n-propyl ketone*, b. p. 53.5°/17 mm.

W. G.

**Properties, Structure, and Derivatives of the Dimeric Diacetyl.** OTTO DIELS, W. M. BLANCHARD, and H. VON DER HEYDEN (*Ber.*, 1914, **47**, 2355—2365).—As an intermediate product in the condensation of diacetyl, Pechmann isolated a colourless oil which was found to be a dimeride of diacetyl, and to yield a trihydrazone. On

account of the latter fact, Pechmann and Wedekind (A., 1895, i, 647) decided in favour of the formula I. It would be strange for an unsymmetrical product to arise from diacetyl by simple means, and such a compound as the above (formula I) should be unstable and intensely coloured. The authors now bring forward evidence in favour of Pechmann's alternative formula II.



In the first place, they find that the compound may be obtained as a colourless solid, but that it develops a yellow colour on melting or distilling, and in many solvents. It seems probable, therefore, that, although the colourless compound can scarcely contain adjacent carbonyl groups, it can readily pass into such a state. The formation of a triphenylhydrazone, a quinoxaline and disemicarbazone, does not really help to decide on the true formula, but it is hoped that two oxygen-free compounds, obtained by the action of hydrazine under different conditions, may throw some light on the question. Many fruitless attempts were also made to determine the presence and number of hydroxyl groups in the aldol, but it was at last discovered that carbethoxycarbimide (A., 1906, i, 237; 1908, i, 613) forms a mono- and a di-derivative. This agrees with the cyclic formula, which is further supported by refractometric evidence, and more readily explains the formation of *p*-xyloquinone by the action of 33% potassium hydroxide on the aldol.

For the preparation of the dimeric diacetyl, *N*-potassium hydroxide was allowed to drop into an ice-cold, aqueous solution of the diketone, when the brilliant yellow colour faded. The product was faintly acidified and submitted to prolonged extraction with ether. The residue from the dried extract was then heated at 80° under reduced pressure to remove diacetyl, and finally distilled in a high vacuum, a fraction with b. p. 95—102°/0.2 mm. being collected. This was left over phosphoric oxide in the cold, when, especially after inoculation, it solidified to a hard mass which was freed from traces of oil by hydraulic pressure. After crystallisation from a mixture of ether and light petroleum, it was obtained in large, well-developed, glistening, colourless, hard crystals. The m. p. varied from 44—46° for slow heating to about 58° for quick heating. The refraction of the super-cooled substance was measured for the red hydrogen line at 29.8°,

$D_4^{20.8}$  being 1.15597, and the observed molecular refraction, 40.20, agreed with the theoretical value, 39.94, based on Clarke's figure, 27.78, for *cyclohexanedione* (T., 1912, 101, 1804).

The *monocarbethoxycarbimide* derivative,  $C_{12}H_{17}O_7N$ , gradually separates when cold, ethereal solutions of the components are mixed. It forms white, velvety needles, m. p.  $109^\circ$ . When the undiluted reagents are mixed, much heat is developed, and a mixture of mono- and di-derivatives is formed. On cooling the ethereal solution, the mono-derivative separates, leaving the *dicarbethoxycarbimide* compound in the mother liquor. The latter forms coarse, fibrous crystals, m. p.  $150^\circ$ .

When an aqueous solution of the aldol is mixed with a solution of hydrazine hydrate in the cold and the water is subsequently distilled under reduced pressure, a syrup is formed, which deposits from methyl alcohol the colourless *hydrazone*,  $C_8H_{12}N_4$ , in stout crystals, m. p.  $161-163^\circ$ . By adding hydrazine hydrate, drop by drop, to the pure aldol, however, a yellow liquid is obtained which solidifies when acidified by 50% acetic acid and cooled in ice. This *hydrazone*,  $C_{16}H_{20}N_6$ , forms brilliant golden-yellow prisms, m. p.  $185^\circ$ , which crystallise in an almost colourless form from very dilute alcohol, but recrystallise from pure alcohol with the original colour. A mixture of the colourless hydrazone with potassium hydroxide and platinised alumina was heated until reaction set in and then distilled, when the *base*,  $C_8H_{12}N_2$ , was collected as a yellow oil, b. p.  $220-230^\circ$ ,  $132^\circ/11$  mm.; it formed a *methiodide*,  $C_9H_{15}N_2I$ , in large, yellow crystals, m. p.  $152^\circ$ .

The *disemicarbazone* of the aldol,  $C_{10}H_{18}O_4N_8$ , was obtained by mixing concentrated aqueous solutions of the aldol and the hydrochloride, in colourless, slender needles, m. p.  $225^\circ$  (decomp.). Similarly, on mixing aqueous solutions of the aldol and *o*-phenylenediamine, the *quinoxaline* (?),  $C_{14}H_{16}O_2N_2$ , separated in glistening, yellow needles, m. p.  $112-113^\circ$ . The *semicarbazone* of the latter,  $C_{15}H_{19}O_2N_5$ , forms well-developed, almost colourless plates, m. p.  $185^\circ$ . J. C. W.

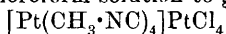
**Problems of Celluloid Chemistry and the Necessity of Colloido-Chemical Views in the Industry.** H. SCHWARZ (*Koll. Chem. Beihefte*, 1914, 6, 90-126).—The possible application of the theories associated with the chemistry of colloids to the problems of the celluloid industry is discussed with special reference to the factors which influence the stability of the substance. In particular, the author deals with the relationship between the stability of celluloid and the stability of the nitrocellulose employed in its production. As a means of determining the presence of small quantities of unstable substances in nitro-cellulose, the "heat-test" is adversely criticised.

The fact that traces of free acid are responsible for the instability of celluloid would seem to be well established, and the methods employed in practice for the neutralisation of the free acid are discussed. It is shown that colloidal ant-acids are particularly efficient in this connexion, and that the activity of these increases with the quantity present. Celluloid itself is regarded as a colloidal mixture of nitrocellulose and camphor.

H. M. D.



**Preparation of Complex Compounds of Bivalent Platinum.** L. TSCHUGAEV (*Compt. rend.*, 1914, 159, 188—189).—By the use of tripropylamine platinochloride, obtained by the double decomposition of tripropylamine hydrochloride and ammonium platinochloride, the author has been able to use organic solvents for the preparation of complex platinum compounds. Thus, this platinochloride reacts with methylcarbylamine in chloroform solution to give the compound,

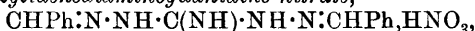


(compare Tschugaev and Teearu, this vol., i, 392). With hydrazine in the same solvent, it yields the compound,  $[\text{Pt}(\text{N}_2\text{H}_4)_4]\text{Cl}_2$ . Tripropylamine platinochloride can also be used for the preparation of platinochlorides from aromatic phosphines, arsines and stibines, which are quite insoluble in water. W. G.

**Preparation of a Stable, Solid Compound of Hydrogen Peroxide and Hexamethylenetetramine.** DIAMALT AKTIEN-GESELLSCHAFT (Austrian Patent 63538).—This compound, which is obtained by dissolving hexamethylenetetramine, with cooling, in hydrogen peroxide solution and precipitation by means of an organic solvent, is moderately stable and possesses antiseptic properties. Its stability is enhanced by the addition of: (1) an anhydride, such as that of lactic or glycollic acid or the acetyl derivative of an aromatic hydroxy-acid, which absorbs the ammonia formed on decomposition, and (2) a protein or polysaccharide, which absorbs the formaldehyde also formed. T. H. P.

**Preparation of Aminoguanidine and of Diaminoguanidine.** GUIDO PELLIZZARI and AUGUSTO GAITER (*Gazzetta*, 1914, 44, ii, 72—77).—The authors have established the conditions under which aminoguanidine hydrogen carbonate (compare Thiele, A., 1899, i, 7) can be obtained simply and in almost theoretical yield from calcium cyanamide, hydrazine sulphate and potassium carbonate. *Aminoguanidine hydrobromide*,  $\text{CH}_6\text{N}_4\cdot\text{HBr}$ , forms colourless, prismatic needles, m. p.  $149^\circ$  (decomp.).

Now that hydrazine hydrate is obtainable of 100% purity, the authors have modified the conditions for the preparation of diaminoguanidine hydrobromide by the action of cyanogen bromide (compare Pellizzari and Cantoni, A., 1905, i, 576). *Diaminoguanidine nitrate*,  $\text{CH}_7\text{N}_5\cdot\text{HNO}_3$ , forms groups of colourless, prismatic needles, m. p.  $143^\circ$ . *Dibenzylidenediaminoguanidine nitrate*,



forms white needles, m. p.  $211\text{—}212^\circ$ , turning an intense red in the light. T. H. P.

**Triaminoguanidine.** GUIDO PELLIZZARI and AUGUSTO GAITER (*Gazzetta*, 1914, 44, ii, 78—85).—The formation of triaminoguanidine hydrochloride by boiling hydrazine hydrate with excess of carbon tetrachloride in a current of ammonia for some days gives a small yield of a preparation difficult to purify (compare Stollé, A., 1904, i, 980). The authors find that triaminoguanidine salts may be obtained readily by heating concentrated alcoholic or aqueous solutions of the salts of either guanidine or its amino- or its diamino-derivative

with the calculated proportion of hydrazine hydrate for two to five hours. Salts of triaminoguanidine react easily with aldehydes, giving salts of the condensation products of the triaminoguanidine with 3 mols. of the aldehydes.

*Triaminoguanidine nitrate*,  $\text{NH}_2 \cdot \text{N} : \text{C}(\text{NH} \cdot \text{NH}_2)_2, \text{HNO}_3$ , forms colourless needles, m. p.  $216^\circ$  (decomp.).

*Tribenzylidenetriaminoguanidine nitrate*,  
 $\text{CHPh} : \text{N} : \text{N} : \text{C}(\text{NH} \cdot \text{N} : \text{CHPh})_2, \text{HNO}_3, 3\text{H}_2\text{O}$ ,  
 forms slender, yellowish-white needles.

*Triaminoguanidine hydrobromide*,  $\text{CH}_8\text{N}_6, \text{HBr}$ , forms colourless, shining needles, m. p.  $232^\circ$  (decomp.), or somewhat lower if the heating is slow.

*Tribenzylidenetriaminoguanidine hydrobromide*,  $\text{C}_{22}\text{H}_{20}\text{N}_6, \text{HBr}, 3\text{H}_2\text{O}$ , forms shining, yellow crystals, and has no definite melting point, but decomposes at about  $145\text{--}150^\circ$ .

Triaminoguanidine hydrochloride has m. p.  $231^\circ$  (decomp.); Stollé (*loc. cit.*) found  $229^\circ$ . Its tribenzylidene derivative crystallises with  $3\text{H}_2\text{O}$ , and the crystals effloresce and lose hydrogen chloride in the air.

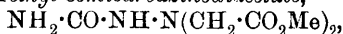
Tribenzylidenetriaminoguanidine forms small, yellow needles m. p.  $198^\circ$ ; Stollé (*loc. cit.*) gave  $196^\circ$ .

*Triaminoguanidine thiocyanate*,  $\text{CH}_8\text{N}_6, \text{HCNS}$ , forms slender, shining needles, m. p.  $136^\circ$ , and the *picrate*,  $\text{CH}_8\text{N}_6, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , long, yellow needles or shining lamellar crystals, m. p.  $171^\circ$ .

Triaminoguanidine sulphate and oxalate are difficult to purify owing to their extremely high solubility in water. T. H. P.

**Action of Chloroacetic Acid on Semicarbazide and Hydrazine.** J. R. BAILEY and W. T. READ (*J. Amer. Chem. Soc.*, 1914, **36**, 1747—1766).—The action of chloroacetic acid on hydrazine and phenylhydrazine has already been studied, but its action on semicarbazide has not hitherto been investigated. The present work was therefore undertaken.

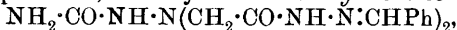
When potassium chloroacetate and semicarbazide are heated together in aqueous solution, semicarbazinodiacetic acid is produced, together with a small quantity of semicarbazinoacetic acid. On evaporating the product of the reaction to dryness and treating the residue with alcohol and hydrochloric acid, the ester of semicarbazinodiacetic acid is obtained. *Methyl semicarbazinodiacetate*,



m. p.  $143.5^\circ$ , crystallises in long needles; the corresponding *ethyl* ester, m. p.  $91^\circ$ , forms thin plates. By the action of hydrazine hydrate (2 mols.) on the methyl ester (1 mol.), *semicarbazinodiacetohydrazide*,



m. p.  $149^\circ$ , is produced, which yields a *dibenzylidene* compound,



m. p.  $178^\circ$  (decomp.). Methyl semicarbazinodiacetate is decomposed by nitrous acid with formation of methyl iminodiacetate (Jongkees, A., 1908, i, 959).

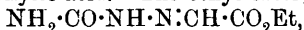
If ethyl or methyl semicarbazinodiacetate is treated with an alcoholic solution of sodium ethoxide, *ethyl 3:5-dihydroxy-1:6-dihydro-1:2:4-*

*triazine-1-acetate*,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{N}<\begin{smallmatrix} \text{N}=\text{C}(\text{OH}) \\ \text{CH}_2\cdot\text{C}(\text{OH}) \end{smallmatrix}>\text{N}$ , m. p.  $138.5^\circ$ , is produced which crystallises in slender needles; the corresponding *methyl ester*, m. p.  $183.5^\circ$ , forms short, stout prisms.

*Semicarbazinodiacetic acid* crystallises in long, rectangular plates and decomposes at  $161^\circ$ ; its *calcium*, *barium*, and *zinc* salts are described.

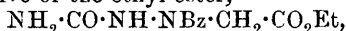
When methyl semicarbazinodiacetate is heated with potassium hydroxide, hydrazinodiacetic acid is produced. A modification of Curtius and Hussong's method (A., 1911, i, 401) of preparing this acid is described which gives a greatly increased yield. Hydrazinodiacetic acid becomes yellow at  $165^\circ$  and decomposes at  $176^\circ$ ; its solubility in water is 1:108 at  $22^\circ$  and 1:46 at  $100^\circ$ . The *barium* and *zinc* salts are described; the *methyl ester* has m. p.  $174.5^\circ$  (decomp.). By the action of phenylthiocarbimide on methyl hydrazinodiacetate, *methyl phenylthiocarbamidoaminodiacetate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Me})_2$ , m. p.  $120^\circ$ , is obtained, which crystallises in long needles. Formaldehyde reacts with hydrazinodiacetic acid with formation of a pale yellow substance which has not been investigated. When hydrazinodiacetic acid is treated with nitrous acid, iminodiacetic acid is produced. Confirmation was obtained of Curtius and Hussong's observation (*loc. cit.*) that hydrazinodiacetic acid is readily decomposed when heated with mineral acids, half the nitrogen of the molecule being eliminated as ammonia, and glycine and nitrilotriacetic acid were isolated from the reaction products.

Methyl and ethyl semicarbazinodiacetates are readily oxidised with potassium permanganate or bromine with formation of esters of the semicarbazone of glyoxylic acid. The ethyl ester,



melts at  $211^\circ$  (decomp.) when heated slowly, and decomposes at about  $218^\circ$  when heated rapidly; Simon and Chavaune (A., 1907, i, 110) state that it has m. p.  $228^\circ$  (decomp.). The corresponding methyl ester has m. p.  $206^\circ$  (decomp.).

When glyoxylic acid semicarbazone is reduced with sodium amalgam and the product esterified by means of alcoholic hydrochloric acid, ethyl semicarbazinoacetate is produced in yield amounting to 66% of the theoretical; the *hydrochloride* of this ester decomposes at  $170^\circ$ . *Semicarbazinoacetic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , has m. p.  $143^\circ$ . The *benzoyl* derivative of the ethyl ester,



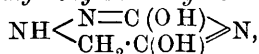
m. p.  $172^\circ$ , forms rectangular plates, and when heated with 10% potassium hydroxide solution it is converted into 3-hydroxy-5-phenyl-*triazole-1-acetic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{N}<\begin{smallmatrix} \text{N}=\text{C}\cdot\text{OH} \\ \text{CPh}\cdot\text{N} \end{smallmatrix}>$ , m. p.  $253-256^\circ$

(decomp.), which furnishes an *ethyl ether*, m. p.  $145^\circ$ . Phenylthiocarbimide reacts with ethyl semicarbazinoacetate to form 2-thio-

1-carbamide-3-phenylhydantoin,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}<\begin{smallmatrix} \text{CS}-\text{NPh} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}>$ , m. p.  $211^\circ$

(decomp.), which crystallises in thin plates. The *nitroso*-derivative of ethyl semicarbazinoacetate,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , has m. p.

99—102° (decomp.). By the action of sodium ethoxide on ethyl semicarbazinoacetate, 3:5-dihydroxy-1:6-dihydro-1:2:4-triazine,



m. p. 221°, is produced, which forms prismatic plates.

Ethyl semicarbazinopropionate (Thiele and Bailey, A., 1899, i, 169) can be obtained from pyruvic acid semicarbazone by a method similar to that used for the preparation of ethyl semicarbazinoacetate; its nitroso-derivative has m. p. 134.5° (decomp.). E. G.

**Amino-acids.** I. A. GEAKE and M. NIERENSTEIN (*Zeitsch. physiol. Chem.*, 1914, 92, 149—153).—The authors find that amino-acids do not undergo methylation when treated, in ethereal suspension, with diazomethane, the amino-acid being recovered unchanged. This is regarded as supporting Willstätter's betaine-structural formula for the amino-acids, for example,  $\text{CH}_2 \left\langle \begin{array}{c} \text{CO}^- \\ \text{NH}_3 \end{array} \right\rangle \text{O}$  instead of  $\text{CH}_2 \left\langle \begin{array}{c} \text{CO}_2\text{H} \\ \text{NH}_2 \end{array} \right\rangle$ .

According to this view, the acetylated amino-acids, possessing a free carboxyl group, might be expected to react with diazomethane, and as a matter of fact, it is found that the methyl ester of carbethoxyglycine is readily formed on treatment of the corresponding acid with diazomethane. H. W. B.

**Transformations of *d*-α-Amino-α-methylbutyric Acid.** EMIL FISCHER and RICHARD VON GRÄVENITZ (*Annalen*, 1914, 406, 1—11).—The addition of hydrogen cyanide to methyl ethyl ketone proceeds so rapidly after the addition of 2 or 3 drops of very concentrated potassium carbonate that cooling is necessary. *dl*-α-Amino-α-methylbutyric acid, ultimately obtained in 72% yield, forms rhombic, apparently holohedral crystals containing H<sub>2</sub>O [*a*:*b*=0.81:1]. The acid and boiling 99% formic acid yield the *formyl* derivative, m. p. 175.5—176° (decomp. corr.), which is resolved into its active components by brucine. The *d*-*formyl* derivative, thus obtained in a pure state, resembles the inactive compound in crystalline form and solubility, but decomposes at a slightly higher temperature. By heating with 10% hydrobromic acid on the water-bath and subsequent treatment with lead oxide, it yields *d*-α-amino-α-methylbutyric acid, colourless needles, containing H<sub>2</sub>O, which sublimes without melting, has  $[\alpha]_D^{19}$  11.0° in water and  $[\alpha]_D^{21}$  7.26° in 20% hydrochloric acid, and is not appreciably racemised by prolonged boiling with water or 2*N*-sodium hydroxide.

*l*-α-Amino-α-methylbutyric acid has been obtained by Ehrlich in 1908 by the partial fermentation of the racemic acid by yeast. The authors' method is less convenient than this, but has the advantages that both the active components can be isolated, and the *d*-acid is obtained in a purer form than Ehrlich's *l*-acid.

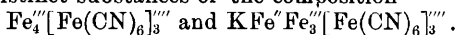
The *d*-acid is converted into optically inactive products by nitrosyl bromide and into *dl*-α-hydroxy-α-methylbutyric acid by nitrous acid; it is useless, therefore, for the study of the Walden inversion.

C. S.

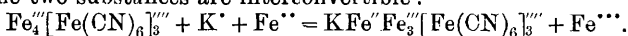
**Action of Carbon Dioxide on Calcium Cyanamide.** C. MANUELLE (*Ann. Chim. Applicata*, 1914, 1, 493—494).—The inefficiency of

calcium cyanamide as a fertiliser and its injurious effect on the labourers who spread it are attributed to the presence of free lime. The author has made investigations to ascertain if these inconveniences are avoidable by replacing the current of nitrogen by one of carbon dioxide during the cooling of the calcium cyanamide and thus converting the free lime into calcium carbonate. It is, however, found that such procedure is accompanied by elimination of a very considerable proportion of the nitrogen of the calcium cyanamide. T. H. P.

**Prussian Blue and Turnbull's Blue.** IV. ERICH MÜLLER (*J. pr. Chem.*, 1914, [ii], 90, 119—135. Compare A., 1909, i, 142, 705; 1911, i, 844; this vol., i, 504).—From the ratio of ferrous to ferric iron in the precipitates formed by the interaction of potassium ferrocyanide and ferricyanide with ferric and ferrous chlorides respectively, the author has drawn the conclusion that Prussian blue and Turnbull's blue are two distinct substances of the composition



In support of this view a series of experiments is described showing that the two substances are interconvertible:



If potassium ferrocyanide is added to an excess of ferric chloride and the mixture is then shaken with ferrous chloride, part of the latter is converted into ferric chloride.

A large excess of the ferrous salt, however, is necessary in order to convert Prussian blue into Turnbull's blue to any appreciable extent. On the other hand, if ferric chloride is added to a mixture of potassium ferricyanide and ferrous chloride, it is partly reduced to the ferrous condition.

Prussian blue can be shaken with ferrous chloride without undergoing change, thus indicating that the presence of potassium salts is necessary for the transformation into Turnbull's blue.

Experiments are also described, showing that the same transformation may be effected by reducing Prussian blue with potassium sulphite in the presence of potassium salts.

According to Woringer (A., 1912, i, 170; this vol., i, 504), sodium ferrocyanide differs from potassium ferrocyanide in that it yields with ferric chloride a basic precipitate, corresponding with the composition  $\text{Fe}_5(\text{OH})_3[\text{Fe}(\text{CN})_6]_3$ , this conclusion being based on the fact that the ratio  $\text{Fe}'' : \text{Fe}'''$  in the precipitate is considerably less than the value (0.75) corresponding with the composition  $\text{Fe}_4'''[\text{Fe}(\text{CN})_6]_3'''$ .

The author has repeated Woringer's observations and finds that the behaviour of sodium ferrocyanide towards ferric chloride is very similar to that of the potassium salt. In both cases when the ferrocyanide is in excess, the ratio  $\text{Fe}'' : \text{Fe}'''$  is greater than 0.75, indicating the presence of sodium or potassium in the precipitate.

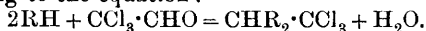
On the other hand, when the ferric chloride is in excess, the ratio, in the case of sodium ferrocyanide, is slightly less than 0.75. This discrepancy has not yet been satisfactorily explained, but experiments are described showing that it is probably to be referred to the presence of chlorine in the precipitate and not to the formation of a basic compound as is assumed by Woringer. F. B.

**Constitution of the Benzene Nucleus with Reference to the Phenomenon of Di-substitution.** BERNARD FLÜRSCHHEIM (*Chem. News*, 1914, 110, 1—2).—A reply to Horton (A., 1914, i, 508). It is pointed out that the special hypotheses advanced to account for the influence of the aldehyde, carbonyl and other unsaturated groups on substitution are quite unnecessary and also erroneous. According to the present author's theory, it is an unsaturated atom attached directly to the benzene nucleus that directs entering groups into the ortho- and para-positions, and this condition is not fulfilled by the carbon atom of the carbonyl group which has much less available affinity left for its union with the nucleus than has, say, the carbon atom of a methyl group, since an increased demand is made on its affinity by combination with an unsaturated atom (bivalent oxygen, trivalent nitrogen, etc.). The fact that the carbon in carbon monoxide is less unsaturated than the carbon in methylene gives independent evidence on this point. G. F. M.

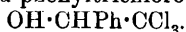
**Action of Chloral, Chloral Hydrate, and Bromal on Certain Organic Compounds in the Presence of Aluminium Chloride.** G. B. FRANKFORTER and W. KRITCHEVSKY (*J. Amer. Chem. Soc.*, 1914, 36, 1511—1529).—In promoting the condensation of organic substances, aluminium chloride not only plays the part of a catalyst in eliminating hydrogen chloride, but may act as a substitute for sulphuric acid, removing water from the reacting components. Its applicability as a dehydrating agent appears to be almost as universal as that of sulphuric acid, and the authors have employed it in preparing condensation products of the aliphatic, benzene, naphthalene, and anthracene series, not only with chloral, but also with chloral hydrate and bromal. The substances described below have been prepared by the following general method. Aluminium chloride is gradually added to the two reacting components at or below 0°, the mixture is kept for twenty-four to seventy-two hours in a freezing mixture, water is then added, the unchanged substances are removed by distillation with steam, and the condensation product is, in most cases, removed by extraction with ether; in a few cases, the substance must be distilled in a vacuum before it can be crystallised.

Pentane and chloral react very violently; the product is a mixture of substances which is being investigated, but is evidently produced by dehydration.

Benzene, toluene, and xylene yield with chloral the same condensation products as are obtained by means of other condensation reagents, formed according to the equation:



The behaviour of benzene and chloral in the presence of aluminium chloride under the authors' conditions is especially interesting because in 1905, Dienesmann, employing the same substances under somewhat similar conditions, obtained phenyltrichloromethylcarbinol,

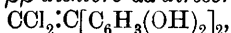


In the case of benzene and toluene under the authors' conditions, dichlorophenylacetaldehyde hydrochloride and the corresponding *p*-tolyl homologue respectively are also produced. Cymene reacts quite

differently from the three preceding aromatic hydrocarbons with chloral, but the products have not been isolated in a pure state.

Ethyl alcohol and chloral react in the cold, with or without the presence of aluminium chloride, to form trichloroacetal, but when the chloride is added at the ordinary temperature, the reaction yields, in addition, acetaldehyde. Benzyl alcohol, chloral, and aluminium chloride at the ordinary temperature yield benzaldehyde and a mixture of two or more chlorinated (unidentified) substances. Phenol in the cold yields trichlorodi-*p*-hydroxyphenylethane.

Resorcinol and chloral in cold carbon disulphide are converted by aluminium chloride into *ββ*-dichloro-*αα*-diresorcyloethylene,



light brown powder, which forms a *tetra-acetate*. Anisole yields trichlorodianisylethane, m. p. 78° (Elbs gives 92°), which is reduced to *pp'*-dimethoxystilbene by zinc and alcoholic ammonia, is converted into *ββ*-dichloro-*αα*-dianisylethane,  $\text{CCl}_2 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2$ , m. p. 109°, by alcoholic potassium hydroxide, and yields trichloro-octanitrodianisylethane, m. p. 173°, yellow crystals, by the action of nitric acid (D 1.5), at 0°. Phenetole yields quite analogous compounds; trichlorodiphenylethane,  $\text{CCl}_3 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OEt})_2$ , m. p. 105°, colourless, hexagonal crystals, dichlorodiphenylethane, m. p. 97°, needles, and trichloro-octanitrodiphenylethane, m. p. 137°, yellow needles.

Phenetole, bromal, and aluminium chloride yield tribromodiphenylethane, m. p. 112°, yellow crystals (octanitro-derivative, m. p. 153°, yellow crystals). Reaction does not occur when aluminium bromide is used in place of the chloride. Phenyl ether, chloral, and aluminium chloride do not yield well-defined products, benzophenone apparently does not react at all, and acetophenone yields an unidentified substance, b. p. 170°/40 mm.

Benzoic acid does not react with chloral and aluminium chloride. Acetic acid, however, yields a product which, by treatment with ether (not water) to remove the impurities, leaves a residue consisting of a substance,  $\text{Al}_2\text{Cl}(\text{OAc})_5 \cdot \text{CCl}_3 \cdot \text{CHO}$ , light yellow powder; the chloral is removed from this by cold alcohol. C. S.

**Action of Trioxymethylene on Various Hydrocarbons in the Presence of Aluminium Chloride.** GEO. B. FRANKFORTER and V. R. KOKATNUR (*J. Amer. Chem. Soc.*, 1914, **36**, 1529—1537).—The action of trioxymethylene is different from that of formaldehyde on hydrocarbons in the presence of aluminium chloride.

By the gradual addition of aluminium chloride to a mixture of benzene and trioxymethylene at 0°, and the decomposition of the product by ice-water, a mixture is obtained from which have been isolated toluene in small amount and diphenylmethane and anthracene in very good yields and in approximately equal molecular proportions. The reaction may be represented by the equation  $4\text{C}_6\text{H}_6 + (\text{CH}_2\text{O})_3 = \text{CH}_2\text{Ph}_2 + \text{C}_{14}\text{H}_{10} + 3\text{H}_2\text{O} + \text{H}_2$ . The reaction with toluene under similar conditions (below 65°) is quite similar, the products containing benzene and toluene in small amount and also ditolylmethane and dimethylantracene, m. p. 225—226°. The interaction of *o*-xylene, trioxymethylene, and aluminium chloride below 65° leads in the preced-

ing manner to the formation of a mixture of substances, from which have been isolated benzene and possibly some toluene, a *dixylylmethane*, b. p. 311—313°, which is highly fluorescent, and a *tetramethylantracene*,  $C_{18}H_{18}$ , decomp. 233—235°, yellow, pearly, monoclinic plates, which can be sublimed and forms solutions with an intense green fluorescence.

Mesitylene and trioxymethylene, under the influence of aluminium chloride below 50°, yield, after treatment of the initial product with water, a *tetramethylantracene*, m. p. 286—287°, a pale yellow, crystalline powder, benzene, toluene, xylene, dimesitylmethane, and durene.

C. S.

**2-Chloro-*m*-dinitrobenzene.** W. BORSCHÉ and D. RANTSCHÉFF (*Annalen*, 1914, **406**, 101).—The m. p. of 2-chloro-*m*-dinitrobenzene is 88°, not 92°, as previously stated (A., 1911, i, 329).

C. S.

**Desmotropism of Nitro-compounds and Nitro-ketones** KURT H. MEYER and PETER WERTHEIMER (*Ber.*, 1914, **47**, 2374—2384).—The bromine titration method, which has helped in the investigation of keto-enol isomerism, has been applied to the study of the desmotropic phenomena connected with nitro-derivatives.

As an example, the isomerisation of phenylisonitromethane in alcoholic solution to the true nitro-derivative may be quoted. The solution to be titrated was treated with a trace of ferric chloride, and 0.1*N*-bromine water was added until the deep colour disappeared. The equilibrium mixture contains the merest traces of the *aci*-form, and the transformation is accelerated by strong acids and is almost instantaneous in the presence of sodium acetate. Nitroethane was also dissolved in alkali, and the *aci*-form liberated by the required amount of acid and studied as above. Here, again, there is no appreciable quantity of the *aci*-compound in the equilibrium mixture, but *p*-nitrophenylnitromethane gradually changes in solution, to a certain extent, into the *aci*-form. In pyridine, the equilibrium mixture contains about 16% of the *aci*-compound, in methyl alcohol 0.21%, in ethyl alcohol 0.18%, and in dilute methyl alcohol 0.79%. Comparing this with keto-enol isomerism, a fundamental difference is apparent. Whereas the enolic form of, say, ethyl acetoacetate is favoured least by water, more by methyl alcohol, and still more by ethyl alcohol, the reverse is the case with isonitro-compounds. This is in accordance with the rule that the proportions of the isomerides depend on their solubilities in the medium, for enols are less soluble than ketones in water, but *aci*-compounds are more soluble than true nitro-derivatives. Thus, on acidifying an aqueous solution of ethyl sodioacetoacetate, the liquid is turbid and becomes clear, but on acidifying an alkaline solution of phenylnitromethane, the liquid is first clear and becomes cloudy.

The study of phenyldinitromethane was rendered more accurate by reason of the fact that the bromo-derivative reacts quantitatively with potassium iodide and can therefore be titrated like ethyl bromoacetoacetate. The equilibrium is influenced by solvents in the above manner, there being 15% of the *aci*-form in 30% methyl-alcoholic solution. Nitroacetic ester does not react with ferric chloride, and

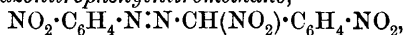


scarcely so with bromine, but nitromalonic ester reacts, not immediately, but very quickly. The fact that bromonitromalonic ester reacts at once with potassium iodide, whilst bromonitroacetic ester does not, is not regarded as due to a difference in constitution. They are the extremes of a series of bromo-ketones, aldehydes and nitro-compounds, in which widely different activities towards potassium iodide are displayed by the bromine atoms.

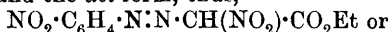
Old alcoholic solutions of  $\omega$ -nitroacetophenone react with ferric chloride or bromine, but not so the fresh solutions, and the bromonitro-derivative can be titrated iodometrically. The equilibrium mixture contains an amount of the labile form which rises from 2·7% in 67% methyl alcohol to 9—10% in indifferent solvents. This corresponds with keto-enol and not with nitro-desmotropism, and, therefore, the labile form in solution is the nitro-enol and not the *aci*-ketone.

Experiments were also carried out which show that nitro-compounds and nitro-ketones react towards diazonium salts in their labile forms. The free derivatives couple very slowly, but the addition of catalysts, like sodium acetate, leads to very speedy combination.

*p*-Nitrobenzeneazonitrophenylnitromethane,



forms orange-yellow crystals, m. p.  $166^\circ$ , and *ethyl benzeneazonitroacetate*,  $\text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CH}(\text{NO}_2) \cdot \text{CO}_2\text{Et}$ , forms orange-yellow crystals, m. p.  $60^\circ$ , and absorbs a little bromine in alcoholic solution. *Ethyl p*-nitrobenzeneazonitroacetate forms long, yellow needles, m. p.  $152^\circ$  (decomp.), and gives yellow solutions in neutral or acid media and red solutions in aqueous or alkaline solvents. The red solutions absorb bromine, and therefore represent equilibria between the azo- or phenyl-hydrazone form and the *aci*-form, thus,



$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{N} : \text{C}(\text{NO}_2) \cdot \text{CO}_2\text{Et} \rightleftharpoons \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}(\text{NO}_2\text{H}) \cdot \text{CO}_2\text{Et}$ .  
*p*-Nitrobenzeneazonitroacetophenone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CHBz} \cdot \text{NO}_2$ , forms pale yellow crystals, m. p.  $137^\circ$ , which give yellow solutions in neutral or acid media and deep red in alkaline or alcoholic solvents.

J. C. W.

**Morphological Studies of Benzene Derivatives. VI. Para-sulphonic Derivatives of Chloro-, Bromo-, Iodo-, and Cyano-benzene.** C. S. MUMMERY (*Proc. Roy. Soc.*, 1914, [4], 90, 455—462).—The sulphonyl chlorides of the three acids containing halogen form an isomorphous series.

$\text{C}_6\text{H}_4\text{Cl} \cdot \text{SO}_2\text{Cl}$ : m. p.  $53 \cdot 5^\circ$ ; monoclinic crystals; [ $a : b : c = 0 \cdot 840 : 1 : 2 \cdot 079$ ;  $\beta = 83^\circ 31'$ ].

$\text{C}_6\text{H}_4\text{Br} \cdot \text{SO}_2\text{Cl}$ : m. p.  $74 \cdot 5^\circ$ ; [ $a : b : c = 0 \cdot 820 : 1 : 2 \cdot 074$ ;  $\beta = 83^\circ 13'$ ].

$\text{C}_6\text{H}_4\text{I} \cdot \text{SO}_2\text{Cl}$ : m. p.  $84^\circ$ ; [ $a : b : c = 0 \cdot 839 : 1 : 2 \cdot 074$ ;  $\beta = 84^\circ 38'$ ].

The following sulphonyl bromide is not isomorphous with the above three compounds.

$\text{C}_6\text{H}_4\text{Cl} \cdot \text{SO}_2\text{Br}$ : m. p.  $56^\circ$ ; monoclinic; [ $a : b : c = 1 \cdot 901 : 1 : 1 \cdot 527$ ;  $\beta = 88^\circ 26'$ ].

The two following sulphonamides form monoclinic isomorphous crystals from acetone.

$\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{NH}_2$ : m. p.  $143.5^\circ$ ; [ $a:b:c=0.629:1:0.603$ ;  $\beta=82^\circ 12'$ ].

$\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\cdot\text{NH}_2$ : m. p.  $165^\circ$ ; [ $a:b:c=0.628:1:0.601$ ;  $\beta=81^\circ 4'$ ].

The sulphanilides have not been completely measured. Their melting points are:  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{NHPh}$ ,  $104^\circ$ ;  $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\cdot\text{NHPh}$ ,  $118^\circ$ ;  $\text{C}_6\text{H}_4\text{I}\cdot\text{SO}_2\cdot\text{NHPh}$ ,  $143^\circ$ .

The sulpho-*p*-toluidides form triclinic crystals.

$\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ : m. p.  $87^\circ$ ; [ $a:b:c=1.020:1:1.096$ ;  $\alpha=106^\circ 6'$ ;  $\beta=93^\circ 50'$ ;  $\gamma=77^\circ 29'$ ].

$\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ : m. p.  $94^\circ$ ;  $\text{C}_6\text{H}_4\text{I}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ : m. p.  $129^\circ$ .

*p*-Cyanobenzenesulphonic acid was prepared from sulphanilic acid by diazotising and treating the diazo-anhydride with a cold solution of cuprous cyanide. Of the derivatives of this acid, the sulphonyl chloride and sulphonamide were measured.

$\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ : m. p.  $109^\circ$ ; rhombic; [ $a:b:c=1.139:1:1.709$ ].

$\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ : m. p.  $167^\circ$ ; rhombic; [ $a:b:c=0.793:1:0.537$ ].

The three following magnesium salts form a well-defined monoclinic isomorphous series.

$(\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_3)_2\text{Mg}, 6\text{H}_2\text{O}$ : [ $a:b:c=3.6870:1:0.9223$ ;  $\beta=93^\circ 12'$ ].

$(\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_3)_2\text{Mg}, 6\text{H}_2\text{O}$ : [ $a:b:c=3.7380:1:0.9094$ ;  $\beta=93^\circ 51'$ ].

$(\text{C}_6\text{H}_4\text{I}\cdot\text{SO}_3)_2\text{Mg}, 6\text{H}_2\text{O}$ : [ $a:b:c=3.7965:1:0.9148$ ;  $\beta=93^\circ 1'$ ].

E. H. R.

**New Compound of Mercuric Acetate and Aniline.** L. VECCHIOTTI (*Gazzetta*, 1914, **44**, ii, 34—38).—2:4-Dimercurioaniline acetate,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{Hg}\cdot\text{OAc})_2$ , obtained by the interaction of aniline and aqueous mercuric acetate, forms mammillary masses of white prisms, m. p.  $206^\circ$ . The action of acetic anhydride converts it into 2:4-dimercurioacetanilide acetate (compare Pesci, A., 1899, i, 908), which gives 2:4-dibromoacetanilide when treated with bromine. 2:4-Dimercurioaniline hydroxide,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{Hg}\cdot\text{OH})_2$ , forms microscopic, white needles decomposing at  $250^\circ$ .

T. H. P.

**Preparation of Arylcarbamic Esters.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 272529).—Esters of arylcarbamic acids may be obtained by the interaction of either (1) alkylamines and derivatives of arylcarbamic acids, or (2) aliphatic amines and halogenated alkyl esters of arylcarbamic acids; they exhibit anæsthetic properties.

*Diethylaminoethanol phenylcarbamate*, obtained from diethylaminoethanol and phenylcarbimide, is a colourless oil with a marked alkaline reaction; its *hydrochloride*, m. p.  $143^\circ$ , picrate, and ferrocyanide were prepared.

*Diethylaminoethanol p-ethoxyphenylcarbamate*, prepared from diethylaminoethanol and *p*-ethoxyphenylurethane, forms strongly alkaline crystals, and its *hydrochloride*, colourless crystals, m. p.  $167^\circ$ .

*Diethylaminoethanol phenylmethylcarbamate*, colourless crystals, giving a neutral aqueous solution, and its *hydrochloride*, m. p.  $136^\circ$ ; *diethylaminoethanol diphenylcarbamate*, and its *hydrochloride*, m. p.  $180^\circ$ ; *piperidinoethanol phenylcarbamate*, an oil, and its *hydrochloride*, m. p.

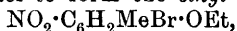
205—207° (decomp.); *piperidinoisopropanol phenylcarbamate*, an oil, and its *hydrochloride*, m. p. 75—77°; *diethylaminoisopropanol phenylcarbamate*, a liquid, and its *hydrochloride*, m. p. 143°; *diethylamino-trimethylcarbinol phenylcarbamate*, m. p. 94°, and its syrupy *hydrochloride*; *tetramethyldiaminopropanol phenylcarbamate*, a colourless, viscous oil, and its *dihydrochloride*, m. p. 226° (decomp.); *diethylamino-dihydroxypropane phenylcarbamate*, m. p. 105—107°, and its *hydrochloride* were also prepared.

T. H. P.

**Manufacture of Ethers of Monohydric Phenols and of Neutral and Acid Ethers from the Chlorinated Substitution Products Corresponding with Aromatic Hydrocarbons.** CHARLES FORLEY and OSKAR MATTER (Fr. Patent, 457843).—Ethers of monohydric phenols and normal and hydroxylated ethers of polyhydric phenols are prepared by heating chloro-derivatives of aromatic hydrocarbons in a closed vessel with alkali phenoxides or alkylloxides. When polychloro-derivatives are used and a deficit of phenoxide or alkyloxide is taken, chlorinated ethers are obtained. The presence of copper sometimes accelerates the reaction.

T. H. P.

**6-Bromo-4-nitro-*m*-cresol and Some of its Derivatives.** L. CHAS. RAIFORD and GLADYS LEAVELL (*J. Amer. Chem. Soc.*, 1914, **36**, 1498—1511).—In 1889, Claus and Hirsch obtained by the bromination of 4-nitro-*m*-cresol a substance, m. p. 93°, which was stated to be 2:6-dibromo-4-nitro-*m*-cresol. It is now shown that the bromination in glacial acetic acid at the ordinary temperature produces a monobromo-compound, which is rapidly precipitated, and 2:6-dibromo-4-nitro-*m*-cresol, m. p. 87°, which remains in the mother liquor and is precipitated by water. The constitution of the latter has been definitely proved by one of the authors and Stieglitz in 1911, who prepared it from 2:4:6-tribromo-*m*-cresol; so Claus and Hirsch's compound, m. p. 93°, cannot have the constitution ascribed to it by these investigators. The present paper deals mainly with the monobromo-compound mentioned above, which is proved to be 6-bromo-4-nitro-*m*-cresol by the evidence recorded below. It has m. p. 126°, crystallises in yellow plates, is slowly volatile with steam, yields 2:6-dibromo-4-nitro-*m*-cresol, m. p. 87°, by further bromination, and forms the following salts: *ammonium*, orange needles; *potassium*, deep red crystals, *sodium*, red needles, and *silver*, dark red solid. The last salt reacts with ethyl iodide in ether to form the *ethyl ether*,



m. p. 124°, almost colourless crystals.

An alcoholic solution of 6-bromo-4-nitro-*m*-cresol is reduced by boiling concentrated hydrochloric acid and stannous chloride to the *hydrochloride*, almost colourless needles, of 6-bromo-4-amino-*m*-cresol, m. p. 145°, almost colourless crystals.

The nitration of 6-bromo-4-nitro-*m*-cresol by nitric acid, D 1.42, and concentrated sulphuric acid yields, by warming, 2:4:6-trinitro-*m*-cresol, or, at the ordinary temperature, 6-bromo-2:4-dinitro-*m*-cresol, m. p. 77°, yellow needles (*ammonium* salt, orange crystals, *potassium* salt, scarlet plates, *silver* salt, scarlet crystals, *ethyl ether*, m. p. 64—65°, almost colourless crystals).

The chlorination of 6-bromo-4-nitro-*m*-cresol in carbon tetrachloride in the presence of iron produces 2-chloro-6-bromo-4-nitro-*m*-cresol, m. p.  $80^{\circ}$ , yellow needles (*potassium* salt, crimson, rhombic crystals). By reduction, the latter yields 2-chloro-6-bromo-4-amino-*m*-cresol, m. p.  $145-146^{\circ}$ , almost colourless scales (*diacetyl* derivative, m. p.  $199^{\circ}$ , colourless needles), which is converted into a *diazo-oxide*,  $C_7H_4ON_2ClBr$ , decomp. above  $155^{\circ}$ , brown needles, by the action of nitrous acid on its hydrochloride. The *diazo-oxide* is converted by the Sandmeyer method with some difficulty into 2:4-dichloro-6-bromo-*m*-cresol, m. p.  $65^{\circ}$ , fawn-coloured needles, which is oxidised to 2:4-dichlorotoluquinone by chromic acid. The formation of a dichlorinated quinone proves that the bromine atom in the original bromonitro-*m*-cresol must be in the *para*-position to the hydroxyl group. C. S.

**Aminohydroxyethylbenzene** [ $\beta$ -Hydroxy- $\alpha$ -phenylethyl-amine]. A. KÖTZ and H. SCHNEIDER (*J. pr. Chem.*, 1914, [ii], 90, 136—140).—On reduction with sodium and alcohol,  $\beta$ -oximino- $\beta$ -phenylethyl alcohol,  $OH \cdot N : CPh \cdot CH_2 \cdot OH$ , is converted into a mixture of  $\beta$ -hydroxy- $\alpha$ -phenylethylamine and  $\alpha$ -phenylethylamine, which may be readily separated by distillation in steam, the last-named base being much more readily volatile than the amino-alcohol.

$\beta$ -Hydroxy- $\alpha$ -phenylethylamine,  $NH_2 \cdot CHPh \cdot CH_2 \cdot OH$ , has b. p.  $261^{\circ}$ , m. p. between  $50^{\circ}$  and  $60^{\circ}$ , and forms a *hydrochloride*, m. p.  $146-147^{\circ}$ , a *carbamide*, m. p.  $167.5^{\circ}$ , and a *N-benzoyl* derivative, m. p.  $150^{\circ}$ , which, when heated with acetic anhydride and sodium acetate, yields  $\beta$ -benzoyl-amino- $\beta$ -phenylethyl acetate, m. p.  $118^{\circ}$ ; the *N-dichloroacetyl* derivative, obtained by the interaction of ethyl dichloroacetate and the amino-alcohol in alcoholic solution, crystallises in white scales.

$\alpha$ -Phenylethylamine forms a *hydrochloride*, m. p.  $158^{\circ}$ , *acetyl* derivative, b. p.  $287^{\circ}$ , *carbamide*, m. p.  $137^{\circ}$ , and a *monomethyl* derivative.

F. B.

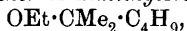
**Preparation of Ethers from Aldehyde or Ketone Acetals and Organo-magnesium Compounds.** A. E. TSCHITSCHIBABIN and S. A. JELGASIN (*Ber.*, 1914, 47, 1843—1853).—It was recently shown (this vol., i, 276) that the alkyloxyl groups in acetals may be replaced by the radicle of an organo-magnesium compound. This reaction is now applied to the preparation of ethers. Formaldehyde acetals yield ethers of primary alcohols, whilst ethers of secondary alcohols are derived from other aldehyde acetals and ethers of tertiary alcohols from ketone acetals. The assumption that the replaceability of the alkyloxyl group depends on the degree of saturation of the oxygen atom is justified, for the acetals of formaldehyde, in which the affinity of the carbon atom of the methylene group must make considerable demands on the residual affinity of the oxygen atoms, are the least reactive, whilst ketone acetals react so readily that both alkyloxyl groups are frequently displaced.

As a rule, the clear, ethereal solution of the organo-magnesium compound was dropped into the warm acetal, the solvent being allowed to distil off. In the case of methylal and ethylal this procedure was not practicable, and sealed tubes were sometimes used. Many attempts

were made to cause them and isobutylal to react with magnesium benzyl chloride. A grey powder was obtained which seemed to be a complex of the reagents, for it reacted vigorously with water, or when heated above  $150^{\circ}$ . On working up the products, it was found that below  $150^{\circ}$  scarcely any replacement of alkylloxyl had taken place, whilst at higher temperatures both groups seemed to be engaged with the formation of complex hydrocarbons.

Ordinary acetal, however, reacted with magnesium phenyl bromide on the water-bath to give a 50% yield of the ethyl ether of phenylmethylcarbinol,  $\text{CHMePh}\cdot\text{OEt}$ , whilst with magnesium isobutyl bromide it yielded the ethyl ether of methylisobutylcarbinol,  $\text{OEt}\cdot\text{CHMe}\cdot\text{C}_4\text{H}_9$ , as a liquid with an intense terpineol-like odour, b. p.  $121\text{--}122^{\circ}$  (corr.),  $D_4^{20}$  0.7767,  $D_{18}^{25}$  0.7612, and with magnesium benzyl chloride it formed the ethyl ether of benzylmethylcarbinol,  $\text{OEt}\cdot\text{CHMe}\cdot\text{CH}_2\text{Ph}$ , as an oil with an intense nerol-like odour, b. p.  $205\text{--}206^{\circ}$ ,  $D_4^{20}$  0.9305,  $D_{18}^{25}$  0.9159. 4-Methylcyclohexanol was converted into the bromide, b. p.  $70^{\circ}/13\text{ mm.}$ , by the action of hydrogen bromide at  $100^{\circ}$ , and the magnesium compound of this was added to acetal. The lowest fraction of the product, b. p.  $101^{\circ}$ , contained apparently methylcyclohexene, and the highest, b. p.  $240\text{--}252^{\circ}$ , dimethyldicyclohexyl, whilst the expected ethyl ether of 4-methylcyclohexylmethylcarbinol,  $\text{OEt}\cdot\text{CHMe}\cdot\text{C}_6\text{H}_{10}\text{Me}$ , a liquid with an odour of aniseed, had b. p.  $197\text{--}198^{\circ}/752\text{ mm.}$ ,  $D_4^{20}$  0.8711,  $D_{20}^{25}$  0.8564.

The authors found it difficult to prepare pure acetone acetal, but obtained over 70% yields by the following means. A few drops of sulphuric acid were added to a mixture of acetone (1 mol.), ethyl orthoformate (1 mol.) and pure alcohol (3 mols.), and, after a day, the liquid was made alkaline with ammonia, diluted with ether, and poured into very dilute ammonia. It reacted with magnesium isobutyl bromide, but the yield of the ethyl ether of dimethylisobutylcarbinol,



was only 10—15%. This ether has b. p.  $140\text{--}142^{\circ}$ ,  $D_4^{20}$  0.7964,  $D_{18}^{25}$  0.7833, and a pronounced odour of dipentene. J. C. W.

**The History of the Quinocarbonium Theory.** F. KEHRMANN and F. WENTZEL (*Ber.*, 1914, 47, 2274—2275).—A claim to the authorship of the quinocarbonium theory as to the structure of the triphenylcarbinol salts (*A.*, 1901, i, 638) in reply to a statement of Schlenk and Marcus (this vol., i, 823) ascribing this theory to Gomberg. D. F. T.

**Cholesterol.** XIX.  $\beta$ -Cholestanol. A. WINDAUS and CL. UBRIG (*Ber.*, 1914, 47, 2384—2388).—Many attempts have been made to reduce the unsaturated sterols to the naturally-occurring, saturated sterols, as represented by coprosterol, but hitherto without success. The authors showed (*A.*, 1913, i, 969) that " $\alpha$ -cholestanol," the compound obtained by boiling cholesterol with sodium and amyl alcohol, is really an amyl derivative. The substance obtained by catalytic reduction, namely, dihydrocholesterol or  $\beta$ -cholestanol, is, however, a normal product, but it is not identical with a known, natural, saturated sterol. The authors have now succeeded in con-

verting cholesterol into coprosterol by chemical means, and in demonstrating the nature of the isomerism existing between  $\beta$ -cholestanol and coprosterol. It is proposed to publish the results in a series of papers, as the subject is complicated. In the present communication, some new derivatives and a new isomeride of  $\beta$ -cholestanol are described.

The following esters of  $\beta$ -cholestanol were prepared: *propionate*,  $C_{30}H_{52}O_2$ , from the anhydride, four- and six-sided crystals, m. p.  $123-124^\circ$ ; *formate*,  $C_{28}H_{48}O_2$ , from the pure acid, long, narrow tablets, m. p.  $83-84^\circ$ ; *benzoate*,  $C_{34}H_{52}O_3$ , from the anhydride, aggregates of needles, m. p. turbid at  $135^\circ$ , clear at  $155^\circ$ , and *cinnamate*,  $C_{36}H_{54}O_3$ , from the chloride, tablets, m. p.  $160-161^\circ$ , and again at  $192^\circ$ .  $\beta$ -Cholestanol was also oxidised by chromic acid in 90% acetic acid at  $60^\circ$ , and the ethereal extract separated into  $\beta$ -cholestanone, m. p.  $128-129^\circ$ , and the corresponding dicarboxylic acid,  $C_{27}H_{46}O_4$ . The latter forms narrow tablets, m. p.  $196^\circ$ , and its *dimethyl* ester, rectangular leaflets, m. p.  $66-67^\circ$ , was prepared by the agency of diazomethane.

$\beta$ -Cholestanol was found to suffer rearrangement to the extent of about 10% on boiling with sodium in amyl alcohol. After removing the solvent in steam, the residue was a solid which gave a precipitate with alcoholic digitonin solution. This consisted of the compound of the unchanged  $\beta$ -cholestanol. The filtrate was concentrated, shaken with ether, and the extract washed several times with water. This aqueous extract was evaporated to dryness and the residue crystallised from alcohol, when  $\epsilon$ -cholestanol was obtained in spikes, m. p.  $181-182^\circ$ ,  $[\alpha]_D^{25} + 33.95^\circ$ . It gives the same colour reactions as  $\beta$ -cholestanol and forms the same ketone, but it is less soluble than its stereoisomeride.

J. C. W.

**Some Fatty-Aromatic Glycols.** H. SIMONIS and P. REMMERT (*Ber.*, 1914, 47, 2307-2311).—By the action of organo-magnesium compounds in excess on phthalaldehydic acids, using anisole as solvent (Simonis and Remmert, this vol., i, 270), dihydric alcohols of the general formula  $OH \cdot CHR \cdot C_6H_4 \cdot CR_2 \cdot OH$  can be obtained. This result is interesting, as the formation of  $\alpha$ -methylphthalide from *o*-phthalaldehydic acid and magnesium methyl iodide in ethereal solution (Simonis, Marben and Mermod, A, 1906, i, 32) is not decisive for the normal structure of the acid as opposed to the possible lactonic structure  $C_6H_4 \cdot \begin{smallmatrix} CH(OH) \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} > O$ , whereas only the aldehydic acid structure is compatible with the results now obtained.

The general method of procedure was to prepare the organo-magnesium compound as usual in ethereal solution, and then to introduce the aldehydic acid dissolved in hot anisole. On evaporating off the ether, a clear solution was finally obtained which, after heating, was submitted to further treatment in the ordinary manner.

The reaction between *o*-phthalaldehydic acid and magnesium ethyl bromide under these conditions produced *o*- $\alpha$ -hydroxypropylphenyldiethylcarbinol,  $OH \cdot CHEt \cdot C_6H_4 \cdot CET_2 \cdot OH$ , a colourless oil, b. p.  $173^\circ/10$  mm., which solidified in needles on a cold day. As is general with the com-

pounds now described, acetic anhydride affects only one hydroxyl group, presumably the secondary one; the *acetyl* derivative is a colourless oil, b. p.  $171^{\circ}/12$  mm. When the dihydric alcohol is heated with hydrochloric acid in acetic acid solution for several hours, dehydration takes place with formation of *triethylphthalan* [1:3:3-*triethyl*-1:3-*di hydroisobenzofuran*],  $C_6H_4 \begin{smallmatrix} \text{CEt}_2 \\ \text{CHEt} \end{smallmatrix} \text{O}$ , a pale yellow oil, b. p.  $115-118^{\circ}/10$  mm.

*iso*Phthalaldehydic acid and magnesium ethyl bromide give *m-a-hydroxypropylphenyldiethylcarbinol*, a colourless oil, b. p.  $174-177^{\circ}/10$  mm.; *acetyl* derivative, b. p.  $178-180^{\circ}/10$  mm. When kept in acetic acid solution saturated with hydrogen bromide at  $15^{\circ}$ , for three days in the dark, one of the hydroxyl groups undergoes esterification, the product, *m-a-bromopropylphenyldiethylcarbinol*,  $CHBrEt \cdot C_6H_4 \cdot CEt_2 \cdot OH$ , being an oil.

Terephthalaldehyde and magnesium ethyl bromide react, giving *p-a-hydroxypropylphenyldiethylcarbinol*, an oil, b. p.  $186^{\circ}/15$  mm.; the *acetyl* derivative, b. p.  $191^{\circ}/14$  mm., and the *p-a-bromopropylphenyldiethylcarbinol*, an oil, were also prepared. D. F. T.

**The Constitution of Dypnopinacone and its Derivatives.** M. DELACRE (*Ann. Chim.*, 1914, [ix], 2, 63-100).—A résumé of work already published (compare A., 1892, 994; 1900, i, 603; 1902, i, 774; 1904, i, 32; 1912, i, 30; Terlinck, 1905, i, 129). W. G.

**The Catalytic Decomposition of Benzoic Acid.** PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1914, 159, 217-220).—The authors have tried the effect of various catalytic agents on the decomposition of benzoic acid by heat. A stream of benzoic acid vapour, obtained by bubbling carbon dioxide through the molten acid, was passed over a column of the catalyst at  $500$  or  $550^{\circ}$ . Cerium and zirconium oxides and the blue oxides of tungsten and molybdenum are without action, whilst barium oxide merely combines with the benzoic acid. Reduced copper at  $550^{\circ}$  readily converts benzoic acid into carbon dioxide and benzene. The same decomposition is brought about by cadmium, zinc or titanium oxides and much more slowly and incompletely by thorium, chromium or aluminium oxides. Lithium carbonate produces carbon dioxide, equal amounts of benzophenone and benzene, and a small amount of anthraquinone. Calcium carbonate and manganous oxide have the same effect, but, in the case of the latter, benzene is the predominant product. Reduced nickel or nickel oxide decomposes the acid vapours at  $550^{\circ}$ , giving carbon dioxide and benzene, which then undergoes rapid dehydrogenation, yielding carbon in a voluminous form and an abundant amount of a mixture of carbon dioxide, hydrogen and methane. Reduced iron has an effect intermediate between that of copper and reduced nickel, the products being benzene with a little diphenyl and the products of dehydrogenation of the benzene. Ferric oxide is first reduced to the metallic state, giving rise to phenol in this process, and then behaves as reduced iron. Ferrous oxide is similarly reduced to the metallic state, but does not produce phenol. W. G.

**Additive Compounds of Organic Acids in Pairs.** JAMES KENDALL (*J. Amer. Chem. Soc.*, 1914, 36, 1722—1734).—In an earlier paper (this vol., i, 858) it was shown by means of the f. p. method that many organic acids form additive compounds with dimethylpyrone and that these compounds should be regarded as true oxonium salts. It was also shown that the degree of dissociation, or, in other words, the relative stability of the salt, is a function of the strength of the acid used.

A study has now been made of the f.-p. curves of a series of weak organic acids with certain strong acids. The weak acids employed were benzoic, *o*-, *m*- and *p*-toluic, phenylacetic, cinnamic, acetic, and crotonic acids, and the strong acids were trichloro-, dichloro-, and chloro-acetic acids. The results show that the tendency towards the formation of additive compounds depends on the difference in the strengths of the two acids used. Acids widely divergent in strength give additive compounds which can be readily isolated, whilst acids of similar strength show little tendency to form compounds.

The reaction is regarded as an oxonium salt formation which may be represented thus:  $R \cdot C(OH) : O \pm + HX \rightleftharpoons R \cdot C(OH) : O < \overset{H}{X}$ . This view is fully supported by the quantitative results obtained. E. G.

**Hydrogenation of Compounds with Aliphatic Ethylenic Linkings in the Presence of Nickel under Moderate Pressure.** ANDRÉ BROCHET and MAURICE BAUER (*Compt. rend.*, 1914, 159, 190—192).—Using the method already described (compare Brochet, this vol., i, 645) the authors have hydrogenated a number of aromatic compounds containing an ethylenic linking in the side-chain and one aliphatic compound.  $\Delta^1$ -Octene readily yields octane. Cinnamic acid, its sodium salt and its methyl ester yield phenylpropionic acid and its corresponding derivatives. The hydrogenation proceeds better with the sodium salt than with the free acid. Piperonylacrylic acid hydrogenates less readily than cinnamic acid, but the conversion readily takes place on using the sodium salt. Anethole, eugenol, and saffrole readily undergo hydrogenation at 60—80°, whilst for *isoeugenol* the ordinary temperature suffices. W. G.

**Hydrogenation under Atmospheric Pressure in the Presence of Nickel of Compounds with Aliphatic Ethylenic Linkings.** ANDRÉ BROCHET and ANDRÉ CABARET (*Compt. rend.*, 1914, 159, 326—329).—The substances containing aliphatic ethylenic linkings which were hydrogenated in the presence of active nickel under a slightly increased pressure by Brochet and Bauer (preceding abstract) also undergo hydrogenation under atmospheric pressure, but in this case the reaction takes place far more slowly and requires a larger amount of the catalyst. W. G.

**Some Nitro- and Amino-derivatives of Salicylonitrile (*o*-Cyanophenol).** H. COUSIN and V. VOLMAR (*Compt. rend.*, 1914, 159, 329—331).—To a cooled solution of salicylonitrile in three times its weight of acetic acid an equal weight of nitric acid in its own weight



of acetic acid is gradually added. A rapid action takes place, two nitro-compounds being formed, which can be separated by fractional dilution. The first to be precipitated on the addition of water is 6-nitrosalicylonitrile, which crystallises from alcohol in golden-yellow prisms, m. p. 132—133°, giving a *potassium* salt in the form of orange-coloured, prismatic needles. Its constitution has been proved by hydrolysis with potassium hydroxide, 6-nitrosalicylic acid being obtained. The second nitro-compound precipitated by water is 4-nitrosalicylonitrile (compare Meyer and Bone, 1893, i, 469). Both nitro-compounds have been reduced by tin and hydrochloric acid, yielding the corresponding amino-compounds. 6-Aminosalicylonitrile crystallises in flattened prisms, m. p. 145° (decomp.), giving a *hydrochloride*, slender, white needles decomposing at 130°. 4-Aminosalicylonitrile crystallises in slender, white needles, m. p. 158—160° (decomp.), giving a *hydrochloride*, prismatic plates, decomposing at 180°. Both bases rapidly become coloured on exposure to light, and they are both diazotised by nitrous acid at 0°, giving diazo-compounds capable of combining with amines and phenols.

W. G.

**Some Reactions of Mercuric Salicylate.** W. OECHSNER DE CONINCK (*Rev. gén. Chim. pure appl.*, 1914, 17, 125—126).—Mercuric salicylate is decomposed by water, methyl or ethyl alcohol, and acetone at their respective b. p.; it is partly decomposed by water or alcohol even at room temperature. After repeated evaporation with boiling water and washing the product with water at 0° until the filtrate has a neutral reaction, the normal salt is converted into *basic mercuric salicylate*,  $C_6H_4 \langle \begin{smallmatrix} CO_2 \\ O \end{smallmatrix} \rangle Hg$ , decomp. 239—240°, amorphous, white powder, which is insoluble in the usual solvents and in the moist state is decomposed by heat into mercury, carbon dioxide, phenol, and oxygen.

C. S.

**Palladosalicylates.** G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 880—885).—In continuation of the previous work (this vol., ii, 375), which showed the existence of palladous acetylacetonate, analogous to the corresponding cupric salt, the author has now prepared palladosalicylic acid and several of its salts, which are similar to the cuprisalicylates obtained by Ley and Erler (*A.*, 1908, i, 177).

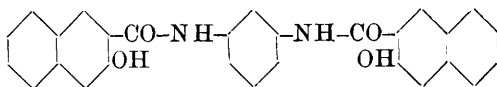
T. H. P.

**Crystals of  $\alpha$ -Ethoxy- $\alpha\alpha$ -diphenylacetic Acid.** A. JOHNSEN (*Centr. Min.*, 1914, 430).—The compound,  $OEt \cdot CPh_2 \cdot CO_2H$ , melting at 114°, crystallises in colourless, anorthic tablets; [ $a:b:c = 1.7019:1:0.8166$ ;  $\alpha = 72^\circ 3'$ ,  $\beta = 116^\circ 2'$ ,  $\gamma = 120^\circ 40'$ ]. There are good cleavages parallel to {100}, {010} and {001}, the other forms observed being {110} and {101}.

E. H. R.

**Preparation of Arylamides of 2-Naphthol-3-carboxylic Acid.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (Fr. Patent, 464478).—Arylamides of 2-naphthol-3-carboxylic acid may be obtained by heating the acid with the corresponding arylamines and a dehydrating

agent, such as phosphorus trichloride or thionyl chloride, in an indifferent liquid (compare this vol., i, 48). The following compounds, all of which give yellow solutions in sodium hydroxide solution, have been prepared: *anilide*, m. p. 243—244°; *o-anisidide*, m. p. 167—168°; *o-chloroanilide*, m. p. 225—226°; *p-chloroanilide*, m. p. 258—259°; *m-chloroanilide*, m. p. 241—242°; *2:5-dichloroanilide*, m. p. 246—247°; *o-toluidide*, m. p. 195—196°; *p-toluidide*, m. p. 221—222°; *α-naphthalide*, m. p. 222—223°;



*β-naphthalide*, m. p. 243—244°; the compound (annexed formula), prepared from tolylene-2:4-diamine, m. p. 261—262°; *ethylanilide*, m. p. 153—154°, and the *o-hydroxyanilide*, m. p. 214—215° (decomp.). The above melting points are uncorrected.

T. H. P

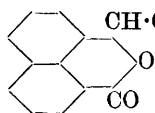
**Manufacture of Salts of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.** OTTO GERNGROSS and HERMANN KAST (Fr. Patent, 464081).—An aqueous solution or suspension of *o*-acetoxybenzoic acid is stirred or shaken with an oxide, hydroxide, carbonate, etc., the mixture being cooled if necessary and the solution being then evaporated in a vacuum and the *o*-acetoxybenzoate separated.

T. H. P.

**The Acid Salts of Dibasic Acids.** É. JUNGFLISCH and PH. LANDRIEU (*Ann. Chim.*, 1914, [ix], 2, 5—56).—A résumé of work already published (compare this vol., i, 13, 416, 657).

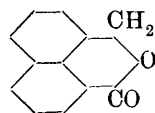
W. G.

**peri-Derivatives of Naphthalene.** VI. G. ERRERA and G. AJON (*Gazzetta*, 1914, 44, ii, 92—98).—In view of the ease with which *perinaphthindantrione* and *dihydroxyketoperinaphthindene* undergo oxidation and reduction in presence of alkali (compare A., 1913, i, 985), the authors have investigated the action of sodium carbonate on the alcoholate of the triketone.

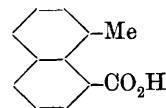


The products obtained comprise: (1) *acenaphthaquinone*; (2) *ethyl naphthalidecarboxylate* (annexed formula), which crystallises in colourless needles or faintly brownish-yellow prisms, m. p. 108—109°.

The corresponding acid,  $C_{13}H_8O_4$ , which may also be obtained by reduction of naphthalonic acid (compare Errera and Cuffaro, A., 1912, i, 273), forms minute, colourless needles, m. p. 210—212°. When heated above its melting point, the acid yields *naphthalide* (annexed formula), which crystallises in yellow needles, m. p. 159—160°, and has an oxygen ring even more stable than that of phthalide.



**Methyl naphthalonate**,  $C_{13}H_6O_5Me_2$ , hard, almost colourless, crystals, m. p. 130—131°, which redden in the light, and the *ethyl ester*,  $C_{13}H_6O_5Et_2$ , colourless needles or faintly brown prisms, m. p. 94—95°, were prepared.



**8-Methylnaphthoic acid** (annexed formula), obtained, together with a little naphthalidecarboxylic acid and acenaphthene, by vigorous reduction of naphthalonic acid with hydriodic acid and phosphorus, forms small, hard prisms or white, flexible needles, melting indefinitely at 130—131°.

T. H. P.

**Some Didepsides of Hydroxybenzoic Acids and of Syringaic Acid.** RICHARD LEPSIUS (*Annalen*, 1914, 406, 11—21).—The following didepsides have been prepared by Fischer's general method: *m*-Methylcarbonatobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\text{Me}$ , m. p.  $151^\circ$  (corr.), colourless needles, prepared by the action of cold *N*-sodium hydroxide (2 mols.) and methyl chlorocarbonate (1.1 mol.) on *m*-hydroxybenzoic acid and subsequent acidification, forms with phosphorus pentachloride a *chloride*, m. p.  $63^\circ$ , colourless needles, which reacts with cold aqueous *m*-hydroxybenzoic acid and *N*-sodium hydroxide (2 mols.) to form 3-*m*-methylcarbonatobenzoyloxybenzoic acid.

$\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p.  $169^\circ$  (corr.), colourless needles. The last substance forms a *chloride*,  $\text{C}_{16}\text{H}_{11}\text{O}_6\text{Cl}$ , m. p.  $91\text{--}92^\circ$  (corr.), and is converted into 3-*m*-hydroxybenzoyloxybenzoic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p.  $199^\circ$  (corr.), by cold *N*-ammonia and subsequent acidification.

The following substances have been prepared by similar methods: 4-*m*-methylcarbonatobenzoyloxybenzoic acid, m. p.  $201^\circ$  (corr.), and its *chloride*, m. p.  $105\text{--}106^\circ$  (corr.); 4-*m*-hydroxybenzoyloxybenzoic acid, m. p.  $239\text{--}240^\circ$  (corr.), with preliminary slight decomp.; 3-*p*-methylcarbonatobenzoyloxybenzoic acid, m. p.  $185^\circ$  (corr.), and its *chloride*, m. p.  $120^\circ$  (corr.); 3-*p*-hydroxybenzoyloxybenzoic acid, m. p.  $254^\circ$  (corr.); methylcarbonatosyringaic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{O}\cdot\text{CO}_2\text{Me}$ , m. p.  $191\text{--}192^\circ$  (corr.), and its *chloride*, m. p.  $123\text{--}124^\circ$  (corr.); ethylcarbonatosyringaic acid, m. p.  $182\text{--}183^\circ$  (corr.), and its *chloride*, m. p.  $75^\circ$ ; methylcarbonatodisyrringaic acid,

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{O}\cdot\text{CO}_2\text{Me}$ , m. p.  $223\text{--}224^\circ$  (corr.); *disyringaic acid*, m. p.  $260^\circ$  (corr.); 4-methylcarbonatosyringaoxyloxybenzoic acid, m. p.  $203^\circ$  (corr.), and its *chloride*, m. p.  $150\text{--}151^\circ$  (corr.); 4-syringaoxyloxybenzoic acid, m. p.  $208^\circ$  (corr.); *p*-methylcarbonatobenzoyloxy-syringaic acid, m. p.  $228\text{--}229^\circ$  (corr.), and its *chloride*, m. p.  $138^\circ$  (corr.); *p*-hydroxybenzoyloxy-syringaic acid, m. p.  $282\text{--}284^\circ$  (decomp. corr.). C. S.

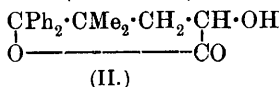
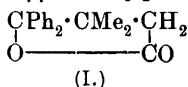
**Stability of Cinnamaldehyde.** H. ADIE PHILLIPS (*Pharm. J.*, 1914, 93, 129—130).—Under the usual conditions prevailing during steam-distillation, cinnamaldehyde, both in the pure state and as a constituent of cinnamon oil, is not oxidised to any appreciable extent.

W. P. S.

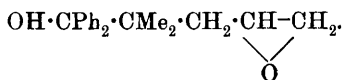
**Syntheses by means of Sodamide.** Propylenedimethylacetophenone Oxide [ $\delta\epsilon$ -Oxido- $\beta$ -benzoyl- $\beta$ -methylpentane] and Some of its Derivatives. New Method of Preparing  $\gamma$ -Ketonic Acids. A. HALLER and (Mme.) RAMART-LUCAS (*Compt. rend.*, 1914, 159, 143—149. Compare this vol., i, 695, 968).— $\delta\epsilon$ -Oxido- $\beta$ -benzoyl- $\beta$ -methylpentane or its dimeride (*loc. cit.*) on oxidation in acetic acid with chromic acid in amount sufficient to furnish 1 atom of oxygen, yields  $\beta$ -benzoyl- $\beta$ -methylpentane- $\delta\epsilon$ -diol, m. p.  $100^\circ$  (*loc. cit.*). If enough chromic acid is used to supply 4 atoms of oxygen, the product in each case is  $\beta$ -benzoyl- $\beta$ -methylbutyric acid,  $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $100^\circ$ . This substance is obtained similarly by the oxidation of *aa*-dimethyl- $\alpha$ -allylacetophenone by means of chromic acid in acetic acid solution.

On treating a mixture of a ketone and chloroacetic acid with sodium ethoxide (compare Darzens, A., 1905, i, 116) or with sodamide (compare Claisen, A., 1905, i, 286) a glycidic ester is obtained. Thus phenyl isopropyl ketone and chloroacetic acid yield ethyl isopropylphenylglycidate, which on saponification yields the corresponding acid, m. p. 73°. If, however, iodo- or bromo-acetic acids are used in place of chloroacetic acid an ester is obtained, b. p. 168—175°/15 mm., which on saponification yields an acid identical with  $\beta$ -benzoyl  $\beta$ -methylbutyric acid. This method can be generalised for the preparation of a series of  $\gamma$ -ketonic acids.

On condensing  $\delta\epsilon$ -oxido- $\beta$ -benzoyl- $\beta$ -methylpentane with magnesium phenyl bromide a compound is obtained, crystallising from light petroleum in needles, m. p. 107—108°, and from ether in prisms, m. p. 122°. Analysis shows it to have the composition  $C_{19}H_{22}O_2$ . It yields an *acetyl* derivative, slender needles, m. p. 119·5°, and a *phenylurethane*, m. p. 116—117°. On oxidation with chromic acid in acetic acid in the cold, it yields a compound,  $C_{19}H_{20}O_3$ , m. p. 155—156°, whilst, if the oxidation is carried out at the boiling point, the product is a compound,  $C_{18}H_{18}O_3$ , m. p. 146—147°. The latter compound can be synthesised by the condensation of magnesium phenyl bromide with ethyl  $\beta$ -benzoyl- $\beta$ -methylbutyrate, thus proving its constitution to be that of  $\gamma\gamma$ -diphenyl- $\beta\beta$ -dimethyl- $\gamma$ -butanolide (formula I), whilst that of the compound  $C_{19}H_{20}O_3$  is  $\delta\delta$ -diphenyl- $\gamma\gamma$ -dimethylpentan- $\alpha$ -ol- $\gamma$ -olide (formula II).

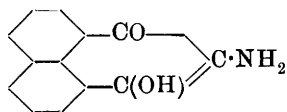


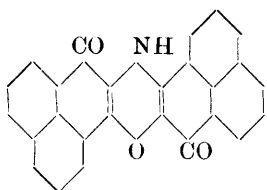
From this it follows that the compound, m. p. 107—108°, obtained by the condensation of magnesium phenyl bromide and  $\delta\epsilon$ -oxido- $\beta$ -benzoyl- $\beta$ -methylpentane, is  $\delta\epsilon$ -oxido- $\beta\beta$ -dimethyl- $\alpha\alpha$ -diphenylpentan- $\alpha$ -ol,



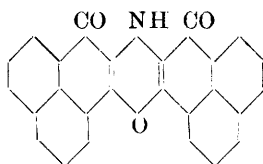
W. G.

**Aminohydroxyketoperinaphthindene. V. G. ERRERA** (*Gazzetta*, 1914, 44, ii, 18—24).—The compound obtained by the action of phenylhydrazine on hydroxyketoperinaphthindene (compare A., 1911, i, 465; 1913, i, 985) has now been purified and is shown to be *aminohydroxyketoperinaphthindene* (annexed formula), which crystallises in shining, golden-brown leaflets, m. p. 260° (decomp.), and is coloured faintly violet by hot water, and more intensely so by alkali carbonates. Solutions of alkali hydroxides dissolve it, giving deep violet solutions, from which acids apparently precipitate the original compound. In sulphuric acid it forms a yellow or reddish solution according to the concentration of the acid. In hot benzaldehyde it is very readily soluble, the solution depositing an additive product (?) in orange needles on cooling. When subjected to prolonged treatment with boil-



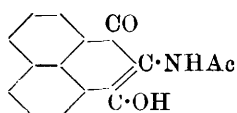


or



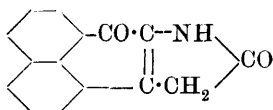
ing alcohol containing 10% of sulphuric acid, it yields the annexed compound, which forms bluish-black needles

or plates, not melting even at 300°.

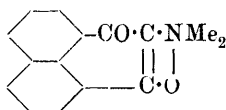


The corresponding *acetyl*amino-derivative (annexed formula) forms orange needles, m. p. 191—192°, and yields an *anhydro*-compound (I.) in yellow needles, m. p. 185—186°, or in reddish-yellow plates or needles containing

benzene of crystallisation; its solutions in alcohol or acetic acid show faint green fluorescence.



(I.)



(II.)

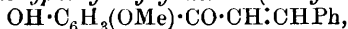
When treated with methyl sulphate in alkaline aqueous solution, the amino-compound is converted into the *betaine* derivative (II), which forms brownish-yellow, opaque laminæ, m. p. 187—188°, with a faint odour of trimethylamine; its hydrochloride forms yellow needles.

T. H. P.

**Chalkones and Hydrochalkones [Phenyl Styryl Ketones and Phenyl Phenylethyl Ketones].** IV. G. BARGELLINI and LYDIA MONTI (*Gazzetta*, 1914, **44**, ii, 25—34).—Further hydrogenated chalkones have been prepared by the method of reduction previously described (A., 1913, i, 59). The same method is applied to the analogous compound, dihydroxybenzylidenecumarone, with which, although the chromophore group,  $\cdot\text{CO}\cdot\text{C}:\text{C}\cdot$ , exists partly in a ring, only the double

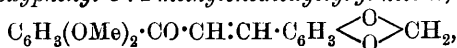
linking becomes saturated, the carbonyl group remaining unaltered.

*2-Hydroxy-4-methoxyphenyl styryl ketone (benzylidenepæonol),*



prepared by the interaction of benzaldehyde and 2:4-dihydroxyacetophenone monomethyl ether (pæonol) in alcoholic solution in presence of sodium hydroxide (compare Emilewicz and von Kostanecki, A., 1898, i, 369), forms yellow crystals, m. p. 106—108°. On reduction it yields 2-hydroxy-4-methoxyphenyl phenylethyl ketone, m. p. 103—104°. In Bargellini and Marantonio's paper (A., 1908, i, 801), the melting points of the mono- and di-methyl ethers of 2:4-dihydroxyphenyl phenylethyl ketone should be interchanged.

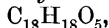
*3:4-Dimethoxyphenyl 3:4-methylenedioxystyryl ketone,*



prepared from 3:4-dimethoxyacetophenone and piperonaldehyde,

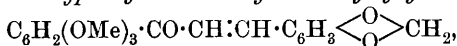
forms pale yellow crystals, m. p. 140—142°, and gives an intense red coloration with concentrated sulphuric acid.

3 : 4-Dimethoxyphenyl 3 : 4-methylenedioxyphenylethyl ketone,



forms white, woolly needles, m. p. 98—100°.

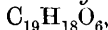
3 : 4 : 5-Trimethoxyphenyl 3 : 4-methylenedioxystyryl ketone,



prepared from 3 : 4 : 5-trimethoxyacetophenone (compare Mauthner, A., 1910, i, 680) and piperonaldehyde, forms pale yellow crystals, m. p. 118—120°, and gives a red solution in concentrated sulphuric acid.

3 : 4 : 5-Trimethoxyphenyl 3 : 4-methylenedioxyphenylethyl ketone,  $\text{C}_{19}\text{H}_{20}\text{O}_6$ , forms colourless leaflets, m. p. 96—98°.

2 : 3 : 4-Trimethoxyphenyl 3 : 4-methylenedioxy styryl ketone,



similarly prepared from 2 : 3 : 4-trimethoxyacetophenone (compare Blumberg and von Kostanecki, A., 1903, i, 644; Mannich and Hahn, A., 1911, i, 648), forms yellow, prismatic needles, m. p. 97—98°, gives a red solution in concentrated sulphuric acid, and on reduction yields the corresponding hydrochalkone, which is an oil and decomposes when an attempt is made to purify it by distillation.

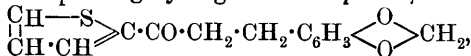
2-Hydroxy-4-methoxyphenyl styryl ketone (compare Woker, von Kostanecki, and Tambor, A., 1904, i, 184), m. p. 98°, may be prepared by the action of sodium hydroxide on 7 : 8-dimethoxyflavanone, m. p. 114—115°, into which it is reconverted by the action of acid. This transformation of a flavanone into a chalkone would appear to be of general character, although only one other instance of such a change has been previously observed (compare Perkin and Hummel, T., 1904, 85, 1459).

2-Hydroxyphenyl 3 : 4-dimethoxystyryl ketone,  $\text{C}_{17}\text{H}_{18}\text{O}_4$ , forms shining, white needles, m. p. 80—82°.

Piperonylideneacetothienone,



prepared from piperonaldehyde and acetothienone in presence of alcoholic sodium hydroxide, forms pale yellow scales, m. p. 127—129°, and gives a red solution in concentrated sulphuric acid. On reduction it yields the corresponding hydrogenated compound,



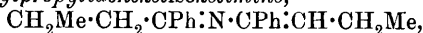
which forms white, tabular crystals, m. p. 50—52°, and is coloured dark garnet-red, but is not dissolved, by concentrated sulphuric acid.

Dihydroxybenzylcumarone,  $\text{C}_6\text{H}_2(\text{OH})_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CH}_2\text{Ph}$ , obtained by reduction of the corresponding dihydroxybenzylidenecumarone, m. p. 221°, forms pale yellow crystals, m. p. about 120° (+  $\frac{1}{2}\text{H}_2\text{O}$ ), or dirty white crystals, m. p. 160—164° (anhydrous). T. H. P.

**Some Ketisocketimines.** CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1914, 159, 149—152. Compare this vol., i, 830).—The

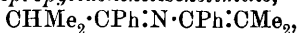
authors have prepared a number of ketisoketimines by heating the corresponding ketimines at  $115^{\circ}$  in a current of hydrogen for several days and separating the products by fractional distillation. They are all very viscous oils, coloured more or less deeply greenish-yellow, and having a slight odour. They are decomposed by hydrochloric acid, yielding one molecule of ammonia and two molecules of the corresponding ketone. They do not evolve gas on treatment with magnesium ethyl bromide.

*Diphenylpropylpropylideneketisoketimine,*



b. p.  $200^{\circ}/12$  mm.;  $D_4^{25.5-29}$  0.9958;  $n_D^{28.5-29}$  1.5809.

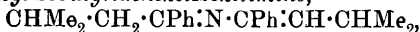
*Diphenylisopropylisopropylideneketisoketimine,*



b. p.  $144-145^{\circ}/4$  mm., obtained from *phenylisopropylketimine*,  
 $\text{NH:CPh}\cdot\text{CHMe}_2,$

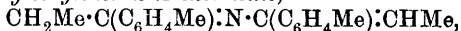
b. p.  $98-100^{\circ}/8$  mm.

*Diphenylisobutylisobutylideneketisoketimine,*



b. p.  $186-187.5^{\circ}/7$  mm.;  $D_4^{29}$  0.9674;  $n_D^{29}$  1.5617.

*Di-p-tolyethyl ethylideneketisoketimine,*



b. p.  $178-179^{\circ}/2.5$  mm., obtained from *p-tolyethylketimine*,  
 $\text{NH:C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\text{Me},$

b. p.  $94-96^{\circ}/2.5$  mm.;  $D_4^{16.5}$  0.9805;  $n_D^{16.5}$  1.5448.

*Diphenylbenzylbenzylideneketisoketimine,*  $\text{CH}_2\text{Ph}\cdot\text{CPh:N}\cdot\text{CPh:CHPh},$

b. p.  $248-250^{\circ}/2$  mm., obtained from *phenylbenzylketimine*,  
 $\text{NH:CPh}\cdot\text{CH}_2\text{Ph},$

white crystals, m. p.  $57^{\circ}$ .

W. G.

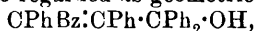
**Reaction Between Magnesium Phenyl Bromide and Unsaturated Compounds Containing a Number of Phenyl Groups.** DOROTHY A. HAHN and RUBY MURRAY (*J. Amer. Chem. Soc.*, 1914, 36, 1484—1497).—Highly phenylated compounds containing phenyl groups in the  $\alpha$ - and  $\beta$ -positions to a carbonyl group offer much greater resistance to the attack of magnesium phenyl bromide than substances containing the same number of phenyl groups in the  $\alpha$ -position only; thus tetraphenylpropenone does not react at all, while benzpinacolin reacts fairly readily. In order to ascertain whether other negative groups exert a similar steric effect, the behaviour of  $\alpha\beta$ -dibenzoylstyrene and of  $\alpha\beta$ -dibenzoylstilbene towards magnesium phenyl bromide has been examined. The result shows that the introduction of a phenyl group in the  $\beta$ -position to a carbonyl group causes resistance to the addition of magnesium phenyl bromide in the 1:4 position ( $\text{O}:\overset{1}{\text{C}}:\overset{2}{\text{C}}:\overset{3}{\text{C}}:\overset{4}{\text{C}}$ ); in agreement with this, Kohler has observed that  $\alpha$ -benzoylstilbene reacts quantitatively and additively in the 1:4 position with magnesium phenyl bromide, whilst tetraphenylpropenone, as stated above, does not react at all.

The reaction between  $\alpha\beta$ -dibenzoylstyrene and ethereal magnesium phenyl bromide leads, after the usual treatment, to the formation of  $\alpha\beta$ -dibenzoyl- $\alpha\beta$ -diphenylethane, m. p.  $256^{\circ}$ , and 2:3:4:5-tetra-

phenylfuran, m. p. 175° (accompanied by their respective products of oxidation,  $\alpha\beta$ -dibenzoylstilbene, m. p. 212°, and dihydroxytetraphenylfuran, m. p. 157°); these two substances are evidently formed by the rearrangement and the dehydration respectively of a primary product,  $\text{CHPhBz}:\text{CPh}:\text{CPh}\cdot\text{OH}$ , resulting from dibenzoylstyrene by addition in the 1:4 position.

$\alpha\beta$ -Dibenzoylstilbene is conveniently obtained in quantity by the following method. The dry ethereal solution containing the additive compound of  $\alpha\beta$ -dibenzoylstyrene and magnesium phenyl bromide is slowly treated with bromine (1 mol.), and the mixture is treated at once with ice and hydrochloric acid, when dibenzoylstilbene is immediately precipitated.

The reaction between  $\alpha\beta$ -dibenzoylstilbene and ethereal magnesium phenyl bromide in the cold leads to the formation of two substances, m. p. 208° and 157° respectively. These are produced by addition in the 1:2 position and are regarded as geometrical isomerides,



for the following reasons: first, either of the two products can be obtained in an average yield of 80% by modifying the conditions of the preparation; secondly, each of the substances, dissolved in acetic anhydride, forms an equilibrium mixture from which both can be isolated by crystallisation; thirdly, the two substances yield identical products of reduction and of oxidation. Thus,  $\gamma$ -benzoyltetraphenyl- $\Delta^2$ -propenol, m. p. 208°, and its isomeride, m. p. 157° (which is the more reactive form), are reduced by stannous chloride and hydrochloric acid, or by hydriodic acid and amorphous phosphorus at 160°, to a substance,  $\text{C}_{84}\text{H}_{26}\text{O}$ , m. p. 185°, large plates, which is probably *pentaphenylbutenyl*

*oxide*,  $\text{O} \begin{array}{c} \text{CPh}_2-\text{CPh} \\ \diagup \quad \diagdown \\ \text{CHPh} \cdot \text{CPh} \end{array}$ ; it reacts with ethereal magnesium phenyl bromide to form, ultimately, a substance,  $\text{C}_{80}\text{H}_{62}\text{O}$ , m. p. 232°, large plates or prisms, which may be *hexaphenylbutenyl ether*,  $(\text{CPh}_3\cdot\text{CPh}:\text{CPh}\cdot\text{CHPh})_2\text{O}$ .

The oxidation of the two isomerides by hot chromic and acetic acids yields benzoic acid, benzil, benzophenone, and a small amount of a substance,  $\text{C}_{27}\text{H}_{22}\text{O}_3$ , m. p. 143°. This substance probably has the

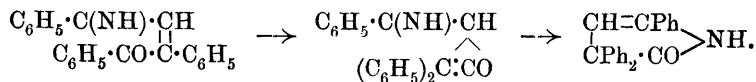
formula  $\text{O} \begin{array}{c} \text{CPh}\cdot\text{CPh}_2\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{CPh}\cdot\text{OH} \end{array}$ , since it yields benzophenone and benzoic acid by further oxidation and is reduced by stannous chloride and hydrochloric acid to benzaldehyde and triphenylvinyl alcohol. C. S.

**Dibenzoylstyrene.** E. OLIVERI-MANDALÀ and E. CALDERARO (*Gazzetta*, 1914, **44**; ii, 85—92).—The action of sunlight on dibenzoylstyrene in benzene solution yields the lactone of triphenylcrotonic acid, which is also obtained by heating the same compound at 300° (compare Japp and Tingle, T., 1897, **71**, 1138). The action of bromine in the light gives the same tribromotriphenylfuran as was obtained by Japp.

The influence of sunlight does not change the action of alcoholic ammonia on this compound, the resulting product, m. p. 180°, undergoing transformation into the isomeric triphenylpyrrolone,



$\text{NH} \begin{smallmatrix} \text{CPh} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CO} - \text{CPh}_2 \end{smallmatrix}$  (compare Japp and Tingle, *loc. cit.*). In view of the explanation suggested by Schroeter (A., 1909, i, 617) for the benzylic acid transposition, the compound, m. p.  $180^\circ$ , and its conversion into triphenylpyrrolone are represented thus:



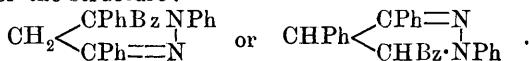
With hydroxylamine, dibenzoylstyrene gives in neutral or alkaline solution a *compound*,  $\text{C}_{22}\text{H}_{17}\text{O}_2\text{N}$ , which crystallises in white leaflets or hard needles, m. p.  $140$ — $141^\circ$ , whilst in acid solution, an isomeric *compound*, crystallising in yellow needles, m. p.  $167$ — $168^\circ$ , is obtained. It is suggested that these compounds are derived from a closed ring,

isooxazoline, and that their structures are  $\text{N} \begin{smallmatrix} \text{CPh} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} - \text{CPhBz} \end{smallmatrix}$  and

$\text{N} \begin{smallmatrix} \text{CPh} \cdot \text{CHPh} \\ \diagdown \quad \diagup \\ \text{O} - \text{CHBz} \end{smallmatrix}$  respectively. Such ring compounds might readily be

formed by isomeric change of the oxime,  $\begin{smallmatrix} \text{C} \cdot \text{CC} - \\ || \\ \text{NOH} \end{smallmatrix} \rightarrow \begin{smallmatrix} > \text{C} \cdot \text{CH} \cdot \text{C} - \\ | \quad \quad | \\ \text{O} \quad \quad \text{N} \end{smallmatrix}$

The compound described by Japp and Klingemann (T., 1890, 57, 662) as dibenzoylstyrenemonophenylhydrazone is remarkably stable towards the action of acids and the author regards it as a pyrazoline derivative of the structure:



Both the carbonyl groups of dibenzoylstyrene react with semicarbazide, giving the *compound*,  $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_6$ , m. p.  $211$ — $212^\circ$  (decomp.).  
T. H. P.

**Certain Derivatives of Iodoanil.** C. LORING JACKSON and ELMER KEISER BOLTON (*J. Amer. Chem. Soc.*, 1914, 36, 1473—1484. Compare Torrey and Hunter, A., 1912, i, 475; Jackson and Bolton, this vol., i, 297, 550).—The substances,  $\text{C}_6\text{X}_2\text{Y}_2\text{O}_2$  (where X is Br or I, and Y is OMe, OEt,  $\text{OCH}_2\text{Ph}$ , OAc, or  $\text{CH}[\text{CO}_2\text{Et}]_2$ ), described in the paper exhibit a surprising resemblance to the corresponding chlorine and bromine compounds; for example, the colour is essentially the same, and the solubilities do not exhibit any qualitative differences. A comparison of the m. p. of corresponding chloro-, bromo-, and iodo-compounds shows that the regularity recorded in two cases by Torrey and Hunter (*loc. cit.*) is not part of a general rule applying to all benzoquinones containing halogens.

The following substances of the type  $\text{C}_6\text{X}_2\text{Y}_2\text{O}_2$  are made usually by the action of di-iododiphenoxy-*p*-benzoquinone on the sodium derivative of the alcohol; in making the dimethoxy- and diethoxy-compounds the first products are the hemi-acetals, which change to the quinones by heating with acetic anhydride: X=I, Y=OMe, light red needles, m. p.  $196^\circ$ ; X=I, Y=OEt, orange-red needles, m. p.  $186^\circ$ ; X=I, Y= $\text{O} \cdot \text{CH}_2\text{Ph}$ , orange-red plates, m. p.  $160^\circ$ ; X=Br, Y= $\text{O} \cdot \text{CH}_2\text{Ph}$ ,

orange-red plates, m. p.  $146^{\circ}$  (in making the last two compounds, ethyl alcohol must be completely absent, otherwise the diethoxy-derivative is obtained);  $X=I$ ,  $Y=NHPh$ , dark purple needles, m. p.  $240^{\circ}$  (decomp.);  $X=I$ ,  $Y=NH\cdot C_6H_4Me(p)$ , dark purple plates, decomp.  $205^{\circ}$  (these two are prepared by heating di-iododiphenoxy-*p*-benzoquinone with alcohol and the necessary amine [rather more than 2 mols.]);  $X=I$ ,  $Y=CH(CO_2Et)_2$ , yellow, fern-like crystals, m. p.  $138^{\circ}$ , (*sodio*-derivative, intensely blue);  $X=Br$ ,  $Y=CH(CO_2Et)_2$ , yellow needles, m. p.  $109^{\circ}$ . The last substance (and also the preceding) cannot be hydrolysed without decomposing, is reduced to the corresponding *quinol*,  $C_6Br_2(OH)_2[CH(CO_2Et)_2]_2$ , m. p.  $183^{\circ}$ , colourless prisms, by phenylhydrazine in toluene, and reacts with bromine in boiling alcohol to form *ethyl dibromo-p-benzoquinone dibromomalonate*,  $C_6Br_2O_2[CBr(CO_2Et)_2]_2$ , m. p.  $172^{\circ}$ , yellow needles.

*Di-iododiphenoxyquinol*,  $C_6I_2(OPh)_2(OH)_2$ , m. p.  $260^{\circ}$ , colourless needles, is prepared by reducing di-iododiphenoxy-*p*-benzoquinone with phenylhydrazine in hot glacial acetic acid. *Dibromodiacetoxy-p-benzoquinone*, m. p.  $205^{\circ}$ , yellow plates, is prepared by heating bromoanilic acid and acetic anhydride. *Silver iodoanilate*,  $C_6I_2O_2(OAg)_2$ , dark red, amorphous substance, prepared from a dilute solution of iodoanilic acid and a slight excess of silver nitrate, is not attacked by cold concentrated nitric acid. *Di-iodoiumino-p-benzoquinone*,  $C_6I_2O_2(NH_2)_2$ , m. p.  $230^{\circ}$  (decomp.), brown, amorphous solid, obtained by heating iodoanil with an excess of alcoholic ammonia, is easily soluble in cold aqueous sodium hydroxide.

*Tetra-iodoquinol*,  $C_6I_4(OH)_2$ , m. p.  $258^{\circ}$  (decomp., beginning at  $238^{\circ}$ ), cream-coloured crystals, prepared from iodoanil and phenylhydrazine in hot glacial acetic acid, rapidly oxidises in the air. The *diacetate*, m. p.  $285^{\circ}$  (decomp., beginning at about  $270^{\circ}$ ), colourless needles, is obtained by heating the quinol with acetic anhydride and sodium acetate or iodoanil with acetic anhydride and a few drops of concentrated sulphuric acid. The action of iodine chloride on *p*-benzoquinone suspended in warm carbon tetrachloride results in the formation of dichlorobenzoquinone, m. p.  $161^{\circ}$ , not the expected iodo-compound. C. S.

**Preparation of Terpenes from their Hydrogen Haloids.** ALFRED MEYER (D.R.-P. 272562).—Hydrogen haloids may be removed from their compounds with terpenes, such as pinene and dipentene hydrochlorides, by heating with kieselguhr in the presence or absence of (1) an absorbent of the hydrogen haloid and (2) a diluent.

T. H. P.

**Oil of *Ocimum pilosum*, Roxb.** KSHITIBHUSAN BHADURI (*J. Amer. Chem. Soc.*, 1914, **36**, 1772—1773).—A specimen of the volatile oil of *Ocimum pilosum*, Roxb., prepared from the whole plant by steam distillation, had  $D_{25}^{25}$  0.8872,  $n_D^{25}$  1.4843, and  $\alpha_D$   $-3.7^{\circ}$ . The greater part distilled at  $205$ — $230^{\circ}$ , and about 10% of it was absorbed by 5% potassium hydroxide. The oil contained citral (41%), citronellaldehyde (34%), limonene, cineole, and a little thymol. E. G.

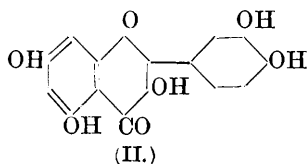
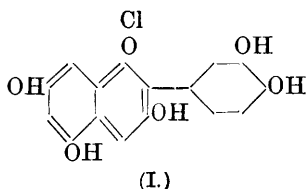
**Oil of Port Orford Cedar Wood and Some Observations on *d*- $\alpha$ -Pinene.** A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1914, 6, 631—632).—The Port Orford cedar (*Chamaecyparis lawsoniana* Parlatores) grows on the coastal regions of Oregon and California and yields an oil having the following approximate composition:  $\alpha$ -*d*-pinene, 60—61%; dipentene, 6—7%; free *l*-borneol, 11%; esters, as borneol acetate, 11.5%; cadinene, 6—7%; loss, 5%. The combined borneol occurs mainly as borneol acetate, but esters of formic and decoic acid are also present. In the old oil, formic, acetic, and decoic acids occur in the free state. The  $\alpha$ -pinene, after purification, yielded the following constants: b. p. 156.0—156.1°;  $D^{15}$  0.8631;  $n_D^{15}$  1.4684;  $[\alpha]_D + 51.52^\circ$ . W. P. S.

**Influence of the Solvent on the Viscosity of Caoutchouc Solutions.** F. KIRCHHOFF (*Kolloid. Zeitsch.*, 1914, 15, 30—36).—Measurements have been made of the viscosity of solutions containing 0.5, 1, 2, and 3 grams of caoutchouc in 100 c.c. of light petroleum, benzene, carbon tetrachloride, trichloroethylene, tetrachloroethane, and pentachloroethane. In general, the viscosity coefficients run parallel with the numbers which afford a measure of the swelling capacity of the various solvents towards caoutchouc (compare Posnjak, A., 1912, ii, 912). In accordance with Hatschek's views (A., 1913, ii, 559), the observed connexion between the viscosity and swelling capacity is probably determined by the combination of the caoutchouc with the solvent. The extent to which this occurs increases with the magnitude of the viscosity coefficient. H. M. D.

**Isolation of the Insoluble [Substances] in Caoutchouc.** GUSTAVE BERNSTEIN (*Kolloid. Zeitsch.*, 1914, 15, 49—50).—The author points out that the method described by Spence and Kratz (this vol., i, 855) for the separation of the insoluble substances in caoutchouc is not novel in so far as it depends on a reduction of the viscosity of caoutchouc solutions. The diminution in viscosity can be brought about in various ways other than by the addition of acids, and furthermore, the addition of sulphuric acid has previously been employed for the estimation of pure caoutchouc in the crude product (compare Marquis and Heim, A., 1913, ii, 884). H. M. D.

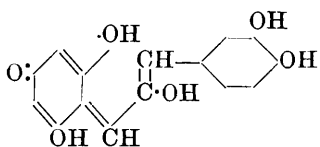
**Biochemical Syntheses of  $\beta$ -Monoglucosides of *m*- and *p*-Xylene Glycols.** EM. BOURQUELOT and AL. LUDWIG (*Compt. rend.*, 1914, 159, 213—215; *J. Pharm. Chim.*, 1914, [vii], 10, 111—116).—These two glucosides have been prepared by the action of emulsin on a solution of the glycol and dextrose in aqueous acetone.  $\beta$ -*m*-Xyleneglycol glucoside crystallises in very slender needles, containing  $1\text{H}_2\text{O}$ , m. p. 85—95°. The anhydride prepared at 100° has  $[\alpha]_D - 46.86^\circ$ .  $\beta$ -*p*-Xyleneglycol glucoside crystallises in prismatic plates, m. p. 159—160°,  $[\alpha]_D - 50.47^\circ$ . Both these glucosides are slightly bitter in taste, and are readily hydrolysed by 3% aqueous sulphuric acid or by emulsin in aqueous solution. Neither reduces Fehling's solution. W. G.

**The Relation between Anthocyanins and Flavones.**  
 RICHARD WILLSTÄTTER and HEINRICH MALLISON (*Sitzungsber. K. Akad. Wiss. Berlin.*, 1914, 769—777).—Anthocyanins are glucosides the colour-components of which (anthocyanidins) have recently been recognised as derivatives of phenylbenzopyrylium (Willstätter, this vol., i, 564). The fission of anthocyanidins into phloroglucinol and phenol-carboxylic acids by alkalis leaves undetermined only the position of the phenyl group in the pyrylium nucleus. Thus cyanidin chloride may be a 2- or a 4-phenylbenzopyrylium derivative. The latter formula is improbable because a substituted benzophenone (maclurin) is not produced by the action of warm alkalis. If, therefore, cyanidin chloride is (I.) its relation to quercetin (II) suggests that the oxida-



tion of anthocyanins should result in the formation of yellow mordant dyes and, conversely, the reduction of flavonols should yield colouring matters of the anthocyanin group. Observations bearing on these relations have been recorded about fifty years ago by Stein and by Hlasiwetz and Pfaunder, and quite recently by Combes, Everest, Wheldale, and Watson and Sen (*I.*, 1914, 105, 389).

The authors have reduced an alcoholic solution of quercetin by 20% hydrochloric acid, magnesium, and a large quantity of mercury at a temperature not exceeding 0°, whereby a *substance*, called *allocyanidin chloride*, violet-red, microscopic needles, is obtained. The chloride readily loses hydrogen chloride and yields *allocyanidin*,  $C_{15}H_{12}O_6$ , which resembles, but is not identical with, cyanidin. *alloCyanidin* is not dihydroquercetin (compare Watson and Sen, *loc. cit.*), but is an



oxonium compound (annexed formula). More important than the examination of *allocyanidin* is the discovery that when the reduction of quercetin by the preceding reagents is effected at 35°, the products are *allocyanidin chloride* and

cyanidin chloride, the latter being identical in all respects with the substance obtained from the cornflower and the rose.

The formation of cyanidin from quercetin has a twofold significance. It is a synthesis of cyanidin, since quercetin has been synthesised by von Kostanecki, Lampe, and Tambor in 1904. Moreover, it proves the constitution of cyanidin chloride (I), establishes almost with certainty the constitutions of the nearly related anthocyanidins, pelargonidin and delphinidin, and leaves for future determination only the orientation of the methyl groups in a number of other anthocyanidins derived from these by the introduction of one or more methyl groups.

It follows from the preceding that an anthocyanidin, in its acid-free form, is isomeric with the flavone derivative which contains in a benzene nucleus one less atom of oxygen. C. S.

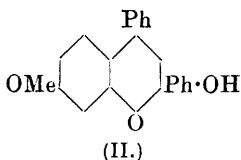
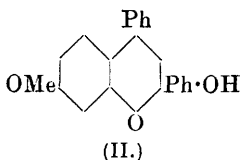
**Resorcinolbenzein (3 - Hydroxy - 9 - phenylfluorone).** F. KEHRMANN and E. LOTH (*Ber.*, 1914, **47**, 2271—2274. Compare Kehrman, A, 1913, i, 1352; Pope, T., 1914, **105**, 251).—The m. p. of the monomethyl ether of resorcinolbenzein is 204°.

Although the preparation of the oxonium bromide of resorcinolbenzein dimethyl ether offers no difficulty, treatment of the alcoholate,  $\text{OMe} \cdot \text{C}_6\text{H}_3 \cdot \text{C}(\text{Ph})(\text{OMe}) \cdot \text{C}_6\text{H}_3 \cdot \text{OMe}$ , with a warm methyl-alcoholic solution of hydrogen chloride gave a yellow, crystalline solid which even after crystallisation from a mixture of methyl alcohol and ether is apparently a mixture of a mono- and a di-hydrochloride. The mono-hydrochloride was finally obtained almost pure by repeatedly grinding the yellow solid with sodium chloride solution, when it remained as an orange-yellow solid. D. F. T.

**The Synthesis of Benzopyrylium Salts.** HERMANN DECKER and PAUL BECKER (*Ber.*, 1914, **47**, 2288—2292. Compare Decker and Fellenberg, A., 1907, i, 950, 1064).—Attempts to replace resorcinol in the synthesis of benzopyrylium salts by phenol have proved unsuccessful, but the monomethyl ether of resorcinol can be applied with satisfactory results.

By passing hydrogen chloride into a solution of resorcinol monomethyl ether and dibenzoylmethane in acetic acid, a clear deep red solution can be obtained which, after keeping for three days and precipitating unchanged material by the addition of an equal bulk of 10% hydrochloric acid, gives on treatment with solid ferric chloride an oily precipitate; this soon crystallises and consists of 7-methoxy-2:4-diphenylbenzopyrylium ferrichloride (formula I), which crystallises from acetic acid in yellow needles, m. p. 186°; the acetic acid solution on the addition of water exhibits a marked yellowish-green fluorescence.

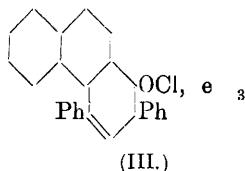
If the ferrichloride is treated with sodium hydroxide solution, ferric hydroxide is precipitated and on passing carbon dioxide through the filtrate a red deposit of a chalkone derivative,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CPh} : \text{CH} \cdot \text{COPh}$ , is produced, arising from fission of the ring of the primarily produced carbinol (formula II). With hydrochloric acid, the chalkone regenerates the original oxonium salt, whilst further treatment with warm sodium hydroxide solution causes its decomposition into acetophenone and 2-hydroxy-4-methoxybenzophenone.



The success of this synthetic process with resorcinol monomethyl ether disposes of the idea that the presence of a hydroxyl group in the para-position is necessary for the reactivity of the hydrogen atom involved in the condensation. On this account the failure of attempts

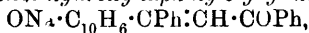
to effect this synthetic reaction with phenol is probably not due to the absence of the second hydroxyl radicle as much as to the unsubstituted hydrogen atom turning the reaction into a different course. Confirmation of this view is supplied by the possibility of effecting a similar condensation, certainly with some difficulty, with  $\beta$ -naphthol, which possesses no hydrogen atom in the para-position to the reactive hydrogen atom.

An equimolecular mixture of  $\beta$ -naphthol and dibenzoylmethane in alcohol was saturated with hydrogen chloride and heated for two hours in a sealed tube at 100°. After five to six days the deep yellow solu-



tion was treated with solid ferric chloride, when 2 : 4 - *diphenylnaphthapyrylium ferrichloride* (formula III) separated in golden-yellow leaflets, m. p. 272—273°, the yield being poor. Corresponding with this salt there is a colourless carbinol which on boiling with sodium hydroxide solution undergoes conversion into the

red sodium salt of *phenyl hydroxynaphthylstyryl ketone*,



the free ketone obtainable by the action of carbon dioxide being recondensed to the oxonium chloride when heated with hydrochloric acid.

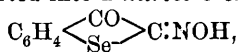
The yellow colour of the benzopyrylium salts is attributed to the C:O: group, and the postulation of other chromophores such as an ortho- or para-quinonoid configuration is regarded as unnecessary.

D. F. T.

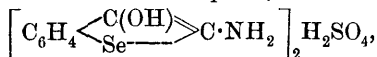
**Aromatic Selenium Compounds. III. Selenonaphthenquinone.** R. LESSER and A. SCHOELLER (*Ber.*, 1914, **47**, 2292—2307. Compare Lesser and Weiss, A., 1913, i, 1184; 1912, i, 642).—The preparation of selenonaphthenquinone, the selenium isologue of isatin, offered some difficulty on account of the sensitiveness of the substance towards most reagents, in which characteristic it resembles the analogous oxygen compound coumarandione. Success was achieved by the application of the method used by Pummerer (A., 1910, i, 510) for isatin and thionaphthenquinone, who condensed indoxyl and 3-hydroxythionaphthen with aromatic nitroso-compounds and then hydrolysed the resulting anils.

In the conversion of *o*-carboxyphenylselenolacetic acid into 3-hydroxy-selenonaphthen by the action of acetic anhydride, it is advisable not to heat above 100—105°. At the ordinary temperature bromine attacks an acetic acid solution of 3-hydroxyselenonaphthen with formation only of a mono-bromo-derivative, whilst at higher temperatures, oxidation is effected with formation of “selenindigo” [2:2'-bisoxyselenonaphthen]. 2-Bromo-3-hydroxyselenonaphthen forms woolly, yellow needles, m. p. 103°; it decomposes on keeping, and when heated with aniline gives only a resinous product. The action of chlorine on an acetic acid solution of the hydroxyselenonaphthen gave rise to no crystalline product other than “selenindigo.”

When treated with the calculated quantity of nitrous acid, 3-hydroxy-selenonaphthen is converted into 2-nitroso-3-oxyselenonaphthen,

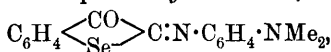


silky, yellow needles, m. p. 154—155°, soluble in most solvents. It is a very stable substance and can be dissolved in warm sulphuric or hydrochloric acid without decomposition; prolonged boiling with 30% sodium hydroxide solution causes the formation of diphenyldiselenide-di-o-carboxylic acid (diselenodisalicyclic acid). When shaken in sodium carbonate solution with methyl sulphate, the nitroso-oxy-selenonaphthen gives a *methyl* derivative, yellow leaflets with a bronze lustre, m. p. 146—147°; it also forms an *acetyl* derivative, yellow needles, m. p. 177—178°, and a *benzoyl* derivative, yellow leaflets, m. p. 184—185°, but the action of hydroxylamine gave only a *substance* of uncertain nature, yellow needles, m. p. 168° (decomp.). Reduction of the nitroso-compound by various agents followed a quite different course from that observed with the corresponding sulphur compound, and did not lead to the desired selenonaphthenquinone; for example, iron and acetic acid gave a product which, on the addition of sulphuric acid, separated from solution in pale yellow tablets; these slowly decomposed above 200°, and apparently consisted of the *sulphate*,



of a very unstable base; the *hydrochloride* closely resembles the sulphate; *perchlorate*, needles; *ferrichloride*, crystalline.

*Selenonaphthenquinone-2-p-dimethylaminoanil*,

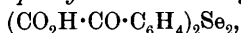


green prisms with metallic lustre, m. p. 166—167°, which give a deep red powder or solution, is slowly formed when a bimolecular proportion of 2*N*-aqueous sodium hydroxide is added to an ice-cold alcoholic equimolecular mixture of 3-hydroxyselenonaphthen and *p*-nitrosodimethylaniline; it is very sensitive towards mineral acids, but a very deliquescent, crystalline, brown *hydrochloride* was prepared. In a similar manner *selenonaphthenquinone-2-anil*, orange-coloured needles or leaflets, m. p. 145—146°, is obtainable from hydroxyselenonaphthen and nitrosobenzene, but a red substance, prisms, m. p. 145—146°, of distinct nature, is concurrently formed in smaller quantity. Both these anils when boiled with the calculated amount of phenylhydrazine in acetic acid solution give the same 2-*benzeneazo-3-hydroxyselenonaphthen*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{Se} \end{array} \text{C}\cdot\text{N}_2\text{Ph}$ , orange-red needles, m. p. 207—208°,

as is obtained by the interaction of 3-hydroxyselenonaphthen and benzenediazonium chloride; this substance dissolves unchanged in concentrated sulphuric acid, but fuming sulphuric acid converts it into a yellow *sulphonic acid*, the salts of which are red. The above anils are also affected analogously by boiling with hydroxylamine hydrochloride in acetic acid solution containing an excess of potassium acetate, the product being the 2-nitroso-3-oxy-selenonaphthen described above.

Selenonaphthenquinone-2-anil proved unsuited to the preparation of selenonaphthenquinone, as it is hydrolysed by mineral acids only when heated, under which conditions the quinone is resinified. With care it is possible to hydrolyse selenonaphthendimethylaminoanil in ice-cold ethereal solution by aqueous hydrochloric acid, so that a good yield of

*selenonaphthenquinone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{Se} \end{smallmatrix} \text{CO}$ , is obtained; this substance forms red or sometimes orange-yellow needles, m. p. 102—103°, which dissolve in organic solvents to a reddish-yellow solution, and in sulphuric acid to a red, gradually passing into a green; it gives with coal-tar benzene a more violet indophenin coloration than does isatin. The quinone is decomposed when dissolved in dilute acetic acid, and the action of dilute aqueous solutions of alkali hydroxides is so marked that, in order to prepare the corresponding quinonic acid, it is necessary to take the ethereal solution of the quinone with very dilute, ice-cold sodium carbonate solution; acidification then liberates *selenonaphthenquinonic acid* (*diphenyldiselenide-di-o-glyoxylic acid*),



orange-yellow, microscopic prisms, which have no definite m. p., and decompose at 200—285°, according to the rate of heating. Esters of this acid are formed when a solution of the selenonaphthenquinone in a primary alcohol is warmed, and the products are identical with those obtained by direct esterification of the acid; the following esters were examined: *methyl* ester, yellow leaflets, m. p. 157—158°; *ethyl* ester, yellow needles, m. p. 125—126°; *propyl* ester, crystals, m. p. 111—112°. The action of phenylhydrazine on selenonaphthenquinone, and also on the above esters, gave rise to complex mixtures, a small quantity of a *substance*, prisms, m. p. 72—73°, being separated from the product yielded by the methyl ester.

Towards *o*-diamines, selenonaphthenquinone is more reactive than thionaphthenquinone (Bezdzik, Friedländer and Koeniger, A., 1908, i, 200), and on mixing with an equimolecular proportion of *o*-phenylenediamine in cold ethereal solution, orange-yellow, microscopic needles, m. p. 320—325°, separate, of *di-2-hydroxy-3-o-quinoxalyldiphenyl diselenide*,  $\left[ \begin{smallmatrix} \text{C}_6\text{H}_4-\text{N} \\ | \\ \text{N}:\text{C}(\text{OH}) \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \right]_2\text{Se}_2$ , that is a structural derivative of the quinonic acid and not of the quinone. In an analogous manner 1:2-naphthylenediamine reacts with the quinone, giving an excellent yield of the corresponding *di-2-hydroxy-3-o-naphthoquinoxalyldiphenyl diselenide*,  $\left[ \begin{smallmatrix} \text{C}_{10}\text{H}_6-\text{N} \\ | \\ \text{N}:\text{C}(\text{OH}) \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \right]_2\text{Se}_2$ , an orange-coloured, crystalline powder, m. p. 352—355°. The esters of the quinonic acid also underwent condensation with these *o*-diamines in acetic acid solution containing hydrochloric acid, and the products were the *hydrochlorides* of the preceding, that of *di-2-hydroxy-3-o-quinoxalyldiphenyl diselenide* having m. p. 350—360° (decomp.).

In boiling ethereal solution, selenonaphthenquinone enters into combination with aniline and with *p*-aminodimethylaniline, giving crystalline *substances*, yellow prisms, m. p. 218—219°, and garnet-red prisms, m. p. 226° (decomp.) respectively, the constitution of which, as well as of a *substance*, red, microscopic prisms, m. p. 205—206° (decomp.), obtained in an analogous manner from thionaphthenquinone and *p*-aminodimethylaniline remains for the present uncertain.

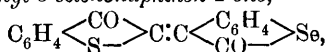
Indigoid dyes were obtained by condensation of selenonaphthenquinone with indoxyl and its isologues, the products being remarkable



for their fusibility; the condensation was effected by the general method of heating the components in equimolecular proportion in acetic acid solution containing a few drops of hydrochloric acid. Indoxyl and the quinone gave "2-indole-3-selenonaphthenindigo"

[2-indoxyl-3-selenonaphthen-2-one],  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} > C:C < \begin{smallmatrix} \text{C}_6H_4 \\ \diagdown \quad \diagup \\ \text{CO} \end{smallmatrix} > Se$ , small, bluish-black prisms, m. p. 241—242°, the chloroform solution of which has a reddish-violet colour with a deep blue fluorescence; fuming sulphuric acid dissolves the substance with violet coloration, producing a red sulphonic acid soluble in water.

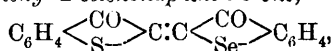
The selenonaphthenquinone and 3-hydroxythionaphthen yielded 3-oxy- $\Delta^2$ -thionaphthenyl-3-selenonaphthen-2-one,



deep reddish-brown needles, m. p. 196—197°, which gives a non-fluorescent deep reddish-violet solution in chloroform and dissolves in fuming sulphuric acid with decomposition.

3-Hydroxyselenonaphthen and the quinone condense together with formation of 2:3'-bisoxyselenonaphthen,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ Se \end{smallmatrix} > C:C < \begin{smallmatrix} \text{C}_6H_4 \\ \diagdown \quad \diagup \\ \text{CO} \end{smallmatrix} > Se$  reddish-brown needles, m. p. 186—187°, the chloroform solution of which is violet-red with a blue fluorescence.

3-Oxy- $\Delta^2$ -thionaphthenyl-2-selenonaphthen-3-one,



was obtained by heating an equimolecular mixture of 3-hydroxyselenonaphthen and 2-bromo-3-ketodihydrothionaphthenquinone (Bzdzyk Friedländer and Koeniger, *loc. cit.*); it forms deep red needles, m. p. near 350°, and in chloroform gives a violet-red colour with blue fluorescence; fuming sulphuric acid dissolves it to a blue solution which contains a carmine-red sulphonic acid soluble in water.

All these dyes can be sublimed without decomposition, and are easily reduced to vats by sodium hyposulphite in alkaline solution, the yellow solutions restoring the dye on exposure to air or more rapidly on treatment with potassium ferrieyanide. D. F. T.

**Alkaloids of Papaver Orientale.** WALTER KLEE (*Arch. Pharm.*, 1914, 252, 211—273).—In 1813 Petit stated that *Papaver orientale* contains narcotine, morphine, and meconic acid. The author has been unable to detect any one of the three. Numerous experiments on the plant at different periods of its existence show that at times of vigorous growth thebaine is almost the only alkaloid present in the root. On the contrary, after the period of blooming and the withering of the aerial parts, a phenolic base and only a little thebaine are present.

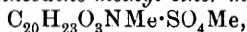
A hot alcoholic extract of the dried, coarsely-powdered roots is diluted with water, the alcohol is evaporated, the fats, resins, and chlorophyll are removed, and the mixture of crude alkaloids (about 0.5% yield) ultimately obtained is readily separated by *N*-sodium hydroxide into a non-phenolic constituent, which is easily identified as thebaine, and a phenolic base. The latter has the formula  $C_{19}H_{21}O_3N$ , and is therefore called *isothebaine*.

*iso*Thebaine has m. p. 203—204°,  $[\alpha]_D^{25} + 285.1^\circ$ , and crystallises in highly refractive, colourless, rhombic crystals  $[a:b:c=0.95145:1:1.61846]$ , which are somewhat sensitive to light. The *hydrochloride*, easily soluble crystals, *sulphate*, m. p. 120—121° (decomp.), small needles, *nitrate*, and *hydrogen l-tartrate*, clusters of short needles, are described. The colour reactions of the alkaloid are: concentrated sulphuric acid, colourless; Erdmann's reagent, pale yellow; Fröhde's reagent, blue, then green, later, dark olive-green, finally, pale green; Mandelin's reagent, pale olive, then olive brown. Quite unique among the *Papaveraceae* alkaloids is the behaviour of *isothebaine* with concentrated nitric acid which produces an intense violet coloration, whereby even a trace of the alkaloid can be detected in the presence of a large quantity of thebaine.

*iso*Thebaine contains, in addition to the phenolic hydroxyl group, two methoxy-groups and a methylimino-group. In deciding his line of attack on the problem of the constitution of the alkaloid, the author has been guided by the inference that *isothebaine*, according to its method of occurrence in the plant, is produced from thebaine. It responds to Pellagri's reaction just as do bulbocapnine and *isocorydine*, and also resembles these two alkaloids in forming an optically inactive *diacetyl* derivative,  $C_{19}H_{19}O_3N\cdot Ac_2$ , m. p. 80—85°, colourless leaflets, by heating with acetic anhydride and anhydrous sodium acetate. There can be little doubt, therefore, that *isothebaine* contains the ring system of morphothebaine and *apomorphine*.

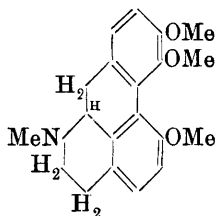
If *isothebaine* is formed from thebaine by rupture of the bridge O-ring and formation of an *isoquinoline* ring, then *isothebaine methyl ether* (assuming the three methoxy-groups are in positions 3:4:6) and morphothebaine dimethyl ether (which is laevorotatory) will be optical antipodes. Morphothebaine and *isothebaine* are practically unattacked by ethereal diazomethane; however, methylation occurs satisfactorily with nascent diazomethane in *isoamyl ether* (Gadamer's method). Neither of the ethers has been obtained in a crystalline state. *Morphothebaine dimethyl ether*, a faintly yellow, resinous substance, has  $[\alpha]_D - 184.8^\circ$  in chloroform, and forms a *hydrogen d-tartrate*, m. p. 205° (decomp.),  $[\alpha]_D 74.3^\circ$  in water, colourless needles. *iso-Thebaine methyl ether* has  $[\alpha]_D + 234.5^\circ$  in chloroform, and forms a *hydrogen l-tartrate*, m. p. 226—227° (decomp.),  $[\alpha]_D + 143^\circ$  in water, colourless needles. The two ethers, although showing many similarities in their colour reactions, are obviously not optical antipodes.

It is equally possible that *isothebaine* may be derived from thebaine by rupture of the bridge O-ring, the substituents (2OMe and OH) being in positions 3:5:6. If this is so, the exhaustive methylation of *isothebaine* should yield the trimethoxyphenanthrene obtained from morphothebaine by Pschorr and Rettberg. An aqueous solution or suspension of the sodium derivative of *isothebaine* is converted by methyl sulphate into *isothebaine methyl ether methosulphate*,



m. p. 237—238°,  $[\alpha]_D + 158.1^\circ$  in water, glistening needles, which is decomposed by boiling aqueous sodium hydroxide, yielding two *methine* bases. One of these has m. p. 104—105°,  $[\alpha]_D - 283.9^\circ$  in ether,

crystallises in stout, colourless needles, and is unsaturated; the other is amorphous and optically inactive. An ethereal solution of the methine bases reacts with methyl sulphate to form *isothebaimethine methyl ether dimethosulphate*,  $C_{19}H_{19}O_3NMe_3 \cdot SO_4Me$ , m. p. 195—196°, colourless needles, which is optically inactive (and is therefore formed from the amorphous methine base) and is converted by warm methyl alcoholic sodium hydroxide into trimethylamine and a *trimethoxyvinyl-phenanthrene*. The latter in acetone at 0° is oxidised by aqueous potassium permanganate to a *trimethoxyphenanthrenecarboxylic acid*, m. p. 170—171°, faintly yellow needles or leaflets, which loses carbon dioxide by heating with glacial acetic acid at 220° under pressure and yields a *trimethoxyphenanthrene*. The *picrate*, m. p. 160°, dark red needles, of the latter is not identical with the picrate, m. p. 109—110°, of 3:5:6 (i.e. 3:4:6)-trimethoxyphenanthrene, but may be the slightly impure picrate, (m. p. 166°) of 3:4:5-trimethoxyphenanthrene.



Assuming this to be correct, the exhaustive methylation of *isothebaine* proves that the group  $\cdot CH_2 \cdot CH_2 \cdot NMe \cdot$  is attached to the phenanthrene nucleus in positions 8:9 and that the (partly methylated) phenolic groups are in positions 3:4:5. *isoThebaine methyl ether*, therefore, has the annexed formula. *isoThebaine* itself may have its phenolic hydroxyl group in position 4 or 5, the former being the more probable.

The oxidation of *isothebaine* or of its methyl ether by alcoholic iodine does not yield products which throw any light on the constitution. C. S.

**Minor Alkaloids in Papaver Orientale.** J. GADAMER (*Arch. Pharm.*, 1914, **252**, 274—280).—In addition to the two chief alkaloids, thebaine and *isothebaine*, isolated from *Papaver orientale* by Klee (preceding abstract), the author has obtained evidence of the presence of several others in extremely minute quantities. At least three of these are phenolic and two are non-phenolic in character. One of the latter is proved to be protopine by its m. p. 204—205°, crystalline form, and colour reactions; the other was accidentally lost before it had been examined.

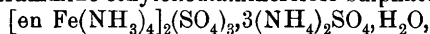
One of the phenolic alkaloids is a *substance*, m. p. about 238—239°, darkening at 209—210°, called *glaucidine*. Its colour reactions are very similar to those of glaucine, and the magnitude of its specific rotation,  $[\alpha]_D$  about 50° in chloroform, indicates that it belongs to the glaucine, not the corytuberine, group of alkaloids. By methylation with nascent diazomethane in *isoamyl ether*, it yields a substance which forms a *hydrogen l-tartrate* exhibiting in its crystalline form and colour reactions a very great similarity to glaucine hydrogen *l-tartrate*; it is impossible to say whether or not the two substances are identical, because the amount of the methylated product is too small for analysis and the colour reactions of glaucine and glaucidine are very similar. C. S.

**Complex Salts of Iron. III.** G. SPACU (*Ann. Sci. Univ. Jassy*, 1914, **8**, 162—204. Compare this vol., i, 573).—*Diaquotetrammine-*

*ferric sulphate*,  $[(\text{H}_2\text{O})_2\text{Fe}(\text{NH}_3)_4]_2(\text{SO}_4)_3$ , reddish-brown powder, is obtained by the action of a rapid current of dry ammonia on finely powdered, hydrated ferric sulphate for several hours at the ordinary temperature. It readily loses ammonia by exposure to the air, is rapidly decomposed by water with the formation of ferric hydroxide, and is insoluble in most solvents except acetic and dilute sulphuric acid; the sulphate radicle is completely ionisable.

By treating the complex salts of iron containing pyridine, ethylenediamine, etc., which have been previously described (*loc. cit.*), with dry ammonia, the author has observed a partial, or in the case of pyridine generally a total, replacement of the basic molecules by ammonia. Thus hydrated tetrapyridineferric sulphate yields a *tetra-aquopyridine-heptammineferric sulphate*, amorphous, brown powder, to which is given the formula  $[(\text{H}_2\text{O})_2\text{Fe Py}(\text{NH}_3)_3][(\text{H}_2\text{O})_2\text{Fe}(\text{NH}_3)_4](\text{SO}_4)_3$ ; this substance, like the other complex salts of iron containing ammonia, is unstable in the air, and is readily decomposed by water. Hydrated aquotripyridineferrous sulphate is converted by ammonia into hydrated *tetrammineferrous sulphate*,  $[\text{Fe}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , brown, amorphous powder.

Ethylenediamine sulphate and hydrated ferric sulphate react in boiling dilute sulphuric acid to form a white, amorphous substance,  $[\text{Fe}_2(\text{en H}_2\text{SO}_4)_2](\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , which reacts quantitatively with barium chloride to produce barium sulphate, and combines additively with dry ammonia (14 mols.) to form a double salt of ammonium sulphate and tetrammine-ethylenediamineferric sulphate,



amorphous, brown powder.

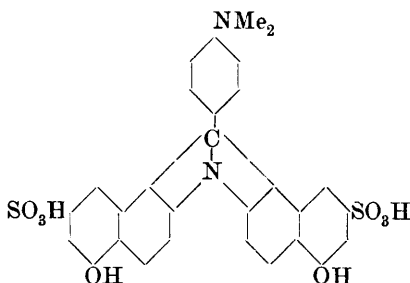
The author gives a list of the 212 complex salts of iron known at the present time and remarks that very rarely does aniline enter into the composition. He describes two such compounds. *Dianilineferrous sulphate*,  $[\text{Fe}(\text{NH}_2\text{Ph})_2]\text{SO}_4$ , prepared by boiling ferrous sulphate with aniline, is a white, amorphous substance which can be kept in the dark and is hydrolysed by water, yielding ferrous hydroxide and, by oxidation, ultimately ferric hydroxide. *Triaquopentananilineferric sulphate*,  $[(\text{H}_2\text{O})_3\text{Fe}_2(\text{NH}_2\text{Ph})_5](\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , prepared by heating aniline and hydrated ferric sulphate on the water-bath, is an amorphous, reddish-brown powder, which can be kept in a desiccator, but is hydrolysed by water.

A mixture of hydrated ferric chloride and an excess of potassium thiocyanate is thoroughly ground in a mortar, at first alone, subsequently with a large excess of pyridine. The product, after being purified and rapidly crystallised from boiling pyridine, is a substance,  $[\text{Fe Py}_4](\text{SCN})_2$ , brilliant, black needles, which is isomeric with the crystalline, yellow thiocyanate obtained by Grossmann and Hunseler in 1905. The two modifications are relatively stable and can be preserved in an atmosphere of pyridine. The black form is labile, but each can be transformed into the other under suitable conditions; thus the black form changes to the yellow by solution in pyridine, whilst the yellow modification is transformed into the black by chloroform. By heating, the two isomerides lose pyridine at different rates; in both cases, the last molecule of pyridine is removed only

with difficulty above 250°. The two substances behave alike towards ammonia, yielding very hygroscopic products which are probably hexammineferrous thiocyanate,  $[\text{Fe}(\text{NH}_3)_6](\text{SCN})_2$ , and towards chlorine water, whereby they are oxidised to ferric salts. The author discusses the nature of the isomerism of the yellow and the black thiocyanates and inclines to the opinion that they are *cis* and *trans* stereoisomerides of the type  $[\text{MA}_2\text{B}_4]$ . C. S.

**Preparation of a Derivative of 2-Phenyl-6-methylquinoline-4-carboxylic Acid of Therapeutic Application.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (Swiss Patent, 64348).—*Methyl 2-phenyl-6-methylquinoline-4-carboxylate*, prepared from the acid by the ordinary methods of esterification, forms white needles, m. p. 91°, yields salts with acids, and has the advantage of tastelessness over the acid itself. T. H. P.

**Preparation of Acridine Derivatives from Aminohydroxynaphthalenesulphonic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 272612).—These derivatives are prepared by the action in the warm of tertiary aromatic amines and formaldehyde, in presence of dilute mineral acid, on 1-aminohydroxynaphthalenesulphonic acids with the 2-position unoccupied or on 2-amino-



hydroxynaphthalenesulphonic acids with the 1-position unoccupied. They are of value for the preparation of colouring matters of various groups.

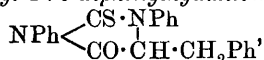
The compound (annexed formula), prepared from 2-amino-5-hydroxynaphthalene-7-sulphonic acid, dimethylaniline and formaldehyde, forms an orange-red, crystalline powder. The analogous compound, obtained from 2-amino-6-hydroxynaphthalene-8-sulphonic acid, diethylaniline and formaldehyde is orange-yellow and the compound from 1-amino-5-hydroxynaphthalene-7-sulphonic acid, dimethylaniline and formaldehyde, olive-green. The colorations given by these compounds with various reagents are described. T. H. P.

**Hydantoins. XXVIII. Synthesis of 1:3:4-Trisubstituted Hydantoins from Ethyl Anilinomalonnate.** TREAT B. JOHNSON and NORMAN A. SHEPARD (*J. Amer. Chem. Soc.*, 1914, **36**, 1735—1742).—During the course of a study of the condensation of hydantoins with aldehydes, it was found that certain hydantoins do not undergo such condensation (Wheeler and Hoffman, A., 1911, i, 500). On investigating some of these cases, results were obtained which rendered it desirable to develop a method for preparing 1:3:4-trisubstituted hydantoins which would not involve the condensation of an aldehyde with a hydantoin. An account of such a method is now given.

*Diethyl benzylanilinomalonnate*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NHPh})(\text{CO}_2\text{Et})_2$ , b. p. 257—260°/50 mm., was obtained as a heavy, yellow oil by the action of

benzyl chloride on the sodium derivative of ethyl anilinomalonate. *Benzylanilinomalonic acid*, m. p. 170—173°, forms clusters of radiating needles; its *potassium* and *silver* salts are described. When the acid is heated above its m. p., it loses carbon dioxide and is converted into *α-anilino-β-phenylpropionic acid*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NHPh})\cdot\text{CO}_2\text{H}$ , m. p. 170—173°, which crystallises in lustrous plates. This acid, however, is most conveniently prepared by boiling an alcoholic solution of the benzylanilinomalonic acid; its *ethyl* ester, b. p. 206—209°/12 mm. or 218—221°/19 mm., m. p. 48—49°, forms stout, hexagonal prisms.

When *α-anilino-β-phenylpropionic acid* is heated with phenylthiocarbimide, *2-thio-4-benzyl-1:3-diphenylhydantoin*,



m. p. 129—130°, is produced which forms needle-like prisms, together with a small quantity of *α-benzylindoxyl*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \text{CH}\cdot\text{CH}_2\text{Ph}$ , m. p. 271—272°, which crystallises in cubical prisms.

*4-Benzyl-1:3-diphenylhydantoin*,  $\text{NPh} \begin{array}{c} \text{CO}\cdot\text{NPh} \\ \text{CO}\cdot\text{CH}\cdot\text{CH}_2\text{Ph} \end{array}$ , m. p. 58—62°, is produced, together with a small amount of *α-benzylindoxyl*, by the action of phenylcarbimide on *α-anilino-β-phenylpropionic acid*; it can also be obtained by desulphurising *2-thio-4-benzyl-1:3-diphenylhydantoin*.

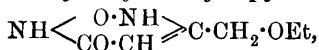
*2-Thio-5-benzyl-7-phenyluramil*,  $\text{CS} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} \text{C}(\text{NHPh})\cdot\text{CH}_2\text{Ph}$ , m. p. 219—220°, obtained by treating an alcoholic solution of thiocarbamide with sodium ethoxide and ethyl benzylanilinomalonate crystallises in stout, prismatic blocks. E. G.

**Pyrimidines. LXXI. Synthesis of the Pyrimidine Nucleoside, 4-Hydroxymethyluracil.** TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1914, **36**, 1742—1747).—In continuation of work on the nucleosides, 4-hydroxymethyltetrahydropyrimidin-2:6-dione (4-hydroxymethyluracil) has been prepared by a method analogous to that used for the preparation of its 5-methyl derivative (A., 1913, i, 656).

When ethyl *γ*-ethoxyacetoacetate (Johnson, A., 1913, i, 588) is condensed with thiocarbamide in presence of sodium ethoxide, *2-thio-4-ethoxymethyltetrahydro-6-pyrimidone*,



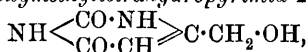
m. p. 180—181°, is obtained which crystallises in large, radiating prisms. On boiling this substance with chloroacetic acid in aqueous solution, it is converted into *4-ethoxymethyltetrahydropyrimidin-2:6-dione*,



m. p. 175°, which forms rhombic prisms; the latter compound is not changed by the action of 10% sulphuric acid at 140°, but when heated with concentrated hydrochloric acid at 100° it is converted into

4-chloromethyltetrahydropyrimid-2:6-dione,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{CH} \end{smallmatrix} \gg \text{C} \cdot \text{CH}_2\text{Cl}$ ,

which crystallises in small, radiating prisms and decomposes at about 214—215°. 4-Hydroxymethyltetrahydropyrimid-2:6-dione,



prepared by treating an aqueous solution of the chloropyrimidine successively with silver sulphate, hydrogen sulphide, barium hydroxide, and carbon dioxide, crystallises in small plates; it begins to melt at about 240°, decomposes at about 254°, and is readily reduced by hydriodic acid in presence of a little red phosphorus with formation of 4-methyluracil.

E. G.

#### Preparation of Acid Triphenylmethane Colouring Matters.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 269214).—Sulphonic acids of alkyl or arylalkyl derivatives of *m*-toluidines or mixtures of them are condensed with aromatic aldehydes containing no alkylamino-group in the para-position to the carbonyl group and the leuco-compounds thus obtained oxidised, or the amines are first condensed with the aldehydes and then sulphonated and oxidised. The acid triphenylmethane colouring matters formed in this way are mostly yellowish-green, and are faster than those prepared in a similar manner from aniline.

T. H. P.

Colour and Ionisation of Crystal violet. ELLIOT Q. ADAMS and LUDWIG ROSENSTEIN (*J. Amer. Chem. Soc.*, 1914, **36**, 1452—1473).—The rate of the development of colour when alkaline solutions of triphenylmethane dyes are acidified has been studied by Biddle (this vol., ii, 115), who calls attention to the complexity of the equilibrium in the case of crystal-violet as a result of the possibility of the formation of mono-, di-, and tri-acid salts. The colour changes produced by the gradual addition of mineral acid to an aqueous solution of a triphenylmethane dye (methyl-violet, crystal-violet, rosaniline, pararosaniline, malachite-green, and aniline-blue) are well-known. The authors observe that these changes in hue are accompanied by another change when the solutions are kept; the intensity of the colour diminishes greatly in strongly acidic or in alkaline solution (only in this case is the substance colloidal), and slowly in weakly acidic solution. Equivalent solutions of all strong acids produce identical effects, and on neutralisation the original colour is in every case restored, in hue at once, and in intensity by keeping. Evidently these changes are produced by reactions, which are completely reversible, of the chromogens with hydrogen or hydroxyl ions (or with water).

The phenomena, which have been fully examined in the case of crystal-violet as admitting of the greatest variety of salt-formation, necessitate two series of measurements, one dealing with the relative proportions of the differently coloured substances in the solution, the other with the variation of the proportions of the colourless substances with the colour of the solution.

The equilibrium between the differently coloured forms of crystal-violet has been examined by means of the spectrophotometer. The

absorption spectra of acidified solutions of the dye indicate that three substances, respectively, violet, green, and yellow, produce the colours of all the solutions. This assumption is substantiated by the fact that the absorption of solutions determined experimentally agrees with the absorption calculated by means of the molecular extinction coefficients; the completeness of the agreement establishes that three absorbing substances are necessary and sufficient to produce the observed absorption of all the solutions. By reasoning based on the fact that the colour of strong electrolytes is almost completely independent of the degree of ionisation, the inference is drawn that the violet, green, and yellow substances (in hydrochloric acid) are  $C_{25}H_{30}N_3Cl$ ,  $C_{25}H_{30}N_3Cl \cdot HCl$ , and  $C_{25}H_{30}N_3Cl \cdot 2HCl$  (or the positive ions produced therefrom) respectively.

The slow changes in colour intensity mentioned above occur at a rate and to an extent which increase with increasing acid concentration. With acid concentrations less than  $N/10,000$  no measurable fading occurs, while in  $N$ -acid the colour almost disappears in the course of an hour. The reactions involved are unimolecular in both directions and are greatly influenced by temperature. The reactions which produce colourless from coloured modifications of the chromogen all occur in solutions extremely dilute with respect to chromogen. On the assumption that the only concentrations which can be changed appreciably are those of the coloured and colourless substances, an equation of a unimolecular reaction is developed and combined with a second equation involving the molecular extinction coefficient, whereby an expression is obtained from which are calculated data supporting the authors' contention that in strongly acidic solutions the principal colourless substance present is the carbinol ion produced by the dissociation of the carbinol trihydrochloride,  $OH \cdot C(C_6H_4 \cdot NMe_2, HCl)_3$ ; in slightly acidic solutions the concentration of the carbinol ion derived from  $OH \cdot C(C_6H_4 \cdot NMe_2)(C_6H_4 \cdot NMe_2, HCl)_2$  constitutes the largest part of the total carbinol concentration. C. S.

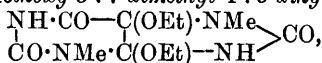
**Derivatives of 3:7-Dimethyluric Acid.** HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1914, 406, 22—59).—3:7-Dimethyluric acid can now be easily obtained from theobromine in more than 50% yield by chlorinating a very finely powdered suspension in chloroform and heating the resulting 8-chlorotheobromine (70—80% yield) with  $N$ -potassium hydroxide (1 mol.) on the water-bath.

5-Chloro-3:7-dimethyl- $\Delta^{4:9}$ -isouric acid,  $\begin{matrix} NH \cdot CO - CCl \cdot NMe \\ CO \cdot NMe \cdot C \equiv N \end{matrix} > CO$ , m. p.

about 168—169° (decomp.), is obtained by vigorously chlorinating 3:7-dimethyluric acid suspended in chloroform, the excess of chlorine being removed by a current of dry air. The substance can be prepared more conveniently, although not in so pure a state, by directing chlorinating theobromine in glacial acetic acid. It deliquesces in moist air, crystallises with difficulty, and is reduced to 3:7-dimethyluric acid by stannous chloride and hydrochloric acid. It liberates iodine from concentrated aqueous potassium iodide, but after solution in water is not affected by this salt, since it reacts with water to form 3:7-dimethyluric acid-4:5-glycol.



5-Chloro-3:7-dimethylisouric acid (prepared by the second method and therefore containing  $C_2H_4O_2$ ) reacts with anhydrous ethyl alcohol at  $0^\circ$  to form 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouric acid,



m. p.  $220-221^\circ$  (decomp.), white, crystalline powder; the corresponding dimethoxy-compound sinters at about  $195^\circ$  and has m. p.  $216-217^\circ$  (decomp.). The ethers are reduced to 3:7-dimethyluric acid by sodium amalgam or hydriodic acid, D 1.96.

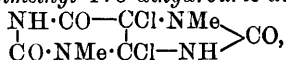
5-Chloro-3:7-dimethylisouric acid is converted by a mixture of alcohol and pyridine at  $0^\circ$  into 5-ethoxy-3:7-dimethylisouric acid, m. p.  $191^\circ$  (decomp.), rectangular plates; the corresponding methoxy-derivative has m. p.  $205-206^\circ$ . The ethoxy-derivative reacts with alcoholic hydrogen chloride or with concentrated hydrochloric acid to form respectively 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouric acid or the semi-ether mentioned below.

4-Hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouric acid, m. p.  $228-229^\circ$ , sintering at  $215^\circ$ , has been prepared in several ways: (i) by the action of concentrated hydrochloric or sulphuric acid on 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouric acid; (ii) by the chlorination of 3:7-dimethyluric acid in anhydrous alcohol; (iii) by the chlorination of theobromine in a cooled mixture of alcohol and chloroform; (iv) by heating to boiling an alcoholic solution of 5-chloro-3:7-dimethylisouric acid containing a few drops of concentrated hydrochloric acid (best method). The substance is extraordinarily stable, being unattacked by concentrated sulphuric acid at room temperature, boiling glacial acetic acid and hydrogen chloride, potassium chlorate and hydrochloric acid, water at  $170^\circ$ , or boiling 2*N*-sodium hydroxide. It yields 1-methylhydantoin by reduction with hydriodic acid (D 1.96), methylparabanic acid by oxidation with nitric acid (D 1.5), on the water-bath, and 3:7-dimethyluric acid-4:5-glycol by heating with concentrated sulphuric acid at  $80-90^\circ$  and subsequent treatment with water. The preceding behaviour and the methods of preparation afford satisfactory proof of the constitution of 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouric acid. Attempts to convert it into the diethoxy-derivative have been unsuccessful; however, it yields an acetyl compound,  $C_{11}H_{16}O_6N_4$ , m. p.  $165^\circ$ , hexagonal plates.

4-Hydroxy-5-methoxy-3:7-dimethyl-4:5-dihydrouric acid, m. p.  $247-248^\circ$ , stout rhombohedra, is prepared by the same methods as the ethoxy-compound and resembles it in behaviour and properties.

4-Hydroxy-5-propoxy-3:7-dimethyl-4:5-dihydrouric acid, m. p.  $203-204^\circ$  (slight decomp.), leaflets, is obtained by boiling 5-chloro-3:7-dimethylisouric acid with propyl alcohol.

4:5-Dichloro-3:7-dimethyl-4:5-dihydrouric acid,



flattened needles or elongated leaflets containing  $C_2H_4O_2$ , sintering at about  $150^\circ$ , and carbonising above  $300^\circ$ , is obtained by vigorously chlorinating 3:7-dimethyluric acid in glacial acetic acid at  $0^\circ$ , and closely resembles 5-chloro-3:7-dimethylisouric acid in its properties

and behaviour. When 3:7-dimethyluric acid is chlorinated at 0° in glacial acetic acid containing water (1 mol.), the product is 5-chloro-4-hydroxy-3:7-dimethyl-4:5-dihydrouric acid, stout prisms containing  $C_2H_4O_2$ , sintering below 100°, and m. p. 180°, which does not exhibit the murexide reaction, and therefore is not a derivative of  $\psi$ -uric acid. The substance is converted into 3:7-dimethyluric acid-4:5-glycol by water, into 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouric acid by alcohol and into 4-hydroxy-3:7-dimethyl-4:5-dihydrouric acid, m. p. 220° (decomp.), stout rhombohedra, by a saturated solution of hydrogen iodide in glacial acetic acid. The last substance is stable to alkalis and to concentrated sulphuric acid at room temperature, and cannot be converted into 3:7-dimethyluric acid by dehydrating agents. Its constitution is deduced from the following reactions. It forms an ammonium salt, m. p. 174—175° (decomp.), slender needles, yields 5-chloro-4-hydroxy-3:7-dimethyl-4:5-dihydrouric acid, 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouric acid, and 3:7-dimethyluric acid-4:5-glycol by chlorination in glacial acetic acid, alcohol, and water respectively, and is converted into 1-methylhydantoin by fission with boiling hydrochloric acid. The last transformation is important, since it proves that the hydroxyl group is in position 4, not 5. C. S.

**Derivatives of 4:5-Dialkyloxy-3:7-dimethyl-4:5-dihydrouric Acid.** HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1914, 406 59—100).—Only about 50% of the theoretical yield of 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouric acid is obtained by chlorinating theobromine in alcoholic solution (preceding abstract). By the addition of ether to the concentrated mother-liquor, a substance,  $C_{10}H_{15}O_6N_3$ , is ultimately obtained, the origin of which is explained below.

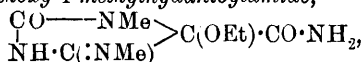
By heating 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouric acid with alcoholic hydrogen chloride on the water-bath until solution is complete, and subsequently adding ether, the hydrochloride,  $C_{11}H_{18}O_5N_4 \cdot HCl$ , m. p. 191—192° (decomp.), leaflets, of a substance is obtained, which proves to be ethyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate,  $\begin{array}{c} CO-NMe \\ | \\ NH \cdot C(:NMe) \end{array} > C(OEt) \cdot CO \cdot NH \cdot CO_2Et$ , m. p. 204—205°, quadratic prisms. The hydrochloride, which can also be prepared by the chlorination of theobromine or 3:7-dimethyluric acid under suitable conditions, loses hydrogen chloride by treatment with water or cold aqueous sodium hydroxide, and yields 3:7-dimethyluric acid by reduction with sodium amalgam. The latter transformation, by suggesting that the hydrochloride is a near relative of 3:7-dimethyluric acid, misled the authors as to the constitution of the carbamate until the discovery was made that hydrochlorides of mixed dialkyloxy-derivatives can be prepared. Thus the hydrochloride, m. p. 190—191° (decomp.), of methyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate, m. p. 210—211°, elongated prisms, is obtained from 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouric acid and methyl-alcoholic hydrogen chloride. In a similar manner have been obtained the hydrochloride, m. p. 204—205° (decomp.), of methyl 4-methylimino-5-methoxy-1-methyl-

*hydantoylcarbamate*, m. p. 188—189°, needles or prisms (*acetyl* derivative, m. p. 184—185°, stout rhombohedra), and the *hydrochloride*, m. p. 179—180° (decomp.), of *ethyl 4-methylimino-5-methoxy-1-methylhydantoylcarbamate*, m. p. 198—199°, long needles.

By boiling with water or dilute hydrochloric acid, the preceding carbamates (in the form of their hydrochlorides) exchange the methylimino-group in position 4 for oxygen. Thus *ethyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate hydrochloride* gives a quantitative yield of methylamine hydrochloride, the other product (the substance,  $C_{10}H_{15}O_6N_3$ , mentioned above) being *ethyl 5-ethoxy-1-methylhydantoylcarbamate*,  $\begin{array}{c} \text{CO} \cdot \text{NMe} \\ | \\ \text{NH} - \text{CO} \end{array} > \text{C}(\text{OEt}) \cdot \text{CO} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , m. p. 170°, stout plates,

which yields methylparabanic acid by oxidation and 1-methylhydantoin by reduction with hydriodic acid, D 1.96, at about 80°. *Methyl 5-methoxy-1-methylhydantoylcarbamate*, m. p. 110—120° (hydrated) or about 177—178° (anhydrous), prisms containing  $H_2O$  or rhombic leaflets (*acetyl* derivative, m. p. 165—166°, stout rhombohedra), *methyl 5-ethoxy-1-methylhydantoylcarbamate*, m. p. 186—187°, stout, double pyramids, and *ethyl 5-methoxy-1-methylhydantoylcarbamate*, m. p. 170—171°, stout crystals, are obtained in a similar manner.

Ethyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate and the other three substances of the same type are attacked by alcoholic ammonia at the carbethoxy-group, ethyl alcohol and carbon dioxide being eliminated and a hydantoylamide being produced. Thus ethyl and methyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamates yield 4-methylimino-5-ethoxy-1-methylhydantoylamide,



m. p. 240—241° (decomp.), leaflets or plates, while methyl and ethyl 4-methylimino-5-methoxy-1-methylhydantoylcarbamates, in the form of their hydrochlorides, yield 4-methylimino-5-methoxy-1-methylhydantoylamide, m. p. 254—255° (decomp.), clusters of elongated prisms. These two hydantoylamides retain their methylimino-group even when they are boiled with concentrated aqueous ammonia or kept with dilute hydrochloric acid for many days; by heating with concentrated hydrochloric acid, however, they undergo extensive decomposition. Solutions of the amides in dilute sodium hydroxide, prepared at room temperature, exhibit an intense biuret reaction. 4-Methylimino-5-methoxy-1-methylhydantoylamide does not form a silver salt or react with methyl sulphate and sodium hydroxide, but is readily acetylated by boiling acetic anhydride, forming the *acetyl* derivative, sintering at 173°, decomp. 184°, long rhombohedra, which can be crystallised from boiling water.

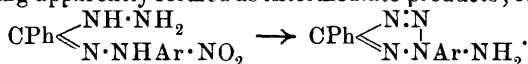
Ethyl and methyl 5-ethoxy-1-methylhydantoylcarbamates are converted by evaporation with concentrated aqueous ammonia into 5-ethoxy-1-methylhydantoylamide,  $\begin{array}{c} \text{CO} \cdot \text{NMe} \\ | \\ \text{NH} - \text{CO} \end{array} > \text{C}(\text{OEt}) \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 206—207°, elongated rhombohedra or rhombic leaflets; 5-methoxy-1-methylhydantoylamide, obtained in a similar manner from ethyl and methyl 5-methoxy-1-methylhydantoylcarbamates, has m. p. 225°, and

forms an *acetyl* derivative, sintering at about  $85^{\circ}$ , m. p.  $110^{\circ}$ , by prolonged boiling with acetic anhydride. The ethoxy- and methoxy-methylhydantoylamides are identical with the products obtained by the ethylation and methylation respectively of 5-hydroxy-1-methylhydantoylamide.

Hypocaffeine is obtained readily and in good yield by passing hydrogen chloride through a fused mixture of *s*-dimethylcarbamide and 5-hydroxy-1-methylhydantoylamide.

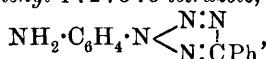
5-Ethoxy-1:3-dimethylhydantoylamide is obtained by treating 5-ethoxy-1-methylhydantoylamide with methyl sulphate and 2*N*-sodium hydroxide; 5-methoxy-1:3-dimethylhydantoylamide, prepared in a similar manner, has m. p.  $198^{\circ}$ . *Ethyl 5-ethoxy-1:3-dimethylhydantoyl-carbamate*, m. p.  $134^{\circ}$ , and *methyl 5-methoxy-1:3-dimethylhydantoyl-carbamate*, m. p.  $161$ — $162^{\circ}$ , prepared by the methylation of the respective monomethyl compounds, are converted into 5-ethoxy- and 5-methoxy-1:3-dimethylhydantoylamides respectively by concentrated aqueous ammonia on the water-bath. C. S.

**New Method of Preparation of Tetrazoles.** G. PONZIO and C. MACCIOTTA (*Gazzetta*, 1914, 44, ii, 63—72).—The action of hydrazine hydrates on nitro-substituted arylhydrazones of  $\omega$ -nitrobenzaldehyde yields amino-derivatives of substituted 1:2:3:5-tetrazoles, hydrazonehydrazides being apparently formed as intermediate products; for instance,



The ease with which this reaction occurs renders it useful for the preparation of tetrazoles unobtainable in other ways. The reaction is to some extent analogous to Dimroth and Merzbacher's synthesis of tetrazoles (A., 1910, i, 897).

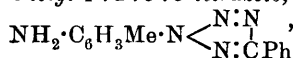
4-Phenyl-1-*p*-aminophenyl-1:2:3:5-tetrazole,



prepared from  $\omega$ -nitrobenzaldehyde-*p*-nitrophenylhydrazone, forms small, white prisms or long needles, m. p.  $164^{\circ}$ , turning yellow in the air. Like the other tetrazole derivatives described below, it gives with mineral acids well crystallised salts, which undergo hydrolysis with greater or less ease. The *sulphate*,  $(\text{C}_{13}\text{H}_{11}\text{N}_5)_2\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ , decomposing at about  $215^{\circ}$ , the *nitrate*,  $\text{C}_{13}\text{H}_{11}\text{N}_5\cdot\text{HNO}_3$ , turning brown at about  $180^{\circ}$  and decomposing at about  $200^{\circ}$ , and the *hydrochloride*,  $\text{C}_{13}\text{H}_{11}\text{N}_5\cdot\text{HCl}$ , turning brown at  $200^{\circ}$ , m. p.  $210^{\circ}$  (decomp.), were prepared. When the diazo-derivative of the sulphate is heated with alcohol, 1:4-diphenyl-1:2:3:5-tetrazole (compare Forster and Cardwell, T., 1913, 103, 870) is obtained.

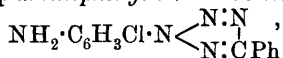
4-Phenyl-1-*o*-aminophenyl-1:2:3:5-tetrazole,  $\text{C}_{13}\text{H}_{11}\text{N}_5$ , prepared from  $\omega$ -nitrobenzaldehyde-*o*-nitrophenylhydrazone, forms flattened, yellow needles, m. p.  $80^{\circ}$ .

4-Phenyl-1-*p*-amino-*o*-tolyl-1:2:3:5-tetrazole,



prepared from  $\omega$ -nitrobenzaldehyde- $p$ -nitro- $o$ -tolylhydrazone, forms white prisms, m. p.  $121^\circ$ , rapidly turning yellow in the air.

4-Phenyl-1- $o$ -chloro- $p$ -aminophenyl-1:2:3:5-tetrazole,



prepared from  $\omega$ -nitrobenzaldehyde- $o$ -chloro- $p$ -nitrophenylhydrazone, forms shining, flattened needles, m. p.  $134^\circ$ . T. H. P.

**The Adsorption of Electrolytes and Colloids by Casein.** HERMAN PALME (*Zeitsch. physiol. Chem.*, 1914, **92**, 177—193).—The author has shaken casein with solutions of ferrocyanic acid, copper acetate, colloidal ferric oxide, and ferric chloride, and has determined the influence of concentration on the amount of material adsorbed by the casein. With the first two substances, the amount adsorbed varied with their concentration in accordance with the formulæ put forward by Arrhenius, Freundlich and Schmidt. In the case of the iron compounds it was found that the amount of iron adsorbed depended on the total quantity of electrolyte in the solution. H. W. B.

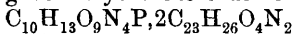
**Myxommucin.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1914, **92**, 144—148).—The mucin was obtained from a tumour by extraction with water and subsequent precipitation with acetic acid. The product after reprecipitation contained C 50.82%, H 7.27%, N 12.24%, S 1.19%, and P 0.25%; and gave positive biuret, Millon's, xantho proteic, Molisch's and Ehrlich's dimethylaminobenzaldehyde reactions. The solution in alkali was precipitated by dilute acid and the precipitate was not soluble in excess of the acid. It contained at least 12% of a carbohydrate which was split off on hydrolysis with a dilute mineral acid and, from the crystalline form and general properties of its hydrochloride, was recognised as glucosamine.

The new mucin differs, in certain particulars, from all known mucins. H. W. B.

**The "Carbohydrate" Group of the True Nucleic Acids.** R. FEULGEN (*Zeitsch. physiol. Chem.*, 1914, **92**, 154—158).—The author draws the conclusion, from a study of the properties of thymic acid, derived from thymonucleic acid, that the so-called carbohydrate group of the nucleic acids is in reality glucal or a similar substance (compare E. Fischer, this vol., i, 252). The reasons for this conclusion are (i) the ease with which the compound is destroyed by dilute mineral acids or alkalis; (ii) the production of a green pine-wood splinter reaction, and (iii) the rapid appearance of an intense reddish-violet coloration with Schiff's reagent. Further, the figures obtained on elementary analysis of nucleic acid agree more closely with the theory on the assumption of glucal instead of hexose groups in the molecule. H. W. B.

**Oxidation of Guanylic Acid to "Xanthylic Acid" by Means of Nitrous Acid.** MARTIN KNOPF (*Zeitsch. physiol. Chem.*, 1914, **92**, 159—162).—Sodium guanylate was treated in aqueous solution with sodium nitrite and acetic acid, and the resulting

xanthylic acid precipitated by the addition of excess of alcohol. The acid after purification gave a crystalline brucine salt,



(needles from 30% alcohol), which began to melt at  $200^\circ$ . Hydrolysis of the raw product gave only xanthine, the absence of guanine showing that the guanylic acid had been completely de-amidised.

H. W. B.

**Action of Some Diastases on the Dextrins.** (Mme.) Z. GRUZEWSKA (*Compt. rend.*, 1914, 159, 343—345).—A comparison of the influence of amylases of animal and vegetable origin on the erythro-dextrin obtained from starch and the achroodextrin from glycogen by the action of hydrogen peroxide. In the case of the amylase in the pancreatic juice of the dog, vegetable amylase, taka-diastase, and the juice of the snail, the ratio between the amounts of sugar obtained from the two dextrins is practically identical with the ratio between the amounts of sugar obtained from starch and glycogen under similar conditions.

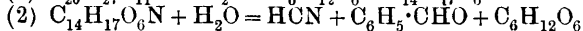
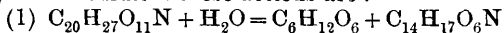
W. G.

**Influence of the Reaction of the Medium on the Action of the Inulase of *Aspergillus niger*.** A. KIESEL (*Ann. Inst. Pasteur*, 1914, 28, 747—757).—Whilst all the acids employed increased the activity of the diastase, a difference was observed between acetic acid and mineral acids. With acetic acid the activation obtained by the neutralisation (to helianthin) of the diastatic solution was changed very slightly up to the point at which the activity was diminished. With mineral acids, the activity increased regularly as the acidity increased. In the case of phosphoric acid the maximum activation was within the limits between  $1/90$  and  $1/72$  mol. gram; with acetic acid between  $1/2000$  and  $1/50$  mol. gram.

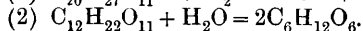
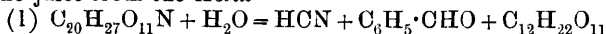
It was to be expected that as the activity of inulase is increased by acids, it would be increased by acid salts still further than by neutral salts. Experiments with hydrogen sodium citrate and disodium citrate showed, however, a reversed effect, the increase obtained with the two salts being respectively 19 and 104%. With dihydrogen sodium phosphate the increase was 131%.

N. H. J. M.

**Coupled Enzyme Actions.** J. GIAJA (*Compt. rend.*, 1914, 159, 274—276).—The hydrolysis of amygdalin by the emulsin of almonds and by the digestive juice of *Helix pomatia* must be considered as the product of two conjoined enzyme actions, the one primary and the other secondary. For emulsin these actions are:



and for the juice from the *Helix*



For emulsin the velocity of production of reducing sugar increases with the concentration of the amygdalin, whilst the velocity of formation of hydrogen cyanide is greater the lower the concentration of

the amygdalin. For the juice of the *Helix*, the velocity of formation of hydrogen cyanide is independent of the concentration of the amygdalin, whilst the velocity of production of reducing sugar increases as the concentration of amygdalin decreases. In each case a low concentration of amygdalin favours the secondary enzyme action.

W. G.

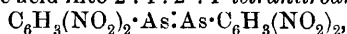
**Action of Chymosin [Rennet] and Pepsin. I. The Clotting-velocity as a Measure of the Amount of Chymosin Present.** OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1914, 92, 119—143).—The author finds that the so-called Time-Law (amount of chymosin  $\times$  clotting-time = constant), which holds good at 37—40°, is not obeyed at lower temperatures. At 20°, the chymosin may be much more active than at 40°, and the product correspondingly too large. The observations were carried out with acid and with neutral and dialysed extracts of stomach, with similar results in every case.

The effect of dilution varies, but usually increases the activity of the enzyme. It is suggested that by dilution inactive enzyme may become active by a process of dissociation.

H. W. B.

**Aromatic Arsenic Compounds. VIII. Some New Reduction Products of 2:4-Dinitrophenylarsinic Acid and a Large Class of New Carbamic Acid Derivatives.** P. KARRER (*Ber.*, 1914, 47, 2275—2283. Compare this vol., i, 890, 891).—By treating an ethereal solution of 2:4-dinitrophenylarsinic acid with phosphorus trichloride and water successively (compare Ehrlich and Berthelm, A., 1910, i, 451) reduction is effected to 2:4-dinitrophenylarsenoxide,  $C_6H_3(NO_2)_2 \cdot AsO$ , a yellow, crystalline solid which is almost insoluble in dilute mineral acids and the common organic solvents, but dissolves in ether or alcohol containing hydrogen chloride, giving dinitrophenylarsenic dichloride and in excess of aqueous sodium hydroxide to a yellow solution. When exposed to sunlight an ethereal solution of the arsenoxide gave an almost black, crystalline deposit of uncertain nature (compare Karrer, this vol., i, 891).

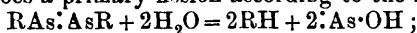
Reduction of hypophosphorous acid in aqueous solution at 50—60°, in the presence of a little potassium iodide as catalyst, converts 2:4-dinitrophenylarsinic acid into 2:4:2':4'-tetranitroarsenobenzene,



which separates in reddish-brown flocks. This substance is easily oxidisable and is very sparingly soluble in all solvents.

A solution of stannous chloride in hydrochloric acid at 70—80°, on the other hand, reduces dinitrophenylarsinic acid to 2:4:2':4'-tetra-aminoarsenobenzene,  $C_6H_3(NH_2)_2 \cdot As \cdot As \cdot C_6H_3(NH_2)_2$ , which, on pouring the reaction product into acetic acid, separates in yellowish-white flocks of the zincichloride. The free base was obtained by dissolving the zincichloride in 2- to 3-N-hydrochloric acid and then adding successively acetic acid and ether, when the base separated as a yellowish-white precipitate. Both the base and the zincichloride are unstable in aqueous solution, rapidly giving a deep reddish-brown precipitate similar to those produced more slowly from solutions of

many organic arsenic compounds on keeping (compare Ehrlich and Berthelm, A., 1912, i, 523), although they are stable in solution in concentrated hydrochloric acid. As, after the decomposition in aqueous solution, the filtrate from the red precipitate is found to contain arsenic and arsenious acids, together with *m*-phenylenediamine, it is believed that the decomposition is a hydrolytic one, in which the molecule undergoes a primary fission according to the scheme



approximately one-quarter of the tetra-aminoarsenobenzene is found to pass into *m*-phenylenediamine, whilst the remainder gives the insoluble brown substance. Although in the dry condition, even in an exhausted space, tetra-aminoarsenobenzene undergoes complete decomposition within forty-eight hours, the base can be coupled in the usual manner of meta-diamines with diazo-compounds, yielding azo-dyes containing arsenic, and when itself diazotised, it gives a precipitate of a reddish-brown substance, probably of the Bismarck-brown type.

A remarkable property of 2:4:2':4'-tetra-aminoarsenobenzene is that its solution in dilute hydrochloric acid when treated with sodium carbonate or hydrogen carbonate gives a precipitate of the base which is soluble in excess, although the resulting solution is unstable, and shortly deposits a flocculent solid. 3:5:3':5'-Tetra-amino-4:4'-dimethylaminoarsenobenzene has already been observed to exhibit similar behaviour (Giemsa, *Münch. Med. Woch.*; 1913, 1074), which is believed to depend on the formation of a carbamic acid derivative. The conclusion is drawn that this solubility in sodium hydrogen carbonate is to be attributed to the amino-groups in the meta-position, and examination reveals the fact that *m*-diamines generally, whether containing arsenic or not, are soluble in sodium carbonate or hydrogen carbonate solution in the presence of free carbon dioxide. This reaction is therefore of great value for the characterisation of meta-diamines, as ortho- and para-diamines do not exhibit this behaviour. That the solutions produced actually contain carbamic acid derivatives and not carbonates of the respective bases is shown by the absence of precipitation on the addition of sodium hydroxide. The solutions of the various carbamic acid compounds vary widely in stability, ranging from that derived from the above-mentioned tetra-aminodimethylaminoarsenobenzene which is very stable to that from 2:4:2':4'-tetra-aminoarsenobenzene which decomposes in a few seconds.

D. F. T.

Preparation of a 3:5:3':5'-Tetra-amino-4:4'-dimethylamino-arsenobenzene. C. F.



BOEHRINGER & SÖHNE  
(Swiss Patent, 64347).—  
This compound (annexed  
formula), m. p. 95° (decomp.),

is prepared from an arseno-benzene derivative containing, in the para-position to the arsenical radicle, the group NRMe, where R represents either a hydrogen atom, or a methyl group, or an acyl radicle; this is treated with a mixture of nitric and concentrated sulphuric acids, and the 3:5-diamino-4-methylnitroaminobenzene-1-arsinic acid thus



obtained is reduced in acid solution. The base has valuable therapeutic properties, as it exerts a pronounced action on trypanosomes and similar disease-producers, whilst its toxic effect on the human organism is less marked than that of other arsenic compounds. The *hydrochloride*,  $C_{14}H_{20}N_6As_2 \cdot 4HCl$ , is a yellowish-green powder and dissolves very readily in water.

T. H. P.

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## Physiological Chemistry.

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**The Influence of the Oxygen Content of the Surrounding Medium on the Gaseous Metabolism and the Rate of Oxidation in the Frog.** ERNST J. LESSER (*Biochem. Zeitsch.*, 1914, **65**, 400—408).—In a series of experiments of twenty-two hours' duration on consecutive days, it was found that the respiratory quotient remained practically constant, although there were variations (10—20%) in the amount of oxygen used (rate of oxidation). The amount of oxygen consumed by the same frogs was found to remain the same, when the oxygen of the atmosphere was reduced, until the amount fell to below about 2·8%. The diminution of the oxygen tension is accompanied, however, with a rise in the respiratory quotient. The author explains these phenomena by assuming that the oxygen pressure in the cells is diminished, and this causes an increased rate of hydrolysis of glycogen. Sugar is thus mobilised and burnt. The rate of hydrolysis by glycogen is not due thus to the rate of oxidation of the organism, but to the oxygen tension in the cell.

S. B. S.

**Substance Hitherto Unknown in Human and Some Animal Serums.** W. FRIEBOES (*Chem. Zentr.*, 1914, i, 2007; from *Deut. Med. Woch.*, 1914, No. 12).—The substance is very similar to the acid saponins; it reduces gold chloride, reacts with Nessler solution, and is precipitated by neutral lead acetate. It is rendered non-poisonous by cholesterol, and less poisonous by bromine and baryta. The name "saponoid" is suggested.

N. H. J. M.

**The "Specific-dynamic Action" of Foodstuffs.** S. CSERNA and G. KELEMEN (*Biochem. Zeitsch.*, 1914, **66**, 63—74).—The intravenous injection of various substances, such as sodium chloride, dextrose, or carbamide increases the gaseous exchanges of eviscerated animals (dogs). This action of various substances on gaseous exchange cannot be due, therefore, as Zuntz has suggested, to increased work of secretion by the alimentary tract, or to increased work of the kidneys. The substances must act, as Tangl has thought, by a general stimulation of the cells, which increases their metabolism of energy and matter.

S. B. S.

**The Behaviour of Amino-acids in the Metabolism of Birds.** K. SZALÁGYI and A. KRIVUSCHA (*Biochem. Zeitsch.*, 1914, **66**, 139—148).—The methods of determining the amino-acids by van Slyke's method in the urine and fæces of birds are described. The urine was collected from fistulæ. To a basal diet of maize was added asparagine, glycine, and molasses with known amino-acid content. All the asparagine was absorbed, as indicated by the amino-acid content of the fæces, when the animals were on the basal diet, and on this diet + the amino-acid. This was not the case with either glycine and molasses, as the addition of these to the basal diet caused an increase of amino-acids in fæces (3·76—9·03%). The increased amount of amino-acids in the urine varied between 2·83 and 6·90% of the amino-acids absorbed, the smallest numbers being obtained with asparagine. S. B. S.

**The Relationship Between the Energy Exchange and the Protein Metabolism During Starvation.** PAUL HÁRI (*Biochem. Zeitsch.*, 1914, **66**, 1—19).—The necessary energy required for maintenance of dogs at their critical temperatures (28°) during the first (second to eighth) days of starvation varies with different individuals between 700 and 1,000 cal. per square metre of body surface. The minimal amount is independent of the size of the animal, but depends on the amount of protein decomposed in the body. The increase of energy depends, not only on the larger amount of protein destroyed, but also on an increased combustion of the fat. This latter phenomenon appears to be due to some specific dynamic action of the decomposed proteins; the degradation products of the latter may perhaps exert some sort of chemical action on the fats, so as to render them liable to combustion.

S. B. S.

**The Energy Exchange on Insufficient Diets.** PAUL HÁRI (*Biochem. Zeitsch.*, 1914, **66**, 20—47).—If a dog, after a short period of starvation, is fed daily with an amount of milk which is insufficient for its energy needs, the daily exchange in chemical energy during this period of chronic underfeeding is either slightly increased or else it shows a gradual apparent decline. It shows an increase in those animals which in the foregoing period of starvation and during the period of underfeeding undergo only a slight loss of proteins, whereas it shows a decline in those animals in which the loss in proteins is relatively high. The milk exerts a specific dynamic action, which can be demonstrated in those animals which have suffered a protein loss, and in which, therefore, the energy necessary for maintenance has diminished. S. B. S.

**The Permanent Intravenous Injection of Peptones and Proteins.** V. HENRIQUES and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1914, **92**, 194—211. Compare this vol., i, 107, 1029).—The author has found it possible to maintain goats alive for two and a-half days after the removal of their intestines. During this time the animals have retained a small amount of nitrogen when fed

by the author's method of permanent intravenous injections with the products of tryptic-ereptic digestion of meat. The agency of the intestinal cells is, therefore, apparently not essential for protein synthesis.

Attempts to maintain nitrogenous equilibrium in goats or calves by intravenous injections of Witte's peptone, casein, and egg-white were usually unsuccessful owing to the acute toxic action of these substances. A positive nitrogen balance was obtained by the injection of serum into a goat, a turkey, and a calf, but in most experiments symptoms of poisoning supervened, resulting in death.

H. W. B.

**Estimations of Tryptophan in Normal and Pathological Kidneys.** ELISABETH KURCHIN (*Biochem. Zeitsch.*, 1914, **65**, 451—459).

—The estimation of tryptophan was made in human kidneys removed from a large number of cases in which the organs were normal and abnormal. The expressed juices and the residues were investigated separately, and were then digested for twenty-four hours with trypsin. The tryptophan in the digest was estimated by means of *p*-dimethylaminobenzaldehyde, the blue colour produced being compared with a standard ammoniacal copper solution according to Herzfeld's method. The tryptophan was found to be somewhat higher in normal than in pathological cases, and increases generally with the age of the individual. The lowest figures were found in a case of chronic interstitial nephritis.

S. B. S.

**Extractives of Muscle. XVI. The Isolation of Carnosine by means of Mercuric Sulphate.** M. DIETRICH (*Zeitsch. physiol. Chem.*, 1914, **92**, 212—213).—Carnosine is precipitated from the aqueous extract of muscle by mercuric sulphate dissolved in 5% sulphuric acid instead of by the more expensive phosphotungstic acid. The addition of two volumes of alcohol and a little ether just before the mercuric sulphate solution greatly increases the rapidity with which the carnosine is precipitated. By this method, 0.17% of crystalline carnosine was obtained from calf's muscle.

H. W. B.

**The Occurrence of Carnosine, Methylguanidine, and Carnitine in Mutton.** J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1914, **92**, 221—227. Compare this vol., ii, 759).—An extract of mutton was analysed by two methods: (1) precipitation of the bases directly with mercuric sulphate in sulphuric acid solution, followed by treatment of the filtrate after removal of the mercury with phosphotungstic acid; (2) treatment with lead acetate, and subsequent isolation of the bases with phosphotungstic acid. Method (1) gave, as in the case of the extract of beef (*loc. cit.*), more purine, carnosine, and carnitine, but less methylguanidine, than method (2). Expressing the results as percentages of the fresh muscle of the sheep, the amount of purine extracted was 0.058, carnosine 0.115, methylguanidine 0.038, carnitine 0.047, and

creatine 0.173. Extract of beef contains three times as much carnosine as extract of mutton. H. W. B.

**Preparation of Carnosine from the Broth Formed During the Sterilisation of Meat by Steam in the Hönnecke Meat-steamer.** J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1914, 92, 228—230. Compare preceding abstract).—By means of the mercuric sulphate process, 22.4 grams of carnosine were obtained from 10.5 litres of broth. This represents about 0.064 gram of carnosine per 100 grams of ox muscle. It follows that during the process of sterilisation about three-fourths of the extractives are retained in the meat. H. W. B.

**The Influence of a Diet Poor in Calcium on the Composition of Growing Bones.** STEPHAN WEISER (*Biochem. Zeitsch.*, 1914, 66, 95—114).—As a result of experiments on young pigs, it was found that a diet poor in calcium caused the increase of body-weight to be 20% less than in control animals fed on a diet with normal calcium content. If the calcium deprivation continued for a longer period, the animals commenced to lose weight. The appearance of the bones of the animals on a calcium-poor diet was also different. They were thinner, deformed, and easily cut with a knife. The growth and weight of the skeleton was not, however, smaller, but the bones were richer in water and poorer in calcium and ash-content when calcium was withheld. The amount of alkalis in the ash in the bones of animals on calcium-poor diet was larger than in the control animals, and they contained more sodium than potassium. S. B. S.

**The Action of Moderators (Buffers) in Altering the Acid-base Equilibrium in Biological Fluids.** MAX KOPPEL and K. SPIRO (*Biochem. Zeitsch.*, 1914, 65, 409—439).—A definition is given of the moderating (buffer) action of substances. The amount  $S$  of an acid added to a solution produces a certain change in the negative exponent of the hydrion concentration  $p$  ( $p = -\log[H]$ ). Suppose a given amount of acid  $\Delta S_0$  produces a change  $\Delta p$  in the absence of a moderator, and the same change is produced by an amount  $\Delta S$  in the presence of the moderator. The moderating action  $P$  can then be indicated by the expression  $\Delta(S - S_0)/\Delta p$ . The following expression for the moderating action of a weak acid is then deduced from the laws of ionic mass reaction,  $P = -Ak_s x / (k_s + x)^2 \log 10$ , where  $x$  = the hydrion concentration,  $k_s$  = the dissociation constant of the acid, and  $A$  is the equivalent concentration in which it is present. From such an expression it is evident that the moderating action of an acid is proportional to the equivalent concentration in which it is present. Where  $x$  is very large (that is, in the case of strong acids) or very small (as in the case of strong bases), the value of  $P$  becomes, therefore, diminishingly small. The maximum is where the value  $x = k_s$ , that is to say, the buffer action of a monobasic acid exhibits its maximum when the hydrion concentration is numerically equal to its dissociation constant. Just half of the acid is then present

as free acid and the other half as salt. All moderators, therefore, act efficiently for a certain value of  $p$ . In the above formula, if  $x = k_s$ ,  $P = -A/4 \log 10$ . From this it follows that the maximal buffer action of all weak acids in the same equivalent concentration is the same, and is proportional to that concentration. For a normal acid  $P = -\log 10/4$ . It is not, therefore, correct to speak of strong or weak "buffers," apart from the concentration, as this buffer action depends only on the position of the substance in the series of  $p$  values.

Owing to the maintenance of a constant neutrality in the organism, just those acids will be effective as buffers the  $k_s$  value of which is near  $10^{-7}$  (that is, the hydrion concentration of the neutral point). It is for this reason that phosphoric and carbonic acids act so effectively in the body fluids, etc.

Similar theoretical deductions have been made as to the buffer action of ampholytes. Here, three cases can be distinguished ( $k_b$  = the basic and  $k_s$  the acid dissociation constants of the ampholyte): (1) When  $k_b \cdot k_s > k_w/16$ . In this case there is only one point of maximal action of the moderator, viz., at the isoelectric point of the ampholyte. (2) When  $k_b \cdot k_s < k_w/16$ . In this case the moderating action is at a minimum at the isoelectric point of the ampholyte. There are in this case two points of maximal action, situated equidistantly from the isoelectric point, and of about the same magnitude. (3) The third case is when  $k_b \cdot k_s = k_w/16$ . This is of theoretical interest only.

The theoretical considerations have also been applied to the determination of the positions of maximal moderating actions in the case of substances with two or more dissociation stages (polybasic acids, etc.).

The theoretical deductions are illustrated by curves showing the moderating action of acetic acid, glycine, and various urines, the  $(S - S_0)$  values being plotted as the ordinates and the  $p$  values on the abscissæ.

S. B. S.

**Does Normal Urine Contain Free Glycerol?** MILAN FARKAŠ (*Biochem. Zeitsch.*, 1914, 66, 115—121).—A method is described for obtaining the glycerol by distillation in steam in a vacuum of the liquid under investigation, the apparatus used for this purpose being figured and described. The glycerol in the distillate was then estimated by the Zeisel-Fanto method. The glycerol was also estimated directly in the urine by the same method, after the latter had been treated consecutively with silver nitrate, barium hydroxide, and carbon dioxide. Only a faint opalescence was obtained in the silver nitrate in the glycerol estimation in 100 c.c. in both cases—no more than was obtained in blank experiments. The conclusion is drawn that the urine contains no free glycerol.

S. B. S.

**The Detection of Peptides in Urine by means of the  $p$ -Cresol-tyrosinase Reaction.** R. CHODAT and R. H. KUMMER (*Biochem. Zeitsch.*, 1914, 65, 392—399).—All normal urines give

a positive reaction with the *p*-cresol-tyrosinase reagent; all urines investigated contain polypeptides, but no tyrosine or peptides yielding tyrosine were found. There is also found in urine a thermolabile substance which inhibits the action both of tyrosinase and trypsin. S. B. S.

**Studies on Water Drinking. XVIII. Relation Between Water Ingestion and the Ammonia, Phosphate, Chloride, and Acid Excretion.** D. W. WILSON and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, **36**, 1774—1779).—Earlier experiments (Wills and Hawk, this vol., i, 223) showed that an increased ingestion of water resulted in a proportional increase in the ammonia excreted in the urine. A further study of this question has now been made, and also of the relationship of the ammonia output to the chloride, phosphate, and acid excretion.

The amount of ammonia excreted again increased with increased ingestion of water. The excretion of chlorides showed only a small variation with the amount of water taken, and, at certain points in the experiments, a retention of chlorides was observed, which was probably due to the effort of the body to maintain the normal osmotic pressure in its various fluids. A similar retention occurred in the case of the phosphates and acids, but, in spite of this tendency to obscurity, the small differences observed were sufficient to show significant increases in the output of both phosphates and acids after the ingestion of large quantities of water. E. G.

**Studies on Water Drinking. XIX. Intestinal Putrefaction as Influenced by the Ingestion of Softened and Distilled Water.** C. P. SHERWIN and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, **36**, 1779—1784).—Experiments are described which show that both softened and distilled water, when taken with meals in quantities of 500—1000 c.c., tend to cause a decrease in putrefactive processes in the intestine as indicated by the urinary indican excretion. It is noteworthy that when the greatest decrease in the indican output occurred, that is, during the period of copious drinking, the ethereal sulphates excreted showed a marked increase. This failure of the indican and total ethereal sulphate values to run parallel to one another affords evidence in favour of the view that indican has a different origin from the other ethereal sulphates. E. G.

**The Chemical Composition and Physical Properties of the Urines of Ducks and Fowls.** KORNELIUS SZALÁGYI and ALEXANDER KRIWUSCHA (*Biochem. Zeitsch.*, 1914, **66**, 122—138).—The urine was in both cases obtained from pre-anal fistulæ. The following factors were determined: total nitrogen, ammonia, carbamide, uric acid, proteins, amino-acids (by van Slyke's method), colloidal substances (by Salkowski's method), carbon (by wet method), caloric values, composition of ash, acidity, specific gravity, osmotic pressure (by freezing-point method), electrical conductivity, surface tension, viscosity, refraction, and rotation of polarised light. S. B. S.

**The Colloidal Nitrogen of the Urine and its Significance for the Clinical Diagnosis of Carcinoma.** P. L. J. DE BLOEME, S. P. SWART, and A. J. L. TERWEN (*Biochem. Zeitsch.*, 1914, **65**, 345—359).—The nitrogen precipitable by Kojo's zinc sulphate method was estimated, and also the purine substances and uric acid contained in this precipitate. In cases of carcinoma, no very definite differences could be detected in the analyses which would serve any purpose of clinical diagnosis. It was found, however, that the amount of non-dialysable nitrogenous substances in the zinc precipitate was considerably higher than that found in the normal.

S. B. S.

**Bactericidal and Antitoxic Action of Lanthanum and Thorium Salts on the Cholera Vibrio. Therapeutic Action of these Salts in Experimental Cholera.** ALBERT FROUIN and D. ROUDSKY (*Compt. rend.*, 1914, **159**, 410—413).—After mixing the microbic emulsion with an equal volume of lanthanum sulphate or thorium sulphate solution, centrifuging the mixture after thirty minutes, and suspending the microbic deposit in a volume of saline solution equal to that of the original emulsion, a guinea-pig was able to survive a peritoneal injection of an amount equal to twice that which proved fatal in eight hours without previous treatment. An injection of three and a-half times the fatal dose killed the guinea-pigs at the end of twenty-four to thirty-six hours when using lanthanum sulphate, but they survived this amount after its treatment with thorium sulphate. Phagocytosis and dissolution of the vibrio in the peritoneum of the guinea-pig is much more rapid in the case of the cultures treated with the above salts. In the case of monkeys, the culture was administered by the mouth after the purgative effect due to an ingestion of sodium sulphate had been produced, and then either six or twelve hours later 40 c.c. of a 2% solution of thorium or lanthanum sulphate was given by the mouth. In the case of the six hours' intervals, the monkeys survived after treatment with either of the salts, but with the twelve hours, the animals died when lanthanum sulphate was administered, but survived when thorium sulphate was used.

W. G.

**The Combustion of Sugar in Pancreatic Diabetes. III. The Sugar Consumption in the Surviving Intestine taken from Dogs with Pancreatic Diabetes.** F. VERZÁR and J. KRAUSS (*Biochem. Zeitsch.*, 1914, **66**, 48—55).—The consumption of sugar by the surviving intestine of dogs suspended in oxygenated Tyrode's fluid to which dextrose had been added was investigated. Intestines from both normal and depancreatized animals were employed. The results obtained were somewhat irregular, little consumption of sugar occurring, as a rule, in the first two hours. No differences could be detected, however, between the sugar consumption of the organs of the normal and depancreatized animals. Sugar did not stimulate the movements of the intestines as it does that of rabbits.

S. B. S.



**The Combustion of Sugar in Pancreatic Diabetes. IV. The Disappearance of the Blood-sugar after Evisceration of Normal Animals and Animals with Pancreatic Diabetes.** J. KRAUSS and M. SEINER (*Biochem. Zeitsch.*, 1914, **66**, 56—62).—There is a disappearance of the blood-sugar after evisceration both of normal and depancreatized animals. The authors confirm in this respect the results of Macleod and Pearce. They direct attention to the fact, however, that it is not justifiable to draw from these experiments the conclusion that sugar can be destroyed in the blood of depancreatized animals. S. B. S.

**The Combustion of Sugar in Pancreatic Diabetes. V. F. VERZÁR** (*Biochem. Zeitsch.*, 1914, **66**, 75—94).—It has been shown that injection of dextrose increases the respiratory quotient of normal animals, but not of depancreatized animals. The possible explanation of this fact is that the depancreatized animals have lost their capacity for burning sugar. There is, however, another possible explanation, viz., that the organism is already overladen with sugar, and therefore the injection of further quantities cannot increase the respiratory quotient. The experiments seem to indicate that the latter explanation is not correct, for if sugar is injected into animals shortly after the removal of the pancreas (one or two days), injection of sugar still causes a rise in the respiratory quotient, although there is marked hyperglycemia. The power of burning the increased sugar injected is only lost some days after the removal of the pancreas. Similar results were obtained with lævulose.

It has been shown by Macleod and Pearce that when the liver is excluded from the circulation of a depancreatized animal the blood-sugar diminishes. The explanation suggested is that the liver exerts an inhibitory action on the sugar destruction, but that this action is paralysed by the pancreas. If this explanation is correct, then the injection of dextrose into a depancreatized animal in which the liver is excluded from circulation should give rise to a higher respiratory quotient. The experiments of the author, however, show that this does not take place. After reviewing various experiments on the subject, he draws the conclusion that an animal with pancreatic diabetes can in some way cause the sugar to disappear, but that it has lost the power of burning it completely so as to yield carbon dioxide. S. B. S.

**Physiological Action of Aromatic Mercury Compounds. IV. FERDINAND BLUMENTHAL and KURT OPPENHEIM** (*Biochem. Zeitsch.*, 1914, **65**, 460—478).—Details are given of the action of a large number of mercury compounds after single and repeated injections into animals. Compounds in which the mercury is both masked and ionised were used. The organs were examined to determine the presence of the mercury. It was found that the liver was the only organ in which the metal was constantly stored, and this happened in all cases with the exception of colloidal mercury and the sodium and mercury salts of diaminodiphenylcarboxylic acid. It appears as if the diamino-group inhibits the deposition of the

metal in the liver. In toxynone (sodium acetylaminomercurobenzoate) this does not happen, as a hydrogen atom of the amino-group is in this case replaced by acetyl. There is no relationship between the toxicity of a compound and its affinity for the tissues. It is assumed that the mercury acts therapeutically by being taken up in the liver, and there converted into a product toxic to spirochetes. As a result of the work on mercury compounds generally, the conclusion is drawn that there is no organic mercury compound which surpasses in its action for the treatment of syphilis the ordinary inorganic medicaments in the same way that salvarsan and atoxyl surpass ordinary arsenic compounds in the treatment of syphilis and sleeping sickness respectively. If such an organic compound might be chosen for therapeutic purposes it is toxynone, as it can be applied intravenously with advantage. S. B. S.

**The Behaviour of Glycuronic Acid in the Organism.** JOHANNES BIBERFELD (*Biochem. Zeitsch.*, 1914, 65, 479—496).—The glycuronic acid was produced by the hydrolysis of menthyl glycuronate, which was obtained by the administration of menthol to rabbits. When administered to rabbits or dogs parenterally (either subcutaneously or intravenously), the acid is excreted almost quantitatively in the urine after a short interval. The same happens to the glycuronic acid produced after administration of menthol or amylen hydrate. Gluconic and saccharic acids are also rapidly excreted in the urine even after parenteral administration of only small doses. Long-continued administration of menthol is only tolerated on a mixed diet, and not on a diet of oats alone. The production of the conjugated acids stops, in the case of rabbits, after a relatively short interval. S. B. S.

**Origin of Creatine in the Animal Body. II. The Behaviour of  $\epsilon$ -Guanido-,  $\epsilon$ -Carbamido- and  $\epsilon$ -Amino- $n$ -hexoic Acids in the Rabbit's Body.** KARL THOMAS and M. H. G. GOERNE (*Zeitsch. physiol. Chem.*, 1914, 92, 163—176).—Feeding rabbits with  $\epsilon$ -guanidohexoic acid did not lead to an increase of the creatinine in the urine, only small amounts of unaltered acid and of a compound, which was found to be  $\epsilon$ -carbamidohexoic acid, being isolated.  $\epsilon$ -Carbamidohexoic acid was prepared synthetically from  $\epsilon$ -aminohexoic acid and urea by boiling with barium hydroxide in a similar manner to that employed by Lippich (A., 1908, i, 861) for the preparation of the carbamido-compounds of the  $\alpha$ -amino-acids. The product was obtained in 88% yield as colourless needles, which, after recrystallisation from water, decomposed at 174—178°. Analysis agreed fairly well with the formula  $C_7H_{14}O_5N_2$ . Hydrolysis with barium hydroxide was carried out in a sealed tube at 140° for four and a-half hours, ammonia and  $\epsilon$ -aminohexoic acid being produced. The carbamido-acid was boiled for two hours with concentrated hydrochloric acid without undergoing any change; it thus differs from the  $\alpha$ -carbamido-acids of Lippich, which in similar circumstances form hydantoin derivatives.

$\epsilon$ -Carbamidohehoic acid administered to rabbits proved to be slightly toxic. About 50% of the acid was regained from the urine, the remainder being utilised in the body. No intermediate products of its metabolism, such as  $\epsilon$ -aminohehoic acid, could be detected.

The ingestion of  $\epsilon$ -aminohehoic acid was also followed by toxic symptoms, and 17% of the amount eaten was recovered from the urine.

The results show that the  $\epsilon$ -guanidohehoic acid metabolised by the rabbit is not first hydrolysed to  $\epsilon$ -aminohehoic acid, but probably becomes oxidised to the lower homologue,  $\epsilon$ -guanido-butyric acid. Since, further, the administration of  $\epsilon$ -aminohehoic acid does not lead to the elimination of  $\epsilon$ -carbamidohehoic acid, the production of this latter substance from  $\epsilon$ -guanidohehoic acid in the organism cannot occur through the intermediate formation of  $\epsilon$ -aminohehoic acid.

H. W. B.

**The Action of  $\beta$ -Iminoazolyethylamine [4- $\beta$ -Aminoethylglyoxaline] and of  $p$ -Hydroxyphenylethylamine on Unstripped Muscle.** G. QUAGLIARIELLO (*Zeitsch. Biol.*, 1914, 64, 263—284. Compare Dale and Laidlaw, A., 1911, ii, 137).—The author has investigated the action of these drugs on the unstripped muscle fibres of the large and small intestine, uterus, artery, and bronchus, the results being recorded graphically. 4- $\beta$ -Aminoethylglyoxaline causes contraction, which may be observed even at a dilution of 1 in 17,500,000 by direct action on the muscle fibres.  $p$ -Hydroxyphenylethylamine acts indirectly through the nervous system, and thus resembles adrenaline in its sympathomimetic action. These results confirm the previous work of Dale and Laidlaw (*loc. cit.*).

H. W. B.

**The So-called Veratrine Contraction. The Action of Aldehydes on the Contraction of Striped Muscle.** FRITZ VERZÁR and MAGDA FELTER (*Pflüger's Archiv*, 1914, 158, 421—442).—The authors find that formaldehyde, glyoxal, acetaldehyde, paracetaldehyde, acraldehyde, and glyceraldehyde produce the same effect as veratrine on the contraction of voluntary muscle. Other aldehydes, including propaldehyde and higher aldehydes and benzaldehyde, are inactive. Some electrolytes, organic acids, and alkaloids also resemble veratrine in producing a delayed relaxation of the contracted muscle fibre, whilst other allied substances are inactive. The results lead the author to suggest that the secondary chemical tetanus brought about, according to von Frey, by the stimulating action of the compound formed by veratrine and an unknown product of muscular contraction, is really due to the stimulating action of veratrine itself acting on the muscle in the hypersensitive state induced by, and immediately following, a contraction.

H. W. B.

## Chemistry of Vegetable Physiology and Agriculture.

**The Metabiotic Action of Ultra-violet Rays. Modification of the Morphological and Biochemical Characteristics of the Anthrax Bacillus. Heredity of Acquired Characteristics.** (MME.) VICTOR HENRI (*Compt. rend.*, 1914, 159, 340—343).—After exposure to ultra-violet rays, several changes are noticeable in the morphological character of the anthrax bacillus. The least stable character is the chain formation of rods. After exposure to the rays, fragmentary filaments, and even isolated elements, could be observed. Then the form of the rods is altered. After irradiation, instead of the elongated rods, cocci, or cocci mixed with more or less elongated rods, are obtained. After irradiation the rods are diminished in diameter, three new forms composed of very slender elements about one-third the size of the normal elements being obtained. The biochemical characteristics similarly undergo alteration. The normal form is stained by Gram's reagent, but after irradiation five forms were obtained which would not take this reagent. The normal anthrax bacillus is white, but after irradiation two new forms were obtained, which gave intense yellow cultures. These new characteristics remained fixed even after 130 to 200 days, new cultures being taken almost daily. It should be noted that when, by culture on special sugar media, fragmentary filaments or cocci are obtained without irradiation, these forms do not remain fixed, but return to the original form by sowing on to an ordinary medium. After inoculation into a guinea-pig of these modified forms, cultures have been obtained from its blood which had all the macroscopic characters of the normal bacillus. Under the microscope the filaments were fragmentary, but the bacillus sporulated actively. W. G.

**The Metabiotic Action of Ultra-violet Rays. Theory of the Production of New Microbic Forms by the Action on the Different Nutritive Functions.** VICTOR HENRI and (MME.) VICTOR HENRI (*Compt. rend.*, 1914, 159, 413—415).—A comparative study of the development of normal anthrax bacillus and two new forms, (1) cocciform- $S_1$ , taking Gram's reagent; (2) slender filaments, not taking Gram's reagent, yellow in colour, which they call anthrax- $\gamma$  (compare preceding abstract). The culture media consisted of mineral salts, together with (a) one of the carbohydrates, dextrose, sucrose, maltose, lactose, or starch; (b) one of the nitrogenous substances, ammonium lactate, ammonium citrate, glycine,  $\alpha$ -alanine, asparagine, or Chapoteaut's peptone; (c) hydrochloric acid or sodium hydroxide at a concentration of  $N/200$ .

Normal anthrax does not develop on media containing ammonium salts or amino-acids as the nitrogenous nutrient, but only in media containing peptone. The form  $S_1$  behaves exactly like normal anthrax. Anthrax- $\gamma$  develops in the presence of both ammonium salts and amino-acids. None of the three forms develops

in an acid medium, but all prefer an alkaline to a neutral medium. Normal anthrax develops better on a medium devoid of carbohydrates than in the same medium with carbohydrates present, and if grown under the latter conditions a whole series of modified forms is obtained. For the form  $S_1$  there is no appreciable difference. Anthrax- $\gamma$  develops best in the presence of carbohydrates, and often it will not grow in a medium containing peptone unless sucrose or maltose are present. Cultures of anthrax- $\gamma$  are very abundant on potato.

After short periods of irradiation, cultures inoculated on media devoid of carbohydrate develop but little, whereas the culture is abundant in the presence of carbohydrate. For longer periods of irradiation the reverse is true.

Apparently, under the influence of the irradiation, the anthrax bacillus loses its capacity for secreting proteolytic enzymes whilst retaining the power of producing amylolytic enzymes. Such a bacillus placed on a nutritive medium would require carbohydrates for its development, and would thus change its mode of feeding, and as a result its form and all its biochemical and biological properties would be modified. A new form would thus be obtained which would retain its acquired characteristics through thousands of generations.

W. G.

**Nitrogen Fixation by *Azotobacter* in Substrata Poor and Rich in Nitrogen.** J. HANZAWA (*Centr. Bakt. Par.*, 1914, ii, 41, 573—576).—Mixed cultures of different strains of *Azotobacter* were found to be more efficient than the same bacteria in pure cultures, especially in aqueous solutions of mannitol.

The nitrogen of humus and small amounts of nitrates were almost without effect on the fixation of nitrogen by pure cultures of *Azotobacter*. In presence of nitrogen amounting to 2.5% of the amount of carbon, nitrogen fixation is retarded, and with large proportions of nitrogen, inhibited. Under natural conditions it seems probable that soil nitrogen can only seldom, if at all, have an unfavourable action on nitrogen fixation.

Some humus substances seem capable of being utilised as source of energy in the fixation of nitrogen. The humus of farmyard manure gave positive results, whilst that of green manure gave negative results.

N.-H. J. M.

**Nitrogen Metabolism of Soil.** H. H. GREEN (*Centr. Bakt. Par.*, 1914, ii, 41, 577—608).—Experiments on ammonification, nitrification, nitrogen fixation, and decomposition of cyanamide, both in soils and in solutions inoculated from soil samples taken at approximately monthly intervals from August, 1912, to August, 1913.

As regards the ammonification of organic manures, bacterial activity showed a rise from August to October, a tendency to fall or remain constant in November, and a rise to a maximum in December. In February activity reached the minimum, and from April to July there was a slight fall, probably continued to a summer minimum in August. The nitrification results were similar, except that the spring maximum was in March, whilst the

decline to a summer minimum commenced in April. The slight variations and the December maximum are attributed to the mild character of the winter of 1912—13. Nitrogen fixation in 1% mannitol was low in August and September; subsequently it was fairly constant, except with samples taken after ploughing. No definite results were obtained in the cyanamide experiments.

Comparison of the results of field-manuring experiments with those of laboratory tests indicates that the latter may be of considerable value in supplying information as to the decomposition processes in soils.

Solution methods were found to be equal to those in which the natural soil is employed as medium, whilst as regards nitrification the solution method gave much clearer indications of seasonal variation.

N. H. J. M.

#### **Antagonism between Anions as Affecting Soil Bacteria.**

C. B. LIPMAN and P. S. BURGESS (*Centr. Bakt. Par.*, 1914, ii, 41, 430—444).—A study of the effects of reciprocal doses of sodium chloride, sulphate, and carbonate on nitrification in the soil. One hundred grams of sandy soil were mixed with 1 gram of dried blood, moistened, and incubated at 30° for one month; at the end of this period nitrates were determined by the aluminium reduction method.

From the results it would appear that marked antagonism exists between the anions of the three salts when the nitrifying power of the soil is the criterion. For the active transformation of organic nitrogen certain combinations of these three common alkali salts are permissible in the soil without retardation, but even with stimulation of the processes of ammonification and nitrification. Thus both ammonification and nitrification may proceed normally in the presence of a total salt content of 0.45%, consisting of 0.20% chloride and 0.25% carbonate. If sodium carbonate is present to the extent of about 0.1%, either 0.2% chloride or 0.35% sulphate may be added to it, and still permit of efficient nitrogen transformation. The work gives definite indications for the combination of alkali salts as a measure in alkali land reclamation.

H. B. H.

#### **Chemical Actions of Citromyces: Utilisation of Nitrogen Compounds and Action of Heavy Metals in the Medium.**

F. ALEX. McDERMOTT (*Chem. Zentr.*, 1914, i, 1893; from *Mycol. Zentr.*, 3, 159—160).—Experiments on the utilisation of uric and hippuric acids and hexamethylenetetramine as sources of nitrogen for *Citromyces glaber* and *C. Pfefferianus*. Development was more rapid in presence of manganese acetate and uranyl acetate, whilst ferric chloride and zinc chloride had a retarding effect.

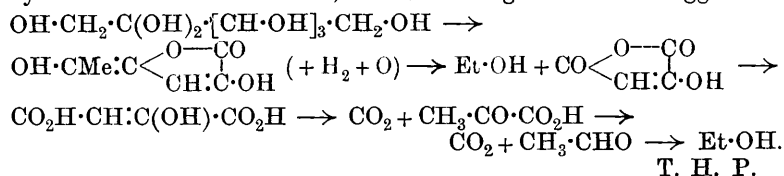
N. H. J. M.

**Fermentation of Certain Sugars by means of *Aspergillus glaucus*, and Considerations on Alcoholic Fermentation.** F. TRAETTA-MOSCA (*Ann. Chim. Applicata*, 1914, 1, 477—492).—Sucrose

is fermented slowly by *Aspergillus glaucus*, and when the solution becomes optically inactive it is found to contain the  $\gamma$ -lactone of a trihydroxyhexadienoic acid.

This lactone,  $\text{OH}\cdot\text{CMe}\cdot\text{C} \begin{smallmatrix} \text{O} \text{---} \text{CO} \\ \text{CH}:\text{C}:\text{OH} \end{smallmatrix}$  (?), forms white, prismatic needles resembling glass-wool, m. p.  $154^\circ$ , and assumes a violet tint in the light. It is acted on by permanganate, and exhibits normal cryoscopic behaviour in water. In alcoholic solution and in presence of palladium-black it takes up 4H at the ordinary temperature, and it yields a *diacetyl* compound,  $\text{C}_6\text{H}_4\text{O}_4\text{Ac}_2$ , long, white needles, m. p.  $102^\circ$ , and a *dibenzoyl* compound,  $\text{C}_6\text{H}_4\text{O}_4\text{Bz}_2$ , white crystals, m. p.  $134\text{--}135^\circ$ . It combines with bromine, giving a *compound*, m. p.  $99^\circ$ , and gives a crystalline, sky-blue *copper salt*,  $\text{Cu}(\text{C}_6\text{H}_5\text{O}_4)_2\cdot\text{H}_2\text{O}$ .

The lactone undergoes fermentation by beer-yeast, yielding alcohol and carbon dioxide, and the author considers it probable that it is formed as an intermediate product in ordinary fermentation, its formation being due to simultaneous reduction and oxidation of the sugar molecule. Thus, for the fermentation of the hydrated form of *lævulose*, the following scheme is suggested:



T. H. P.

**Analogy between the Nutritive Value of Different Substances for *Penicillium glaucum* and their Narcotic Action.** H. I. WATERMAN (*Chem. Zentr.*, 1914, i, 1844—1845; from *Folia Microbiol.*, 2, Heft 3).—Several narcotics, such as phenol, *m*- and *p*-hydroxybenzoic acids, and protocatechuic acid, in solutions of low concentration, are very suitable as sources of carbon for *Penicillium glaucum*.  
N. H. J. M.

**Causes of the Growth of Plants. III.** G. A. BOROVNIKOV (*Kolloid. Zeitsch.*, 1914, 15, 27—30. Compare A., 1913, i, 324, 571).—Observations have been made on the rate of growth of seedlings in water and in solutions of various electrolytes with the object of ascertaining the connexion between this and the concentration of the cell sap, which was determined by the freezing-point method. The results show that, in general, an increase in the rate of growth is accompanied by a slight reduction in the concentration of the cell sap. This relationship is considered favourable to the view that the swelling of the protoplasmic colloids as a result of the absorption of water is one of the most important factors concerned in the growth of plants. It is supposed that the protoplasm passes through three different stages during the growth of the cell, these stages being distinguished as the solid, the gel, and the sol phases.

H. M. D.

**The Mechanism of the Exchanges Between the Plant and the Exterior Medium.** P. MAZÉ (*Compt. rend.*, 1914, 159, 271—274).

—The author has grown maize plants in aseptic mineral solutions containing 2 or 5% of sucrose. When the concentration of the sugar had reached to such a degree that the plants only tolerated it with difficulty, they lost their turgescence in sunlight and suffered from a lack of water. At this stage the sugar content of the nutritive solution and of the juices of the roots, stem, and leaves was determined. The results showed that there was no relationship between the sugar content of the nutritive solution and of that of the different plant juices. The author draws the conclusion that the laws of osmosis do not entirely control the exchanges taking place, but that it is the chemical work of the plant which controls them. By suppressing this chemical work as far as possible by growing the plants in diffused light, results were then obtained showing a fairly close relationship between the sugar content of the nutritive solution and of the different juices. From this he draws the conclusion that the plant, instead of enriching itself in sugar, lives on its reserves. Further, that the plant constitutes a system permeable to water and to substances that it contains in solution or colloidal suspension, but that the permeability is capable of regulation, not only in the organs which are in contact with the external medium, but also in the different tissues which compose the plant. W. G.

**The Theory of the Bioelectric Current.** H. ROHONYI (*Biochem. Zeitsch.*, 1914, 66, 248—257).—A series of electrometric measurements were carried out with the chain

Hg, HgCl, N/10-KCl	Solution of electrolyte of constant concentration.	KCl-solution, variable concentration.	N/10-KCl, HgCl, Hg.
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As a result, the conclusion is drawn that Loeb and Beutner (A., 1912, ii, 663, 1087; 1913, ii, 801, 802; this vol., i, 357) are in error in holding as characteristic the changes in the so-called bioelectric potential with changes in the salt concentration; these are produced in any chain containing an aqueous salt solution and a salt-free aqueous or non-aqueous solution of an electrolyte. The explanation of the phenomena offered by Loeb and Beutner, which involves the assumption of a plasma membrane of lipid character, is not therefore necessary. It is sufficient to assume that the membrane contains none or only small quantities of salt ions, but has adsorbed in traces electrolytes of acid character. S. B. S.

**The Permeability by Ions and the Membrane Potential.** H. ROHONYI (*Biochem. Zeitsch.*, 1914, 66, 231—247).—The permeability of membranes by ions does not indicate that there are marked differences in the rate of wandering of the ions through that membrane. It was shown by experiment that the *E.M.F.* of a precipitation membrane investigated in an ordinary chain,

Hg, HgCl, N/10-KCl	CuSO <sub>4</sub>	Copper ferrocyanide gel.	K <sub>4</sub> Fe(CN) <sub>6</sub>	N/10-KCl, HgCl, Hg
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is an ordinary diffusion *E.M.F.* The membrane in the chain plays the same part as an electrolyte-free aqueous medium, and the *E.M.F.* is the same if the membrane is replaced by water in the above chain. The membrane in this experiment was prepared by passing a capillary U-tube from the copper sulphate to the ferrocyanide solutions and allowed to form at the end of the U-tube.

S. B. S.

**Influence of Various Salts on Heliotropism.** INES MARCOLONGO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1913, [iii], 19, 226—235).—Examination of the influence of various nitrates, phosphates, and sulphates of potassium, sodium, calcium, and magnesium on green and etiolated seedlings of *Sinapis alba*, *Avena sativa*, and *Phaseolus multiflorus* shows that these salts enhance the heliotropism and shorten the time of reaction of the etiolated plants, but diminish the heliotropism and increase the time of reaction of the green plants. The maximum retardation or prolongation of the time of reaction and the greatest effect on the heliotropism are produced by a solution containing potassium, calcium, and magnesium cations, and the anions of nitric, phosphoric, and sulphuric acids. These influences are to be attributed to chemical actions of the nutritive salts, but there may be also a physico-chemical effect due to the concentration of the liquid, since sodium chloride exerts an action analogous to some extent to that of the above salts.

T. H. P.

**Distribution of Compounds with Simple Carbon Chains in the Vegetable Kingdom.** HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1914, 28, 1—9).—Amongst the carbon compounds with unbranched open chains occurring in plants, those with two, six, and eight carbon atoms are the most widely distributed. With regard to the formation of other substances, the compounds with two and six carbon atoms are the most important. This, and the genetic relation of the various carbon chains to one another, is in accordance with the assumption that a double carbon chain, glycolaldehyde, is an important intermediate compound in the assimilation of carbon dioxide.

W. P. S.

**Importance of the Alkaloids of *Papaver somniferum* for the Life of the Plant.** A. MÜLLER (*Arch. Pharm.*, 1914, 252, 280—293).—The function of alkaloids in plants is an unsolved problem. Are they excretory products with a protective function? Are they produced, during the chemical processes occurring in the plant cells, from complex nitrogenous compounds, and then remain as essentially unimportant debris, or can they again be employed in chemical transformations, especially for the regeneration of albumin?

Although the first query might be answered affirmatively for several reasons, as, for example, the fact that alkaloids are usually localised in the peripheral parts of plants, yet the theory is opposed to other equally well-known facts, for example, an alkaloid may be fatal to one creature and innocuous, or nearly so, to another.

The author attempts to answer the second query by an examination of the poppy in the following manner. In the first place, poppy seeds do not contain any alkaloids. The scheme he adopts is to estimate the alkaloidal nitrogen in the whole plant, and also in its various organs at different periods of its growth, in plants grown under natural conditions, and also in others cultivated in a non-nitrogenous nutrient solution. Methods are described for the quantitative extraction of the alkaloids and for the estimation of their nitrogen by Kjeldahl's process. The experiments must be repeated at the same period of growth in different years, because the alkaloidal content is materially affected by weather conditions, the amount decreasing in wet or cloudy weather and increasing in sunny weather.

It is found that in plants grown under natural conditions alkaloids can be detected in the plant about fourteen days after germination; the amount increases (subject to fluctuations caused by weather conditions) until after blooming the swelling of the seeds by reserve albumin begins. As the seeds ripen, the amount of alkaloid decreases in the capsules, stem, and leaves without, however, completely disappearing.

The cultivation of the plants under artificial conditions is effected by cutting through the stem of a blooming plant above the root under water and placing the plant in a non-nitrogenous nutrient solution. As it was found that alkaloids do not pass into the nutrient solution, the plants only require to have fresh sections cut off every five days, renewal of the nutrient solution, and spraying with distilled water; in this manner they thrive well, and by artificial pollination attain to complete ripeness. A diminution in the alkaloidal content can be detected even after ten days in the whole plant, and also in the leaves and stem. After forty-eight days, when the seeds have ripened, the leaves and stem are quite free from alkaloids, while the capsule walls contain traces which can be detected qualitatively, but are too small to be estimated.

It follows from the preceding that the alkaloids of *Papaver somniferum* are utilised in synthesising albumins during the ripening of the seeds, and therefore are not specific excretory products. C. S.

**Constituents of *Andrographis paniculata*.** KSHITIBHUSAN BHADURI (*Amer. J. Pharm.*, 1914, 86, 349—354).—This common bitter plant growing throughout the plains of India contains two bitter principles, which may be obtained by extracting the plant with alcohol and distilling the extract with steam; the residue in the flask consists of an aqueous portion, which on cooling deposits yellow-coloured crystals (bitter *A*), and a solid mass, from which a second bitter principle (bitter *B*) may be extracted by hot water. The substance *A* had m. p. 206°, contained hydroxyl groups, and had the formula  $C_{19}H_{28}O_5$ . The substance *B* consisted of a white amorphous powder, m. p. 185°, and had the formula  $C_{19}H_{51}O_5$  [ $? C_{19}H_{52}O_5$ ]; the name *kalmeghin* is proposed for it. A white

substance having acid properties is liberated when substance *B* is treated with an acid. The plant also contains a small quantity of an essential oil and a resin. W. P. S.

**Distribution of Nitrates in *Phytolacca* (*Pircunia dioica*) during the Winter Rest and During Growth.** R. SPALLINO (*Ann. Chim. Applicata*, 1914, 1, 502—505).—The results of tests made by means of "nitron" and of diphenylamine show that *Pircunia dioica* is very rich in nitrates, which are, however, not found in the young leaflets at the beginning of spring, when the temperature is still unfavourable. At a later stage the leaflets, like all other parts of the young shoots, contain nitrates in quantity. Subsequently these salts partly disappear, so that: (1) the nitrates function as a reserve material, and (2) the absence of nitrates from the very young leaflets is probably related to the fact that the synthetic processes are still inactive. T. H. P.

**The Physical-chemical Properties of the Alcohol-soluble Proteins of Wheat and Rye.** JULIUS GRÖH and GUSTAV FRIEDL (*Brochem. Zeitsch.*, 1914, 66, 154—164).—The following physical methods were employed. Estimations of viscosity, surface tension, rotatory and refractory powers, and protective action on colloids by (a) Zsigmondy's gold method; (b) the protective action on a platinum sol, as measured by the catalytic action of the latter on hydrogen peroxide, a new method not yet described in detail. The gliadin was obtained in fractions by two methods: (a) by the fractional separation from alcoholic solution; (b) by a method described previously by König and Rintelen. It was found, as a result of physical-chemical examination of the fractions, that gliadin consists of only one protein, although fractions may be contaminated by lecithins. The gliadin from strong and weak glutens is identical. Several proteins are contained in the rye meal, which have not been isolated; a protein identical with gliadin was not obtained. It appears as if the rye does not contain gliadin.

S. B. S.

**Arsenic and Manganese in Some Plant Products Used as Animal Foods.** F. JADIN and A. ASTRUC (*Compt. rend.*, 1914, 159, 268—270. Compare A., 1913, i, 233, 948).—The authors have extended their estimations of manganese and arsenic in plants to the common fodder plants, finding both metals present in every case. The results are tabulated, giving the amounts present in the fresh and dry weights, and in the case of manganese in the ash of lucerne, sainfoin, vetches, clover, potatoes, mangolds, poplar leaves, chestnut, rice, maize, barley, oats, bran, meadow hay. W. G.

**Nicotine in the By-products of the Culture of Tobacco.** E. CHUARD and R. MELLET (*Compt. rend.*, 1914, 159, 208—210. Compare A., 1912, ii, 979).—A notable quantity of nicotine is contained in the waste products from tobacco grown according to the Swiss method (*loc. cit.*). Experiments have been performed to

determine the effect on the yield of nicotine in these waste products of (1) allowing the axillary buds to grow instead of removing them as formed; (2) only removing the large leaves and leaving in the earth the trunks bearing newly-formed buds; (3) applying sodium nitrate to these plants thus partly harvested. The results show that: (1) the plants not deprived of their buds give a smaller yield of nicotine and of a poorer quality; (2) the yield of nicotine in plants left in the soil after the harvest, and bearing newly-formed buds, is markedly higher than in those completely harvested; (3) treatment with sodium nitrate does not modify the relative yield of nicotine in the different organs of the plant in a regular manner, but increases the total yield of each plant.

W. G.

**Properties of Soil Grains and the Plasticity of Soils.** ALBERT ATTERBERG (*Koll. Chem. Beihefte*, 1914, 6, 55—89).—A discussion of the properties of soils in so far as these depend on the size of the grains and on the relative proportions of gravel, sand, silt, and clay. According to the manner in which the properties vary with the size of the grain, the most rational basis for a classification of the grains into groups is afforded by the following ranges of the diameter: 2.0—0.2—0.02—0.002 mm.

The methods employed in the mechanical analysis of soils are referred to, and a new form of sedimentation apparatus is described. The final section of the paper deals with the plasticity of clays and the classification of clays according to their "plasticity numbers."

H. M. D.

**Volatilisation of Ammonia from Soils.** O. LEMMERMANN and I. FRESSENIUS (*Landw. Jahrb.*, 1913, 45, 127—154).—All soils differ from each other in their power of absorbing ammonia, and the action of calcium carbonate on the volatilisation of ammonia from soils is variable, according to the nature of the soil, sometimes increasing and sometimes diminishing the loss of ammonia.

In some soils the effect of calcium carbonate depends on the amount of ammonium carbonate added; in these soils, calcium carbonate acted favourably only in presence of larger amounts of ammonium carbonate, and increased the loss of ammonia when only small amounts of ammonium carbonate were added.

Absorption of ammonium salts, in the soils examined, depends mainly on the exchange of the bases of the zeolitic substances of the soil. The amount of available potassium seems to influence the action of calcium carbonate.

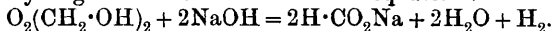
N. H. J. M.

## Organic Chemistry.

**Chemistry of Nascent Methylene.** E. SERNAGIOTTO (*Gazzetta*, 1914, 44, i, 587—597).—Methyl alcohol reacts violently with phosphoric oxide, and a series of hydrocarbons (cyclic and unsaturated) of the type  $(CH_2)_n$  is formed. Gaseous, liquid and solid members of this series are present, but oxygenated products are absent, as also is ethylene.

R. V. S.

**Dimethylenediol Peroxide (Diformal Peroxide Hydrate).** H. J. H. FENTON (*Proc. Roy. Soc.*, 1914, [A], 90, 492—498).—By the evaporation of approximately equal volumes of concentrated solutions of hydrogen peroxide and formaldehyde at a low temperature in a vacuum over sulphuric acid, a substance,  $C_2H_6O_4$ , m. p. about  $65^\circ$ , large, rectangular plates or prisms, is obtained, which responds only very faintly to tests for hydrogen peroxide and formaldehyde, and is regarded as an "atomic" compound such as *dimethylenediol peroxide*,  $O_2(CH_2 \cdot OH)_2$ . The substance undergoes little, if any, change in the dark at the ordinary temperature, and dissolves unchanged in water or acetic acid, the solutions giving normal molecular weights by the cryoscopic method, in the former solution even after forty-eight hours at  $0^\circ$ . The crystals explode at about  $70^\circ$ , and take fire in contact with reduced iron, platinum black, or warm copper oxide; they are slowly decomposed by exposure to bright sunlight. Treatment of the aqueous solution of the substance with platinum black causes a rapid decomposition of the potential hydrogen peroxide and a solution of pure formaldehyde remains. Aqueous alkalis cause the evolution of a volume of hydrogen in accordance with the equation:



There seems to be no doubt that the compound is identical with that which Legler, in 1881, obtained amongst the products of slow oxidation of ether.

C. S.

**The Lecithin of Egg-Yolk.** J. D. RIEDEL (*Chem. Zentr.*, 1914, i, 1896; from *Riedel's Ber.*, 1914, 15—16).—Pure distearyl-lecithin may be prepared by extracting lecithin-albumin with light petroleum, then with ether, drying it under reduced pressure, and extracting the dry substance with methyl alcohol (compare A., 1912, i, 744); the methyl-alcoholic solution is concentrated under reduced pressure and precipitated with acetone, these operations being repeated a few times. The clear methyl-alcoholic solution is then cooled in a freezing mixture, filtered to remove phosphatides, and the lecithin in solution is converted into hydrolecithin. This is dissolved in chloroform and methyl acetate is added, when distearyl-lecithin is precipitated as a white powder. It is insoluble in acetone and methyl acetate, soluble in chloroform, sparingly so in cold methyl alcohol, ethyl alcohol, and ethyl acetate, and may be crystallised from its hot ethyl acetate solution.

W. P. S.

**Oxidation of Certain Fatty Acids with Branched Chains.** HENRY STANLEY RAPER (*Biochem. J.*, 1914, 8, 320—327).—A scheme of oxidation is suggested by the author which explains the results so far obtained in studying the katabolism of  $\alpha$ -methylated fatty acids such as *isobutyric*,  $\alpha$ -methylbutyric and  $\alpha$ -methylvaleric acids, and also acids, such as  $\gamma$ -methylvaleric acid, which by oxidation at the  $\beta$ -position would yield  $\alpha$ -methylated acids. The rule of  $\beta$ -oxidation is applied to these acids with the proviso that the carbon atom of that methyl group which is in the  $\beta$ -position, undergoes oxidation first. The derivative of malonic semialdehyde [formylacetic acid] produced would, by loss of carbon dioxide, give rise to the normal aldehyde of the demethylated fatty acid, and by subsequent oxidation, or the Cannizzaro reaction, to the normal acid itself.

In support of this view as a possible biochemical process it is shown that ammonium *isobutyrate* on oxidation with hydrogen peroxide yields amongst other products propaldehyde, and that ammonium  $\alpha$ -methylbutyrate yields similarly butaldehyde.

The possibility of this scheme being applied to the katabolism of propionic acid is suggested, since this acid is similarly constituted as regards the position of its methyl group to the  $\alpha$ -methylated acids.

H. W. B.

**Purification and Melting Points of Saturated Aliphatic Acids.** P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1914, 18, 463—467).—Several higher fatty acids have been carefully purified and their melting points redetermined. It has been found that the purest acids after distillation even under very low pressure as a rule do not show their maximum melting point. In order to obtain the maximum, several recrystallisations from acetone are required.

Undecolic acid, prepared by reduction of undecenoic acid with hydrogen and palladium, has b. p.  $164^{\circ}/15$  mm., m. p.  $29-30^{\circ}$ . Its amide has m. p.  $103^{\circ}$ . Lauric acid recrystallised from acetone has m. p.  $47.5-48^{\circ}$ . Tridecic acid,  $C_{13}H_{26}O_2$ , prepared by oxidation of  $\alpha$ -hydroxymyristic acid, has b. p.  $202-203^{\circ}/17$  mm., and m. p.  $50-51^{\circ}$ . Myristic acid has m. p.  $57.5-58^{\circ}$ . Methyl  $\alpha$ -hydroxypalmitate has m. p.  $59-60^{\circ}$ . Ethyl  $\alpha$ -hydroxypalmitate has m. p.  $55.5-56.5^{\circ}$ . Pentadecic acid, prepared by oxidation of  $\alpha$ -hydroxypalmitic acid, has m. p.  $53-54^{\circ}$ . Palmitic acid has m. p.  $63.5-64^{\circ}$ . H. W. B.

**Preparation and Properties of the Ammonium Salts of Organic Acids.** IV. LEROY McMASTER (*J. Amer. Chem. Soc.*, 1914, 36, 1916—1925).—In earlier papers (Keiser and McMaster, A., 1913, i, 248; McMaster, A., 1913, i, 444; this vol., i, 481) an account has been given of the preparation of the normal ammonium salts of various organic acids by passing ammonia into solutions of the corresponding acids in alcohol or ether. In continuation of this work, the author has prepared normal ammonium *palmitate*, *stearate*, *oleate*, *elaidate*, *aconitate*, *salicylate*, *m*-hydroxybenzoate, *p*-hydroxybenzoate, *p*-methoxybenzoate,  $\beta$ -phenylpropionate, *hippurate*, *o*-toluate, phenylacetate, mandelate, and *uvitate*. In some of these cases, the salts were prepared by passing ammonia into a solution of the acid in acetone.

E. G.

**Cerebronic Acid.** IV. **The Constitution of Lignoceric Acid.** P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1914, 18, 477—480. Compare A., 1913, i, 889).—The hydrocarbon tetracosane obtained by the reduction of lignoceric acid has m. p. 51—51·5° and has been considered to be identical with *n*-tetracosane. The latter compound has now been prepared by the action of magnesium on dodecyl iodide and found to have m. p. 55°. The hydrocarbon from lignoceric acid must therefore be *isotetracosane*, which is in accordance with the views of Meyer (A., 1913, i, 1151).

*Dodecyl iodide*,  $C_{12}H_{25}I$ , has b. p. 145—150°/0·7 mm. It is converted by Grignard's reaction into *n-tetracosane*,  $C_{24}H_{50}$ , m. p. 55°, b. p. 237—240°/15 mm.

Ethyl lignocerate is reduced to *isotetracosyl alcohol*,  $C_{24}H_{49}\cdot OH$ , b. p. 220°/0·8 mm., m. p. 72°. The corresponding *isotetracosyl iodide*,  $C_{24}H_{49}I$ , has m. p. 48°, and by reduction gives *isotetracosane*,  $C_{24}H_{50}$ , shining plates, m. p. 51—51·5°, b. p. 222—225°/9 mm. H. W. B.

**Clupanodonic Acid.** J. D. RIEDEL (*Chem. Zentr.*, 1914, i, 1882; from *Riedel's Ber.*, 1914, 23—27).—The fatty acids obtained by the hydrolysis of brown Japanese sardine oil (iodine number 195) are brominated in light petroleum, the insoluble bromo-acids are treated with ether, and the residual octabromides, suspended in 96% alcohol, are treated with zinc dust. Clupanodonic acid,  $C_{18}H_{38}O_2$ , iodine number 365—370, thereby obtained in 12·7% yield is an oil with a fishy odour, which acquires after a time the odour of cod-liver oil. Since the acid yields stearic acid and products of lower m. p. by treatment with hydrogen and colloidal palladium, it is probably not an individual substance but a mixture of a derivative of stearic acid and one or more substances,  $C_{18}H_{38}O_2$ , containing branched chains. C. S.

**Ferric Compounds of Some Hydroxy-acids of the Fatty Series.** I. AD. PAIRA (*Ber.*, 1914, 47, 1773—1776).—The compounds described are analogous in constitution to the salts of salicylato-ferric acid prepared by Weinland (A., 1913, i, 1189). *Potassium diglycollatoferrate*,  $[Fe(O\cdot CH_2\cdot CO_2)_2]K, H_2O$ , is obtained as an apple-green precipitate when very concentrated solutions of ferric chloride and potassium glycolate are mixed; from diluter solutions the salt is precipitated by means of alcohol. The corresponding *sodium* salt has  $\frac{1}{2}H_2O$  of crystallisation.

When a mixture of ferric hydroxide (1 mol.) and glycollic acid (6 mols.) is kept cold and in the dark for a long time, a micro-crystalline, green powder of *diglycollatoferric acid*,  $[Fe(O\cdot CH_2\cdot CO_2)_2]H$ , is obtained; it is readily decomposed by water and liberates carbon dioxide from carbonates.

By the addition of sodium carbonate (0·5 mol.) to a solution of ferric chloride (1 mol.) and sodium tartrate (1 mol.), a yellow, sparingly soluble precipitate of *tartratoferric acid*,  $(C_4H_2O_6Fe)H$ , is obtained, which is readily soluble in alkalis; it is also obtained by the interaction of ferric hydroxide and tartaric acid. The *sodium* and *potassium tartratoferrates*,  $(C_4H_2O_6Fe)Na, 5H_2O$  and  $(C_4H_2O_6Fe)K, \frac{1}{2}H_2O$ , are obtained either from the free acid and the appropriate alkali, or from

ferric chloride and the alkali tartrates. They are very soluble in water, but can be recrystallised from dilute alcohol. Concentrated solutions, when dried on a glass plate, give large, brownish-yellow scales.

T. S. P.

**Thorium Ammonium Oxalate.** C. JAMES, C. F. WHITTEMORE, and H. C. HOLDEN (*J. Amer. Chem. Soc.*, 1914, **36**, 1853—1856).—Brauner (T., 1898, **73**, 961) has described two thorium ammonium oxalates,  $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$  and  $2\text{Th}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$ .

A study of the solubility curves of thorium and ammonium oxalates in presence of each other at  $25^\circ$  has now been made, and has indicated that at this temperature only two thorium ammonium oxalates exist (compare Hauser, A., 1912, i, 827).

E. G.

**Cryoscopic Studies on Complexes of Molybdic Acid.** I. A. MAZZUCHELLI and C. RANUCCI (*Gazzetta*, 1914, **44**, ii, 116—149. Compare A., 1913, ii, 817).—Cryoscopic and, in some cases, conductivity measurements have been made in order to ascertain the conditions of ionisation and polymerisation of the complexes formed by tartaric, malic, quinic and oxalic acids and their alkali salts with molybdic acid.

The molybdotartaric acids apparently undergo both marked ionisation, the extent of which increases with the content of molybdenum trioxide, and also polymerisation, but the degrees to which these changes occur cannot be determined exactly. Comparison of the results obtained with Grossmann and Krämer's polarimetric and conductivity data (A., 1904, i, 850) leads to the conclusion that this behaviour is due to association between the anions and the undissociated molecules where these exist in proportions which do not differ greatly. It seems beyond doubt that in very dilute solutions of molybdotartrates and in the more concentrated ones of molybdotartaric acids, the molecular weights tend to assume their simple values. Similar behaviour was observed by Pick (A., 1912, ii, 1131) in the case of hydrofluoric acid. Analogous relations, although less well defined, hold with the complexes formed by malic acid, but the available data are here less numerous.

Schneider's molybdoquinic acid,  $2\text{C}_7\text{H}_{12}\text{O}_6 \cdot \text{MoO}_3$ , and its potassium salt have the simple molecular weights and undergo marked ionisation, which varies considerably with the concentration. Cryoscopic, conductivity and polarimetric measurements render improbable the existence of a second acid of the composition  $\text{C}_7\text{H}_{12}\text{O}_6 \cdot \text{MoO}_3$ .

Monomolybdo-oxalic acid, its sodium salt, and also sodium dimolybdo-oxalate have the simple molecular weights and are normally ionised.

T. H. P.

**Synthetic Preparation of *dl*-Glyceraldehyde.** EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1914, **36**, 1908—1916).—A detailed description is given of a method of obtaining crystalline glyceraldehyde in large quantities. The method followed is essentially that of Wohl (A., 1898, i, 556) and Wohl and Neuberg (A., 1901, i, 12), but certain modifications are recommended, especially in the manipulation



of the glyceraldehyde itself, which facilitate the production of the compound and its isolation in a crystalline form. E. G.

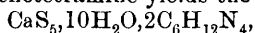
**Biochemical Preparation of  $\beta$ -Ethyl Galactoside.** EM. BOURQUELOT and G. MOUGNE (*J. Pharm. Chim.*, 1914, [vii], **10**, 157—163. Compare A., 1913, i, 498).—The conditions most suitable for the formation of the galactoside are as follows: Two litres of 80% ethyl alcohol are mixed with 100 grams of galactose and 16 grams of emulsin, and the mixture is kept at  $38^{\circ}$ ; after eight days, a further quantity of emulsin is added, and the action allowed to proceed for a month. The mixture is then filtered, the filtrate is evaporated under reduced pressure, and the excess of galactose destroyed by fermentation with bottom yeast in the presence of dextrose.

$\beta$ -Ethyl galactoside crystallises in colourless needles,  $[\alpha]_D^{20} - 7.21^{\circ}$ , m. p.  $161-162^{\circ}$ . W. P. S.

**The Most Appropriate Experimental Conditions for the Preparation of  $\alpha$ -Methyl Glucoside and  $\alpha$ -Ethyl Glucoside.** A. AUBRY (*J. Pharm. Chim.*, 1914, [vii], **10**, 202—207. Compare this vol., i, 144).—In the laboratory  $\alpha$ -methyl glucoside is best prepared by working with the following proportions of reagents. To 1800 grams of methyl alcohol is added a solution of 500 grams of dextrose in 4 litres of distilled water, and then 3 litres of a 10% maceration of dried bottom yeast, and the whole is made up to 10 litres. The mixture is allowed to ferment at  $18-20^{\circ}$  until the rotation of the solution, which to start with is  $+5^{\circ}18'$ , has increased to  $11^{\circ}30'$ , this taking about six weeks. The liquid is then neutralised with calcium carbonate, boiled and filtered, and the filtrate distilled to half its volume under reduced pressure. The excess of dextrose is destroyed by fermentation with baker's yeast, the liquid again neutralised, boiled and filtered, the filtrate being evaporated to dryness under reduced pressure. From the dry residue, the  $\alpha$ -methyl glucoside is extracted with alcohol and allowed to crystallise, the yield being 150—200 grams.  $\alpha$ -Ethyl glucoside is similarly prepared, using the same proportions, the final purification being carried out by crystallisation from ethyl acetate, and finally from acetone. W. G.

**Calcium Polysulphides.** G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 8—12).—In investigating the polysulphides of calcium the author has made use of the fixation of labile hydrated salts by means of hexamethylenetetramine (compare Barbieri and Calzolari, A., 1911, i, 184).

The interaction of ammonium pentasulphide and calcium chloride in presence of hexamethylenetetramine yields the compound,



which forms non-hygroscopic, orange-yellow prisms and dissolves in water with partial decomposition and separation of sulphur. Use of a solution of ammonium polysulphide less rich in sulphur results in the formation of the compound,  $\text{CaS}_4, 10\text{H}_2\text{O}, 2\text{C}_6\text{H}_{12}\text{N}_4$ , which crystallises in orange prisms and dissolves in water without apparent alteration.

Either of these compounds or a mixture of them is obtainable by the action of hexamethylenetetramine on calcium polysulphide solutions prepared from sulphur and either lime or calcium hydrosulphide; the solutions thus obtained may contain calcium polysulphides with lower proportions of sulphur, but these would appear to form readily soluble additive compounds with hexamethylenetetramine. T. H. P.

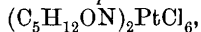
**Anhydrification of Glycine.** L. BALBIANO (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 893—896).—The assumption made by Maillard ("Genèse des Matières protéiques et des Matières humiques. Action de la glycérine et des sucres sur les acides  $\alpha$ -aminés," Paris) that the action of glycerol on glycine (compare Balbiano and Trasciatti, A., 1900, i, 632; Balbiano, A., 1901, i, 454) is merely that of a dehydrating agent is shown to be inaccurate; when heated with naphthalene or cymene, glycine is also converted more or less completely into an anhydride. T. H. P.

**New Physiologically Active Derivatives of Choline.** ARTHUR JAMES EWINS (*Biochem. J.*, 1914, 8, 366—373).—The following new bases all resemble muscarine in their physiological action, but not one of them is identical with the natural base. *Formylcholine*,  $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CHO}$ , is obtained by boiling a solution of choline chloride in formic acid, and isolated in the form of its *platinichloride*,  $(\text{C}_6\text{H}_{14}\text{O}_2\text{N})_2\text{PtCl}_6$ , orange-red octahedra from hot water, m. p. 255—256°. The *aurichloride*,  $\text{C}_6\text{H}_{14}\text{O}_2\text{N}\cdot\text{AuCl}_4$ , forms thin, golden-yellow hexagonal plates, m. p. 175°. *Choline propyl ether*,  $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPr}$ , is prepared by acting on  $\beta$ -iodoethyl propyl ether (Karvonen, A., 1909, i, 202) with alcoholic trimethylamine solution. The *platinichloride*,  $(\text{C}_8\text{H}_{20}\text{ON})_2\text{PtCl}_6$ , crystallises in orange-red prisms, m. p. 246°. *Choline ether*,  

$$\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH})_2$$

prepared by treating  $\beta\beta$ -di-iodoethyl ether with a slight excess of alcoholic trimethylamine solution, when the *iodide*,  $\text{C}_{10}\text{H}_{26}\text{ON}_2\text{I}_2$ , crystallises in thin, rectangular plates, m. p. 275°. The *chloride* forms rhombic plates, m. p. above 280°. The *platinichloride* crystallises in clusters of small prisms, m. p. 226° (decomp.); *aurichloride*, golden-yellow, rhombic plates, m. p. 269°. *Trimethyl- $\beta$ -cyanoethylammonium hydroxide*,  $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$ , is prepared from  $\beta$ -chloropropionitrile and trimethylamine. The *chloride*,  $\text{C}_6\text{H}_{13}\text{N}_2\text{Cl}$ , separates in prisms, 228—229° (decomp.); *platinichloride*, brownish-yellow, aggregated octahedra, m. p. 249—250° (decomp.); *aurichloride*, thin, golden-yellow needles, m. p. 213—214°. *Trimethyl- $\beta$ -aminoethylammonium hydroxide*,  $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , is obtained by heating choline nitric acid ester with the calculated amount of ammonia in alcoholic solution. The *aurichloride*,  $\text{C}_5\text{H}_{15}\text{N}_2(\text{AuCl}_4)_2$ , crystallises in yellowish-brown, rectangular prisms, m. p. 263°. *N-Dimethyloxazolinium hydroxide*,  $\text{OH}\cdot\text{NMe}_2\cdot\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2\quad\text{O} \end{matrix}$ , was prepared by treating dimethylaminomethyl alcohol with one molecular proportion

of ethylene chlorohydrin. The hydroxycholine first produced then loses one molecule of water. The *platinichloride*,



orange-red, rectangular prisms, has m. p. 237—238°; *aurichloride*,  $\text{C}_5\text{H}_{12}\text{ON}\cdot\text{AuCl}_4$ , golden-yellow prisms, m. p. 279°; *mercurichloride*,  $\text{C}_5\text{H}_{12}\text{ON}\cdot 2\text{HgCl}_2$ , hexagonal prisms, m. p. 244—245°.

The following ethers of "formo-choline" [trimethylhydroxymethylammonium hydroxide] are prepared by the action of trimethylamine on the corresponding iodomethyl ethers. The *methyl ether*,  $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{OMe}$ , was analysed in the form of its *iodide*,  $\text{C}_5\text{H}_{14}\text{ONI}$ , white, glistening, hygroscopic plates, m. p. 84°; *platinichloride*,  $(\text{C}_5\text{H}_{14}\text{ON})_2\text{PtCl}_6$ , orange-red, rhombic prisms, m. p. 234° (decomp.); and *aurichloride*,  $\text{C}_5\text{H}_{14}\text{ON}\cdot\text{AuCl}_4$ , golden-yellow needles, m. p. 135—136°. The *iodide of ethyl ether*,  $\text{OEt}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ , thin plates, has m. p. 94°; *platinichloride*, orange-red, m. p. 241—242°; *aurichloride*, golden-yellow leaflets, m. p. 138—139°. The *propyl ether iodide*,  $\text{OPr}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ , needles, m. p. 108°; *platinichloride*, orange-red needles, m. p. 236—237°; *aurichloride*, golden-yellow leaflets, m. p. 114°. The *butyl ether iodide*,  $\text{C}_4\text{H}_9\cdot\text{O}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ , glistening plates, m. p. 98°; *platinichloride*, orange-red octahedra, m. p. 243—244°; *aurichloride*, golden-yellow leaflets, m. p. 81°.

H. W. B.

**Imide of Chlorocamphoric Acid.** ANNA MANNESSIER (*Gazzetta*, 1914, 44, i, 697—703. Compare Oddo and Mannessier, A., 1910, i, 399).—When camphorimide is heated for four hours at 120—125° in a sealed tube with phosphorus pentachloride and light petroleum, chlorocamphorimide, m. p. 292—293°, is formed, identical with that obtained by Scheiber and Knothe (A., 1912, i, 542) in another way. The substance is very stable; it is not affected by boiling concentrated potassium hydroxide, or by sodium acetate and acetic acid. The *silver salt*,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{NClAg}$ , was prepared. The *methyl derivative*,  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{NCl}$ , forms prismatic crystals, m. p. 146—147°. The *acetyl derivative* (prepared by the action of acetic anhydride),  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{NClAc}$ , has m. p. 160°, and is very unstable. The *benzoyl derivative* can be prepared only by means of the Grignard reaction; it crystallises in needles, m. p. about 200°.

*Bromochlorocamphorimide*,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{NClBr}$ , forms acicular crystals, m. p. 172—174°, and is prepared by the action of bromine on the chloroimide in alkaline, aqueous-alcoholic solution. R. V. S.

**Chlorodithiocamphorimide.** ANNA MANNESSIER (*Gazzetta*, 1914, 44, i, 703—706. Compare preceding abstract and Oddo and Mannessier, A., 1910, i, 399).—When chlorocamphorimide is heated at 200—220° with phosphorus pentasulphide until the evolution of gas ceases, and the mass then extracted with benzene, *chlorodithiocamphorimide*,  $\text{C}_{10}\text{H}_{14}\text{NS}_2\text{Cl}$ , is obtained; it forms golden-yellow scales, m. p. 179·5°. When it is boiled for some hours with alkali hydroxides, the solution on acidification deposits a white, amorphous *substance*, m. p. 205°. Chlorothiocamphorimide dissolves unchanged in concentrated

sulphuric acid, giving a rose-red coloration. When heated at  $250^{\circ}$  for three hours in a sealed tube with quinoline, it reacts with this substance. On reduction with sodium and alcohol, chlorothiocomphorimide yields camphidine.

R. V. S.

**The Blue Iron-cyanogen Compounds.** H. E. WILLIAMS (*J. Chem. Met. Min. Soc. S. Africa*, 1914, 15, 1—5).—See P., 1913, 29, 32.

**Action of Nitric Acid on Iodoanil.** LATHAM CLARKE and E. K. BOLTON (*J. Amer. Chem. Soc.*, 1914, 36, 1899—1908).—By the action of nitric acid on chloranil, Stenhouse (T., 1870, 8, 6) obtained chloropicrin and oxalic acid. It has now been found that the action of nitric acid on iodoanil is quite different; the products in this case are iodic anhydride and di-iodomaleic acid, but neither iodopicrin nor oxalic acid can be detected.

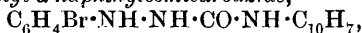
*Sodium di-iodomaleate* forms small, white plates. The *aniline salt*,  $C_2I_2(CO_2H)_2 \cdot NH_2Ph$ , decomposes at about  $152^{\circ}$ ; when heated with glacial acetic acid it is converted into the *phenylimide*,  $C_2I_2(CO)_2NPh$ , m. p.  $171$ — $172^{\circ}$ , which crystallises in small, yellow prisms, and reacts with aniline to form anilinomalephenylimide. In preparing di-iodomalephenylimide, another *compound*, m. p.  $261^{\circ}$ , is sometimes obtained which forms small, yellow needles and is probably anilino-iodomalephenylimide. When di-iodomaleic acid is heated with *p*-toluidine and glacial acetic acid, *p*-toluidinomale-*p*-tolylimide is produced. By the action of phenylhydrazine on di-iodomaleic acid, the *phenylhydrazide*,  $C_2I_2(CO)_2N \cdot NHPh$ , m. p.  $170^{\circ}$ , is obtained together with a smaller quantity of a *substance*, m. p.  $226^{\circ}$  (decomp.).

When di-iodomaleic acid is heated with water at  $100^{\circ}$  in a sealed tube, there are obtained carbon dioxide, formaldehyde, hydriodic acid, a little free iodine, and a brown oil from which two white, crystalline substances can be isolated. These substances were not completely investigated, but one of them, m. p.  $95$ — $96^{\circ}$ , may possibly be di-iodoacetic acid, and the other, m. p.  $182$ — $184^{\circ}$ , penta-iodoethane.

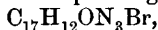
E. G.

**Azoimide of  $\alpha$ -Naphthylcarbamic Acid.** Action of Grignard's Reagent on the Azoimides of Carbamic Acid. E. OLIVERI-MANDALÀ (*Gazzetta*, 1914, 44, i, 662—670).— *$\alpha$ -Naphthylcarbamoyle-azoimide*,  $C_{10}H_7 \cdot NH \cdot CO \cdot N_3$ , is obtained by the interaction of  $\alpha$ -naphthylcarbimide and azoimide (or sodium azoimide and hydrochloric acid) in ethereal solution; it forms silky crystals, m. p.  $119$ — $120^{\circ}$ . When treated with an alcoholic solution of phenylhydrazine, it yields *phenyl- $\alpha$ -naphthylsemicarbazide*,  $NHPh \cdot NH \cdot CO \cdot NH \cdot C_{10}H_7$ , which forms silky crystals, m. p.  $225$ — $226^{\circ}$ . The semicarbazide is oxidised by ferric chloride to the corresponding *azo-compound*,  $C_{17}H_{13}ON_3$ , which begins to decompose at  $170^{\circ}$ , but melts sharply at  $183$ — $184^{\circ}$ .

*$\alpha$ -Naphthylcarbamoyle-azoimide* reacts with *p*-bromophenylhydrazine, giving *p*-bromophenyl- *$\alpha$ -naphthylsemicarbazide*,



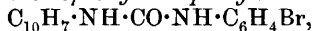
m. p. 230°. On oxidation with ferric chloride, or, better, by the action of nitrous acid, it yields the corresponding azo-derivative,



which forms golden-yellow leaflets, m. p. 163—164°.

On treatment with bromine in benzene solution, 4-bromo- $\alpha$ -naphthylcarbamoylazoimide,  $\text{C}_{11}\text{H}_7\text{ON}_4\text{Br}$ , is obtained; it forms silky needles, m. p. 150° (decomp.). When treated with aniline, it yields *s*-phenyl-4-bromo- $\alpha$ -naphthylcarbamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\text{Br}$ , which forms acicular crystals, m. p. 235° (decomp.). When boiled with alcoholic sodium hydroxide, 4-bromo- $\alpha$ -naphthylcarbamoylazoimide yields *s*-di-4-bromo- $\alpha$ -naphthylcarbamide,  $\text{CO}(\text{NH}\cdot\text{C}_{10}\text{H}_6\text{Br})_2$ , which crystallises in silky needles, m. p. 145—146°.

On boiling *p*-bromoaniline with  $\alpha$ -naphthylcarbamoylazoimide in alcoholic solution, *s*-*p*-bromophenyl- $\alpha$ -naphthylcarbamide,



m. p. 232°, is obtained.

When ethylcarbamoylazoimide is subjected to the Grignard reaction with magnesium phenyl bromide, ethylbenzamide,  $\text{NH}\cdot\text{Et}\cdot\text{COPh}$ , is produced. Similarly, from phenylcarbamoylazoimide, phenylbenzamide is obtained. Phenylcarbamoylazoimide and magnesium ethyl iodide yield phenylpropionamide.

R. V. S.

The Question of Priority in Connexion with the Replacement of Alkylloxy by means of Magnesium Alkyl Haloids. ERNST SPÄTH (*Ber.*, 1914, 47, 2260—2261).—A denial of the claim for priority recently advanced by Tschitschibabin and Jelgasin (this vol., i, 1065).

J. C. W.

Study of the Reaction of Alkali Salts of Sulphonic Acids with Alkali Phenoxides by Dry Distillation. EDGAR H. NOLLAU and LLOYD C. DANIELS (*J. Amer. Chem. Soc.*, 1914, 36, 1885—1891).—The preparation of phenols by the interaction of alkali sulphonates and hydroxides suggested that aromatic ethers should be similarly obtainable from alkali sulphonates and phenoxides. Experiments have therefore been carried out on the dry distillation of alkali sulphonates with alkali phenoxides and have shown that this is a convenient method for preparing aryl ethers of phenols. The yields are smaller than those obtainable by Ullmann and Sponagel's method (*A.*, 1907, i, 38), but, in some cases, the compounds used can be more directly prepared. The reaction probably takes place in accordance with the equation:  $\text{R}\cdot\text{SO}_3\text{M} + \text{R}'\cdot\text{OM} = \text{R}'\cdot\text{OR} + \text{M}_2\text{SO}_3$ , in which R may be the phenyl radicle or one of its homologues, provided that no long side-chain is present, or a methyl group, whilst R' may be a phenyl or aminophenyl radicle.

The following ethers have been prepared by this method: Diphenyl ether; phenyl *p*-tolyl ether; phenyl *o*-4-xyllyl ether,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OPh}$ , m. p. 35—37°, b. p. 104—105° (corr.)/49.4 mm., which forms short, colourless needles; *p*-aminodiphenyl ether; phenyl *o*-amino-*p*-tolyl ether,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OPh}$ , b. p. 102—104°/67.4 mm.; phenyl thymyl ether; and anisole.

E. G.

Dibenzylthioresorcinol and Dibenzylthioquinol [1:3- and 1:4-Dibenzylthiolbenzenes]. CESARE FINZI (*Gazzetta*, 1914, **44**, i, 598—607).—[With VITTORIA FURLOTTI].—1:3-Dibenzylthiolbenzene has m. p.  $60^{\circ}$  (Zincke and Krüger, A., 1913, i, 45, gave  $50^{\circ}$ ). When an ethereal solution of the substance is treated with bromine, a dibromo-derivative,  $C_{20}H_{16}S_2Br_2$ , is obtained; it crystallises in large tablets, m. p.  $107^{\circ}$ . When 1:3-dibenzylthiolbenzene is kept in contact with concentrated nitric acid, a mononitro-derivative,  $C_{20}H_{17}O_2NS_2$ , is obtained; it forms yellow prisms, m. p.  $92^{\circ}$ .

1:4-Dibenzylthiolbenzene,  $C_6H_4(S \cdot CH_2Ph)_2$ , is obtained by condensation of thioquinol with benzyl chloride in the presence of sodium hydroxide. It forms lustrous scales, m. p.  $127^{\circ}$ . When treated with hydrogen peroxide, potassium dichromate and acetic acid, or nitric acid, it yields the sulphoxide,  $C_{20}H_{18}O_2S_2$ , m. p.  $241^{\circ}$ . On treatment with hydrogen bromide or hydrogen iodide, the sulphoxide yields only 1:4-dibenzylthiolbenzene. The sulphone,  $C_{20}H_{18}O_4S_2$ , is obtained by boiling an acetic acid solution of 1:4-dibenzylthiolbenzene with hydrogen peroxide; it becomes brown at  $280^{\circ}$  and melts at about  $310^{\circ}$ .

1:4-Dibenzylthiolbenzene reacts readily with bromine in chloroform solution, yielding a perbromide,  $C_{20}H_{18}S_2Br_4$ , which is a red, crystalline substance, m. p.  $85^{\circ}$ . On keeping or on boiling with alcohol, the perbromide loses all its bromine, leaving 1:4-dibenzylthiolbenzene. When the perbromide is boiled with water or alkali, however, the sulphoxide m. p.  $241^{\circ}$  is formed.

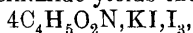
1:4-Dibenzylthiolbenzene periodide,  $C_{20}H_{18}S_2I_4$ , forms brown crystals, m. p.  $120^{\circ}$ . It is much more stable than the perbromide. It decomposes very slowly when boiled with water, rapidly when boiled with alkali, but 1:4-dibenzylthiolbenzene is formed, not the sulphoxide. The sulphoxide is produced, however, when the periodide is shaken with silver acetate in acetic acid solution. R. V. S.

Periodides of Acid Amides and their Additive Products with Metallic Salts. Substances of Exceptionally High Molecular Weight. F. J. MOORE and RUTH M. THOMAS (*J. Amer. Chem. Soc.*, 1914, **36**, 1928—1937).—In the course of an investigation of benzoyl-bromoamide (Moore and Cederholm, A., 1906, i, 831), an attempt was made to prepare benzoyliodoamide for comparison by dissolving iodine in an aqueous solution of sodium hydroxide, adding powdered benzamide and acidifying with acetic acid. Instead of the desired compound, however, a periodide,  $3C_6H_5 \cdot CO \cdot NH_2 \cdot NaI \cdot I_2$ , was produced, which crystallised in long, slender, green needles. This substance can be readily prepared by heating a mixture of benzamide, sodium iodide, and iodine with water or nitrobenzene. The corresponding potassium compound, m. p.  $128$ — $130^{\circ}$ , was also prepared. A perbromide of similar character was obtained from benzamide, potassium bromide, and bromine. Benzamide, potassium bromide, and iodine yield a compound which forms greyish-green needles. Dibenzamide, potassium iodide, and iodine furnish a green substance, resembling the corresponding benzamide compound. The compound,  $2C_6H_5 \cdot CO \cdot NH_2 \cdot HI \cdot I_2$ , was obtained in the form of flakes with a greenish-black iridescence.

The barium and copper compounds,  $6C_6H_5 \cdot CO \cdot NH_2 \cdot BaI_2 \cdot I_4$  and

$8C_6H_5 \cdot CO \cdot NH_2, CuI, I_6$ , are described. Cobalt and nickel iodides yield similar products. The compounds,  $(3C_6H_5 \cdot CO \cdot NH_2, KI, I_2)_6$  (or 7),  $HgI_2$ , m. p. about  $50^\circ$ , and  $(3C_6H_5 \cdot CO \cdot NH_2, KI, I_2)_6, PbI_2$ , are remarkable for their exceptionally high molecular weight, that of the latter being 5160. A crystalline compound of benzamide, mercuric iodide, hydrogen iodide, and iodine was prepared, but was too unstable for analysis.

Indications were obtained of the formation of similar periodides from *p*-toluamide, *p*-bromobenzamide, phthalimide, benzenesulphonamide, and various anilides. Succinimide yields the compound,



which has already been described by Piutti (A., 1896, i, 364).

E. G.

**Dinitro-*m*-arylsalicylic Acids, Mononitro-*m*-arylsalicylic Acids, and *m*-Nitroxanthenes, and their Derivatives.** ATTILIO PURGOTTI (*Gazzetta*, 1914, 44, i, 641—646).—The *m*-dinitroarylsalicylic [dinitro-*o*-aryloxybenzoic] acids described below are prepared by heating sodium 2-chloro-3:5-dinitrobenzoate with the sodium derivatives of phenols and cresols at a temperature not greater than  $140^\circ$ .

3:5-Dinitro-2-phenoxybenzoic acid,  $OPh \cdot C_6H_2(NO_2)_2 \cdot CO_2H$ , forms pale yellow crystals, m. p.  $148^\circ$ . Its ethyl ether has m. p.  $98^\circ$ .

3:5-Dinitro-2-*o*-tolylloxybenzoic acid forms pale yellow crystals, m. p.  $130^\circ$ . Its ethyl ether has m. p.  $88^\circ$ .

3:5-Dinitro-2-*m*-tolylloxybenzoic acid crystallises in yellow needles, m. p.  $164^\circ$ .

3:5-Dinitro-2-*p*-tolylloxybenzoic acid has m. p.  $157.5^\circ$ .

When 3:5-dinitro-2-phenoxybenzoic acid is treated with concentrated sulphuric acid on the water-bath, it does not yield the corresponding xanthone; at a higher temperature (about  $150^\circ$ ) it is sulphonated, yielding the sulphonic acid,  $SO_3H \cdot C_6H_4 \cdot O \cdot C_6H_2(NO_2)_2 \cdot CO_2H$ , which crystallises in scales, m. p. above  $350^\circ$  (decomp.).

The following acids were obtained from 2-chloro-3-nitrobenzoic acid in the same way as those already described, but copper powder must be added as a catalyst and a temperature of  $170^\circ$  is needed.

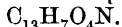
3-Nitro-2-phenoxybenzoic acid forms colourless needles, m. p.  $168^\circ$ .

3-Nitro-2-*o*-tolylloxybenzoic acid forms colourless leaflets, m. p.  $187$ — $188^\circ$ . The corresponding *m*- and *p*-acids have m. p.  $172^\circ$  and  $165^\circ$ , respectively.

3-Nitro-2-methylisopropylphenoxybenzoic acid (from thymol) forms colourless leaflets, m. p.  $177^\circ$ .

3-Nitro-2-*m*-hydroxyphenoxybenzoic acid has m. p.  $212^\circ$ .

3-Nitro-2-phenoxybenzoic acid when treated with sulphuric acid on the water-bath readily yields the corresponding nitroxanthone,

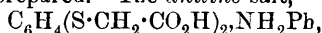


This on reduction with ammonium sulphide give the aminoxanthone,  $C_{13}H_9O_2N$ , which forms yellow laminæ, m. p.  $205^\circ$ , and gives an acetyl-derivative,  $C_{14}H_{11}O_3N$ , m. p.  $178^\circ$ . The aminoxanthone can be diazotised. The solution of the diazo-compound on boiling yields hydroxyxanthone. The diazo-compound gives a yellow precipitate with phenol, and a scarlet precipitate, m. p.  $255^\circ$ , with  $\beta$ -naphthol.

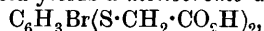
R. V. S.

**Sulphosalicylic Acid and its Hexamethylenetetramine Salts.** J. D. RIEDEL (*Chem. Zentr.*, 1914, i, 1896—1897; from *Riedel's Ber.*, 1914, 17—23).—When crystallised from water and dried below 100°, sulphosalicylic acid contains 2H<sub>2</sub>O, and has m. p. 108—115°; the anhydrous acid is obtained by drying the substance at 105° for a long time; it decomposes at about 200°. The ready solubility of sulphosalicylic acid in water does not afford a means of detecting the presence in it of salicylic acid, since the solubility is not affected by quantities of up to 4% of the latter. *Hexal* (primary) and *neohexal* (sec.-hexamethylenetetramine sulphosalicylate) each contain 1H<sub>2</sub>O. The former decomposes at about 190° and the latter at 180° (compare this vol., i, 45). *Hexal* may be obtained in the anhydrous state by drying under reduced pressure at 100°, but *neohexal* decomposes under these conditions. Anhydrous *neohexal* may, however, be prepared from anhydrous sulphosalicylic acid, hexamethylenetetramine and absolute alcohol; it crystallises in prisms, m. p. 180°. W. P. S.

***m*- and *p*-Phenylenedithiolacetic Acids.** C. FINZI (*Gazzetta*, 1914, 44, i, 579—587. Compare this vol., i, 294).—*m*-Phenylenedithiolacetic acid, C<sub>6</sub>H<sub>4</sub>(S·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, can be obtained by the condensation of thioresorcinol with chloroacetic acid in alkaline alcoholic solution; it crystallises in triclinic prisms, m. p. 132°. The *silver* salt, C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>S<sub>2</sub>Ag<sub>2</sub>, was prepared. The *aniline* salt,



has m. p. 134°. The acid yields a *monobromo*-derivative,



m. p. 164°. When the acid is oxidised with hydrogen peroxide, the corresponding *sulphoxide* and *sulphone* are obtained as white, amorphous substances. Their *silver* salts have the compositions C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>S<sub>2</sub>Ag<sub>2</sub> and C<sub>10</sub>H<sub>8</sub>O<sub>8</sub>S<sub>2</sub>Ag<sub>2</sub>, respectively.

*p*-Phenylenedithiolacetic acid, C<sub>6</sub>H<sub>4</sub>(S·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, is obtained by the condensation of thioquinol and chloroacetic acid in alcoholic solution; it crystallises in slightly yellow prisms. The *sodium* salt, C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>S<sub>2</sub>Na<sub>2</sub>, and the *silver* salt, C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>S<sub>2</sub>Ag<sub>2</sub>, were prepared. The *aniline* salt, C<sub>6</sub>H<sub>4</sub>(S·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>·2NH<sub>2</sub>Ph, forms long prisms which soften at 123° and are completely melted at 163°. The *sulphoxide* has m. p. 168° (decomp.) and gives a *silver* salt, C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>S<sub>2</sub>Ag<sub>2</sub>. The *sulphone* has m. p. 226° (decomp.) and gives a *silver* salt, C<sub>10</sub>H<sub>8</sub>O<sub>8</sub>S<sub>2</sub>Ag<sub>2</sub>. *p*-Phenylenedithiolacetic acid does not react with bromine.

As thioquinol is present in all samples of thioresorcinol, small quantities of *p*-phenylenedithiolacetic acid are produced in the preparation of *m*-phenylenedithiolacetic acid; their removal can be effected by carrying out the condensation in particular conditions which are described. R. V. S.

**Identity of Hydronaringenin with Phloretin.** H. HEINRICH FRANCK (*Chem. Zentr.*, 1914, ii, 253—254; from *Beitr. Phys.*, 1, 179—186).—By the catalytic hydrogenation of naringenin (Tutin, T., 1910, 97, 2054) in alcoholic solution with palladous chloride and hydrogen, a dihydronaringenin identical with phloretin was obtained.



The *tetra-acetyl* derivative forms prismatic plates, m. p.  $96^{\circ}$ . When heated with aqueous potassium hydroxide in a reflux apparatus, dihydronaringenin yields phloroglucinol and *p*-hydroxycoumaric acid.

Phloretin obtained by the hydrogenation of naringenin failed to induce glycosuria when 1.5 gram was given to a dog (10 kilos.). The positive results obtained with commercial phloretin are due to the presence of phlorrhizin which was found in amounts up to 30%.

N. H. J. M.

**Catalytic Decomposition of Borneol in the Presence of Metals and of Metallic Oxides.** J. ALOY and V. BRUSTIER (*J. Pharm. Chim.*, 1914, [vii], 10, 49—51).—Borneol is converted into camphor and hydrogen when it is slowly passed over hot, finely-divided copper. The yield of camphor increases regularly from  $240^{\circ}$  to  $280$ — $300^{\circ}$ , and is quantitative at the latter temperature if the vapours are led sufficiently slowly over the copper. Above  $300^{\circ}$ , the proportion of camphor decreases; at  $350^{\circ}$  it is still considerable, but above  $400^{\circ}$  yellow liquids are formed resembling the terpenes. With reduced nickel, camphor is obtained at  $350^{\circ}$ , whilst at  $450^{\circ}$  liquid terpenes are produced. Iron gives less satisfactory results.

The behaviour of borneol in the presence of the oxides of aluminium, tungsten, uranium, and thorium has also been studied; the latter gives the best yields. The experiments are performed in the same manner as with the metals; the most favourable temperature is  $350^{\circ}$  and must not exceed  $400^{\circ}$ . The product is a pale yellow liquid, b. p.  $150$ — $180^{\circ}$ ,  $D^{20}$  0.8637,  $n^{20}$  1.472,  $\alpha_D + 1.46^{\circ}$ . On fractionation it yields pinene, b. p.  $156$ — $160^{\circ}$ ,  $D^{20}$  0.871,  $n^{20}$  1.472, and a smaller portion, b. p.  $175$ — $180^{\circ}$ , the nature of which could not be definitely proved.

Terpenes are also formed by the decomposition of borneol in the presence of copper at about  $400^{\circ}$ , and the product can be separated into bicyclic terpenes, b. p.  $155$ — $160^{\circ}$ ,  $D^{20}$  0.860, and monocyclic hydrocarbons, b. p.  $170$ — $175^{\circ}$ ,  $D^{20}$  0.850.

H. W.

**Action of Ammonium Hydrogen Sulphide on Thujone and on Carone.** C. AGOSTINELLI (*Gazzetta*, 1914, 44, ii, 111—115).—When heated in alcoholic solution with ammonium hydrogen sulphide, thujone is transformed into *isothujone*, this then reacting further with the sulphide to form a mixture of polysulphides; among the products of decomposition of the latter, only *thioisothujone* could be detected.

Under similar treatment, carone yields no isomeride, although its transformation into carvenone, which is effected readily by the action of heat or of concentrated sulphuric acid, would be expected. The products obtained were sulphides of the compositions  $(C_{10}H_{17})_2S$  and  $C_{40}H_{65}S_5$ .

T. H. P.

**Essential Oil of *Artemisia arborescens*, L.** T. JONA (*Ann. Chim. Applicata*, 1914, 2, 63—68).—Distillation of 2 quintals of the dried shoots of *Artemisia arborescens* yielded 1140 grams of a dark blue, somewhat viscous, aromatic oil,  $D^{15}$  0.9458, saponification number 29.3, acid number 9.8, ester number 19.5, ester number after acetylation

50.0; it remains clear at  $-15^{\circ}$ . The oil contains: (1) 13.94% of alcohols of the formula  $C_{10}H_{18}O$ , consisting of thujol and a small proportion of another alcohol, which is apparently borneol; 8.58% of the alcohols are in the free state and the remaining 5.36% in the form of esters of fatty acids. (2) Formic, acetic, isovaleric, pelargonic, palmitic and stearic acids, partially esterified by the above alcohols. (3) About 13% of  $\beta$ -tanacetone. (4) Various hydrocarbons of high boiling points.

T. H. P.

Oils of the Coniferæ. I. The Leaf and the Twig Oils of Cuban and Longleaf Pines and the Cone Oil of Longleaf Pine. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1914, 6, 723—727).—The percentage compositions of the oils were found to be as follows:

	Cuban. Leaf and twig.	Longleaf.		
		Leaf and twig.	Leaf.	Cone.
Furfuraldehyde.....	trace	trace	trace	trace
<i>l</i> - $\alpha$ -Pinene.....	4	8—9	2	39—40*
<i>l</i> -Camphene.....	10	13—14	12—13	12
<i>l</i> - $\beta$ -Pinene.....	35—36	44	50	25
Dipentene.....	8	5	5	6—7
Bornyl ester (as acetate).....	3.5	2.4	2	1.4
Free alcohol (as <i>l</i> -borneol)...	11.4	10.0	9.8	7.6
<i>d</i> -Cadinene.....	18—19	10—11	11	1—2
Loss, etc....	9	6	7.5	6.5

\* *d*- $\alpha$ -Pinene.

W. P. S.

Components of Essential Oil of *Santolina chamæcyparissus*. L. FRANCESCONI and N. GRANATA (*Gazzetta*, 1914, 44, ii, 150—162. Compare A., 1911, i, 1001; 1912, i, 38).—This essential oil contains two isomeric unsaturated ketones, termed  $\alpha$ - and  $\beta$ -santolinenones. The  $\alpha$ -compound is optically inactive and probably racemic, since its molecule contains an asymmetric carbon atom and its hydroxylamino-oxime can be separated by means of *d*-camphorsulphonic acid into the two antipodal forms. The  $\beta$ -ketone is also inactive and probably racemic. The oil contains further a levorotatory  $\gamma$ -ketone, yielding a dextrorotatory oxime. These three ketones do not combine readily with sodium hydrogen sulphite or with free hydrazine and do not yield crystalline products with phenylhydrazine, bromophenylhydrazine or bromine. With hydroxylamine, the  $\alpha$ -compound gives first the oxime and then the hydroxylamino-oxime, but no simple hydroxylamine; the  $\beta$ -ketone yields no hydroxylamino-oxime, but a liquid oxime or the hydroxylamine, one or the other predominating according to the conditions; the  $\gamma$ -compound gives only an oxime, and appears to be saturated and of the camphor type. The separation of the three ketones is described.

Like most oximes of saturated and unsaturated ketones, those of  $\alpha$ - and  $\beta$ -santolinenones yield the corresponding ketones when treated with acids, which do not effect isomerisation of these ketones. Consequently the double linking cannot be so placed that it migrates readily, its  $\alpha:\beta$ -position being thus confirmed. The oxime of

$\gamma$ -santolinenone is not easily converted into the ketone by the action of acid and thus resembles camphoroxime.

$\gamma$ -Santolinenoneoxime,  $C_{19}H_{17}ON$ , forms large, rounded prisms, m. p. 116—117°,  $[\alpha]_D + 41^\circ$ . Its hydrochloride forms long prisms, m. p. 148—151°,  $[\alpha]_D + 64.31^\circ$ . T. H. P.

**Mesobilirubin.** HANS FISCHER (*Ber.*, 1914, 47, 2330—2333).—It was recently stated (this vol., i, 888) that bilirubin, like hæmin, may be reduced to a substance which yields methylethylmaleimide on subsequent oxidation. This substance, mesobilirubin, is now described. When shaken with sodium amalgam, it is further reduced to hemibilirubin, and, on the other hand, it is formed when hemibilirubin is heated with potassium methoxide. The by-product II, which is formed during the reduction of the bile pigment to hemibilirubin, also yields mesobilirubin under the latter conditions. There is, therefore, the same connexion between these compounds that there is between hæmin, mesoporphyrin and porphyrinogen, and it is suggested that the name "hemibilirubin," which gives a wrong idea of the relative weight of the molecule, should give place to *mesobilirubinogen*.

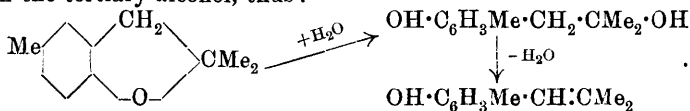
For the preparation of *mesobilirubin*,  $C_{32}H_{38}O_6N_4$  or  $C_{33}H_{42}O_6N_4$ , bilirubin was dissolved in 0.1*N*-sodium hydroxide and shaken with colloidal palladium in presence of hydrogen, using three portions of 2 c.c. of a 1% solution of the preparation for 5 grams of the pigment. The new pigment was then precipitated by acetic acid and obtained in sulphur-yellow, slender, felted needles or stout prisms, m. p. 315° (decomp.) which responded to Gmelin's reaction, but not to Ehrlich's aldehyde test.

During the distillation of a mixture of the esters of bilirubin and isophenopyrrolicarboxylic acids (this vol., i, 430) a deep yellow compound separated, which is now identified as an oxidation product, namely, *methyl xanthobilirubate*,  $C_{18}H_{24}O_3N_2$ . It forms slender prisms, m. p. 212°. J. C. W.

**The Pigments of Fusarium.** BEZSSONOFF (*Compt. rend.*, 1914, 159, 448—450).—Using the method of Willstätter and Miegl (compare A., 1907, i, 865) the author has isolated two pigments from the colouring matter of *Fusarium orobanchus*, one a yellow anthocyanin pigment, soluble in water and alcohol, the other a red carotene. The latter is identical with that described by Willstätter and Miegl, with respect to its behaviour towards solvents, being, however, more soluble in chloroform than in carbon disulphide. It crystallises in plates. It changes colour in solution under certain conditions, a violet modification being obtained in alcoholic solution, reddish-violet in solution in benzene, and yellow after boiling in cymene. The three modifications show a broad absorption band at the left of the spectrum and two narrow bands between this and the middle of the spectrum, all the bands showing gradual displacement in passing from the violet to the yellow modification. The yellow anthocyanin pigment crystallises on evaporating its aqueous solution, and is always accompanied by sugar. It behaves as a weak acid and readily combines with bases.

W. G.

**1:1:4-Trimethylcoumaranone.** K. VON AUWERS (*Ber.*, 1914, 47, 2334—2350).—In continuation of a study of 1-alkylcoumaranones (compare A., 1912, i, 1009) attempts have been made to prepare a 1:1-dialkyl derivative. In view of the mobility usually displayed by a halogen atom when attached to a tertiary carbon atom, it was expected that *m*- $\alpha$ -bromoisobutyryl-*p*-cresol,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$ , would even more readily suffer condensation to a coumaranone than do the  $\alpha$ -halogenated *o*-acetyl- or *o*-propionyl-phenols. Indeed, it did not seem to be improbable that the coumaranone would be formed directly during the preparation of the butyryl derivative by the condensation of  $\alpha$ -bromoisobutyryl bromide with *p*-tolyl methyl ether. However, the sole product of this Friedel-Craft's synthesis is the above *m*- $\alpha$ -bromoisobutyryl-*p*-cresol (80% yield), which is all the more remarkable since, under the influence of aluminium chloride, the bromine might at least have been replaced by chlorine. When treated with zinc dust and acetic acid, the compound simply yielded *m*-isobutyryl-*p*-cresol (future communication), whilst, under the influence of alkaline agents, it merely exchanged bromine for hydroxyl, to form the tertiary alcohol,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{OH}$ . Strange to say, this compound was quite stable towards such dehydrating agents as formic acid, phosphorus trichloride, 30% sulphuric acid, alcoholic hydrogen chloride or potassium hydrogen sulphate. Since the desired condensation could not be effected by the above schemes, the action of organic bases on the  $\alpha$ -bromoisobutyryl-*p*-cresol was tried. It was found that dimethyl- and diethyl-anilines bring about the desired end, whereas pyridine, in an unaccountable manner, yields *p*-hydroxytoluic acid. The most characteristic derivative of the new 1:1:4-trimethylcoumaranone is the semicarbazone. It was expected that this compound would yield 1:1:4-trimethylcoumaran when heated with sodium ethoxide, which seemed, at first, to be the case, for an apparently indifferent oil of the right percentage composition was obtained. Later, this was recognised, however, as a weak phenol, namely, 2-hydroxy-5- $\omega$ -trimethylstyrene (compare *o*-hydroxy- $\alpha\alpha$ -diphenylethylene, Stoermer and Kippe, A., 1904, i, 182), formed by the addition of water to the coumaran, with opening of the ring, followed by elimination of water from the tertiary alcohol, thus:



This phenol was also synthesised by the action of magnesium isopropyl bromide on *p*-homosalicylaldehyde. Most of its derivatives proved to be oils, but it yielded the well-defined 4- $\omega$ -trimethylstyroxycetic acid when warmed with chloroacetic acid.

The above compounds form material for spectro-chemical investigations which will be described later.

*m*- $\alpha$ -Bromoisobutyryl-*p*-cresol,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$ , is a pale yellow oil, b. p. 154°/12 mm., 156—157°/13 mm., 166—167°/22 mm.,  $D_4^{22.3}$  1.3669,  $D_4^{20}$  1.370,  $n_D$  1.56400,  $n_D$  1.57141,  $n_B$  1.59245,  $n_Y$  1.61218, at 22.3°,  $n_D^{20}$  1.5724, and its *acetate* has b. p. 182—183°/17 mm.,  $D_4^{25.7}$  1.3173,  $D_4^{20}$  1.324,  $n_D$  1.52435,  $n_D$  1.52883,  $n_B$  1.54054, at 25.7°.

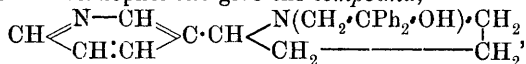
$n_D^{20}$  1.5314. The cresol gradually dissolves in dilute aqueous sodium hydroxide, yielding *m*-*a*-hydroxyisobutyryl-*p*-cresol, which crystallises from light petroleum in small, flat, yellow, sparkling prisms, m. p. 55—56°. It has b. p. 161—162°/18 mm.,  $D_4^{25}$  1.0943,  $n_a$  1.52824,  $n_D$  1.53470,  $n_B$  1.55342,  $n_\gamma$  1.57053 at 54°, gives a violet coloration with ferric chloride, and is readily oxidised by hydrogen peroxide to acetone and *p*-hydroxytoluic acid. Its *diacetate*,  $C_{15}H_{18}O_5$ , forms glistening, rhombic plates and long, flat needles, m. p. 57°, b. p. 182—187°/18 mm., and its *methyl ether*,  $OMe \cdot C_6H_3Me \cdot CO \cdot CMe_2 \cdot OH$ , prepared by means of methyl sulphate or sodium and methyl iodide, separates from light petroleum in long, flat, lustrous prisms, m. p. 51—51.5°, b. p. 160—164°/24 mm. The *semicarbazone*,  $C_{12}H_{17}O_3N_3$ , is quickly formed at 30—40°, and crystallises in slender needles, m. p. 227—228° (decomp.). The *semicarbazone* of the methyl ether,  $C_{13}H_{19}O_3N_3$ , may be prepared from the foregoing semicarbazone, but more readily from the methyl ether, in slender, white needles, m. p. 188—189°.

1 : 1 : 4-*Trimethylcoumaranone*,  $C_6H_3Me \langle \begin{smallmatrix} CO \\ O \end{smallmatrix} \rangle CMe_2$ , is best prepared by boiling the above *m*-*a*-bromoisobutyryl-*p*-cresol with diethylaniline, pouring the solution into cold, dilute sulphuric acid, converting the distilled oil into the semicarbazone, decomposing this by means of concentrated oxalic acid solution and redistilling. It forms colourless, lustrous prisms, m. p. 34—35°, b. p. 137°/10 mm., 145°/18 mm. The physical constants for two specimens are given, the more trustworthy being b. p. 159.5—161.5°/26 mm.,  $D_4^{20.6}$  1.1144,  $D_4^{20}$  1.115,  $n_a$  1.54868,  $n_D$  1.55475,  $n_B$  1.57109,  $n_\gamma$  1.58711, at 20.6°,  $n_D^{20}$  1.5550. It is quickly oxidised by hot hydrogen peroxide to *p*-homosalicylic acid. Its *semicarbazone* forms small, white, glistening needles, m. p. 232°, and its *oxime* has m. p. 128—129°, and sublimes on the water-bath. When the semicarbazone is heated with sodium and alcohol at 160—170° for some hours, it is converted into 6-hydroxy-3-*ω*-trimethylstyrene, which separates, when the solvent is removed and the residue is diluted with water, as a pleasant smelling, colourless oil, b. p. 114—117°. A purer specimen, b. p. 121—121.4°/13 mm., was obtained by the interaction of magnesium isopropyl bromide and *p*-homosalicylaldehyde. The tertiary carbinol which is first formed gradually suffers the necessary loss of water on distillation under 20 mm. pressure, but it is best not to attempt to expedite this by using dehydrating agents. The compound is a phenol for it dissolves in concentrated sodium hydroxide, forms a *methyl ether*,  $C_{12}H_{16}O$ , b. p. 117.2—117.6°/11 mm., and reacts with chloroacetic acid in alkaline solution, yielding 4-methyl-2-isobutenylphenoxyacetic acid,  $CO_2H \cdot CH_2 \cdot O \cdot C_6H_3Me \cdot CH : CMe_2$ , in silky, white needles, m. p. 80—81°. J. C. W.

Organic Syntheses by Means of Sunlight. X. Behaviour of Vegetable Alkaloids towards Ketones. E. PATERNO [with G. CHIEFFI and R. DE FAZI] (*Gazzetta*, 1914, 44, ii, 99—111. Compare this vol., ii, 321).—The following pairs of compounds have been exposed to the action of light for some months and the resulting products investigated.

Coniine and benzophenone yield benzopinacone, indicating that the alkaloid loses hydrogen.

Nicotine and benzophenone give the compound,



crystallising in needles, m. p. 151—153°.

Sparteine and acetophenone yield acetophenonepinacone and a gelatinous base, the *platinichloride* of which has the composition,  $\text{C}_{15}\text{H}_{26}\text{N}_2\text{C}_8\text{H}_8\text{O}_2\text{H}_2\text{PtCl}_6$  (?); the base exhibits colloidal properties and shows shining, red granules of ultramicroscopic dimensions.

Sparteine and benzophenone give benzopinacone and a yellow base, which is apparently an additive compound.

Piperine and benzophenone yield benzopinacone, a white compound, m. p. 158—165°, and a small proportion of a yellow compound, m. p. about 200°.

Papaverine and acetone remain without apparent change.

Strychnine and acetophenone yield an amorphous, yellow compound, turning brown but not melting at 280°, and forming a *picate* which corresponds with that of a compound of 1 mol. of strychnine with 2 mols. of the ketone. On prolonged exposure to air at 100°, this compound loses about 10% of its weight, and when left under a bell-jar in presence of acetophenone, absorbs the latter in large proportion, as much as 76% being taken up in about three and a-half months. The compound has marked emulsifying properties.

Strychnine and benzophenone seem to yield a polymeride of strychnine capable of absorbing large proportions of the ketone. The resulting product is a yellow, amorphous substance which does not melt at 300°.

Narceine and acetone give: (1) A base which forms shining laminae, m. p. 231—232°, and is apparently a dehydrated narceine of the formula  $\text{C}_{23}\text{H}_{25}\text{O}_7\text{N}$ ; its *platinichloride* and *picate*, m. p. 186—187°, were analysed; cryoscopic measurements in acetic acid gave indefinite results; (2) a base,  $\text{C}_{23}\text{H}_{25}\text{O}_7\text{N}$  (?), which crystallises in plates, m. p. 156—160°, and forms a *hydrochloride*, m. p. 196—197°, and a *platinichloride*.

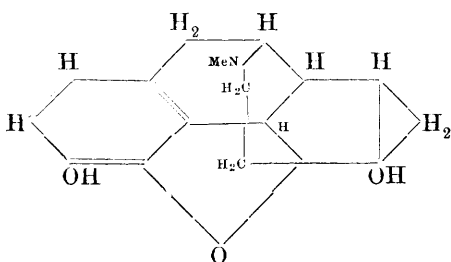
Narceine and acetophenone yield an intensely reddish-brown, amorphous powder, beginning to decompose at about 220°.

Narceine and benzophenone give a reddish-brown crystalline compound which is being examined further.

T. H. P.

Investigations of the Morphine Alkaloids. I. J. VON BRAUN [with O. KRUBER and E. AUST] (*Ber.*, 1914, 47, 2312—2330).—According to the formulæ usually assigned to morphine and thebaine (compare Knorr and Hörlein, A., 1907, i, 789) there is, in each case, a double linking in the  $\beta\gamma$ -position with regard to the nitrogen atom. The author has shown, in a number of papers (compare A., 1910, i, 189) that cyanogen bromide readily ruptures such a chain at the nitrogen atom, rather than remove a methyl group from that atom. Applying this reaction to acetylated  $\alpha$ -methylmorphimethine (indefinite, dark oils are formed if the hydroxyl groups in these alkaloids are not

protected), which has no double linking in the  $\beta\gamma$ -position, it is found that the compound behaves like trimethylamine or dimethylaniline, the basic group,  $\cdot\text{NMe}_2$  being converted into the non-basic group  $\cdot\text{NMe}\cdot\text{CN}$ . This shows that the complicated structure of the other parts of the molecule does not interfere with the specific action of the cyanogen bromide. Thebaine, however, does not lose the *N*-methyl group, but seems to combine directly with the reagent. Morphine and codeine, on the other hand, in the form of their acetyl derivatives, do not suffer rupture of the ring, but exchange a *N*-methyl group for cyanogen. Dihydromorphine, dihydrocodeine, and, probably, tetrahydrothebaine (Oldenberg, A., 1913, i, 1093) behave in the same way. The author therefore draws the conclusion that the particular double linking in morphine and codeine is not in the  $\beta\gamma$ -position, that is



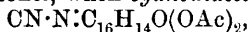
either 8:14 or 13:14, and suggests that, in contrast to thebaine, there is no double linking, but rather a bridge between the atoms 6 and 8. The annexed formula is therefore proposed for morphine. This would help to explain many of the problems connected with the constitution of morphine;

among others, the facts that it is very difficult to eliminate hydrogen chloride from chloromorphide and to combine bromine with the alkaloid.

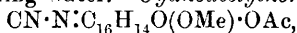
The cyano-acetyl derivatives, obtained from morphine and codeine, have also been hydrolysed, first to the acetyl-free compounds, and finally to normorphine and norcodeine. The discovery of the latter substance (*N*-demethylcodeine) by Diels and Fischer (this vol., i, 989) has led the author to give the present early account of what was intended to be an exhaustive study of these compounds.

Cyanogen bromide (1 mol.) is added to a concentrated chloroform solution of acetylmethylmorphimethine (1 mol.) and warmed for two hours. On diluting the solution with ether, the methobromide of the base separates, together with some of the non-basic *cyano*-derivative,  $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}_2$ . The latter is present in the filtrate, and crystallises from alcohol in silvery leaflets, m. p. 108°. The residue, insoluble in ether, is almost completely soluble in hot water, from which the *acetylmethylmorphimethine methobromide*,  $\text{C}_{22}\text{H}_{23}\text{O}_4\text{NBr}$ , separates, on cooling, in white scales, m. p. 207—208°. The acetyl-cyano-derivative dissolves at once in a solution of sodium methoxide, and, on adding water immediately, the non-acetylated *cyano*-derivative,  $\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_2$ , separates. This forms an ice-flower-like mass of crystals, m. p. 119°.

Diacetylmorphine (heroin) also reacts with cyanogen bromide under the above conditions. On diluting with ether, the whole of the product separates. Part is soluble in cold alcohol and consists of heroine methobromide, which could not be purified. The residue may be crystallised from hot alcohol, when *cyanodiacetylnormorphine*,



separates as a crystalline powder, m. p.  $240^{\circ}$ , the yield being 75—80 grams from 100 grams of diacetylmorphine and 40 grams of cyanogen bromide. *Diacetyldihydromorphine*,  $C_{21}H_{25}O_5N$ , prepared from the product of the catalytic reduction of morphine, m. p.  $167^{\circ}$ , forms *cyanodiacetyldihydronormorphine*,  $C_{21}H_{22}O_5N_2$ , in long, silky needles, m. p.  $138$ — $139^{\circ}$ . The chloroform solution of the product in the case of acetylcodeine is best evaporated to dryness and freed from the methobromide by boiling water. *Cyanoacetylnorcodeine*,



forms minute crystals, m. p.  $184^{\circ}$ . *Acetyldihydrocodeine*,  $C_{20}H_{25}O_4N$ , m. p.  $120^{\circ}$ , yields *cyanodiacetyldihydronorcodeine*,  $C_{20}H_{22}O_4N_2$ , in glistening crystals, m. p.  $227$ — $228^{\circ}$ .

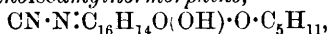
In order to remove the acetyl groups from cyanodiacetylnormorphine, it is best to dissolve the substance in a solution of potassium hydroxide (2 mols.) in 50% alcohol at  $50^{\circ}$ , and, after five minutes, not longer, to dilute with cold water and acidify with acetic acid. *Cyanonormorphine*,  $CN \cdot N : C_{16}H_{14}O(OH)_2$ , separates as a fine powder, m. p.  $295$ — $296^{\circ}$ , which is not indefinitely stable in alkaline solution. It can be directly acetylated to the mother substance, and, like morphine, it yields a *monobenzoyl* derivative,  $C_{24}H_{20}O_4N_2$ , m. p.  $265^{\circ}$ , which is insoluble in alkalis. The analogous hydrolysis of cyanoacetylnorcodeine is best effected by dissolving the substance in warm, concentrated hydrochloric acid and diluting after five minutes. *Cyano-norcodeine*,  $CN \cdot N : C_{16}H_{14}O(OMe) \cdot OH$ , m. p.  $263^{\circ}$ , is also easily prepared by the methylation of cyanonormorphine.

The further hydrolysis of these cyano-derivatives presented many difficulties, but may be accomplished by warming the compounds with 6% hydrochloric acid for several hours, when the salts of the bases crystallise on cooling. Starting with codeine, it is possible to obtain a 38% yield of pure norcodeine in a few days, whereas Diels and Fischer's method gives a 16% yield. Norcodeine (*N*-demethylcodeine),  $NH : C_{16}H_{14}O(OMe) \cdot OH$ , crystallises in leaflets, m. p.  $184^{\circ}$ . The sulphate, nitrate, and acetate are readily soluble, the sparingly soluble *hydrochloride*, m. p.  $309^{\circ}$ , crystallises with  $3H_2O$ , the *platinichloride* forms yellow leaflets, m. p.  $239^{\circ}$ , and the *hydriodide*, m. p.  $257^{\circ}$ , combines with  $2H_2O$ . Acetic anhydride gives rise to a diacetyl derivative, but phenylthiocarbimide attacks only the imino-group, forming a *phenylthiocarbamyl* derivative,  $C_{17}H_{18}O_3 : N \cdot CS \cdot NHPh$ , m. p.  $210^{\circ}$ , whilst the addition of sodium nitrite to an acid solution precipitates the *nitroso*-derivative,  $C_{17}H_{18}O_4N_2$ , which crystallises in yellow leaflets, m. p.  $246^{\circ}$ . *Normorphine*,  $NH : C_{16}H_{14}O(OH)_2$ , m. p.  $262$ — $263^{\circ}$ , could not be obtained quite pure, for it is appreciably soluble only in hot water or alcohol, and decomposes under such treatment. It is unstable towards alkalis, but yields a number of well-defined derivatives. The *hydrochloride*,  $1H_2O$ , has m. p.  $305^{\circ}$ , the *platinichloride*,  $3H_2O$ , m. p.  $230$ — $231^{\circ}$ , the *sulphate*,  $3H_2O$ , is fairly soluble, the *triacyetyl* derivative forms tablets, m. p.  $164^{\circ}$ , the *dibenzoyl* derivative forms white leaflets, m. p.  $208^{\circ}$ , and the *phenylthiocarbamyl* derivative is a colourless powder, m. p.  $245^{\circ}$ . The assumption that the oxide ring remains intact through all these changes is justified by the conversion of normorphine and norcodeine, by direct methylation,



into codeine methiodide and then, by the action of alkali, into  $\alpha$ -methylmorphimethine.

Cyanonormorphine reacts with *iso*amyl iodide in presence of sodium ethoxide to form *cyanoisoamylnormorphine*,

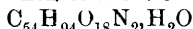


m. p. 225°, which may be hydrolysed as above to *O*-*iso*-*amylnormorphine*,  $\text{NH}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OH})\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$ , m. p. 100°; this forms a sparingly soluble *hydrochloride*, m. p. 278°, and a *nitroso*-derivative, m. p. 186°.

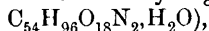
The alkylation of the imino-group of norcodeine is easy. Thus, on boiling the compound with  $\beta$ -phenylethyl iodide in chloroform, *N*-*phenylethyl*norcodeine,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OMe})\cdot\text{OH}$ , is obtained. This is isolated by adding sodium carbonate solution, extracting with chloroform, dissolving the residue from the evaporated extract in acetic acid, and adding sodium nitrite, when a solution of the nitrite of the tertiary base and a precipitate of nitrosonorcodeine are obtained. The latter is extracted with hot water, and the combined solutions of the nitrite are rendered alkaline. The new base has m. p. 114°, the *hydrochloride*, m. p. 277°, is sparingly soluble, and the *platimichloride* has m. p. 216—217°.

The experiments with thebaine and tetrahydrothebaine were somewhat indefinite. J. C. W.

**Solanum Sodomæum.** VI. GIUSEPPE ODDO and MARCELLO CESARIS (*Gazzetta*, 1914, **44**, i, 680—690. Compare A., 1911, i, 670; Oddo, A., 1911, i, 671).—When solanine-*s* of the formula



is boiled with dextrose for a long time and then recrystallised, it is found to have taken up two atoms of hydrogen (formula



although its physical and chemical properties are unchanged. The action of the dextrose is not a reduction, but a separation of impurities which contain less hydrogen. When solanine-*s* which has been purified as far as possible with water and alcohol is boiled with ether and benzene, a small quantity of a saturated *hydrocarbon*,  $\text{C}_{18}\text{H}_{38}$ , which forms colourless, silky needles, m. p. 58—60°, is obtained. In another experiment the hydrocarbon was accompanied by a white, nitrogenous *substance*, m. p. about 300°. The solanine-*s* recovered after this treatment and purified with water and alcohol has the composition  $\text{C}_{54}\text{H}_{96}\text{O}_{18}\text{N}_2\cdot\text{H}_2\text{O}$ . Solanine-*s* may crystallise with one or with two molecules of water. Solanine-*s* absorbs traces of carbon dioxide when kept in contact with air. R. V. S.

**Solanine-*s*.** VII. Identification of the Second Hexose Formed on Hydrolysis. GIUSEPPE ODDO and MARCELLO CESARIS (*Gazzetta*, 1914, **44**, i, 690—696. Compare preceding abstract).—The authors have definitely identified the second hexose formed on hydrolysis of solanine-*s* and find that it is dextrose. R. V. S.

**Sphingosine.** III. The Oxidation of Sphingosine and Dihydrosphingosine. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1914, **18**, 481—484. Compare A., 1912, i, 284, 575; this vol., i,

308).—The authors show that the tridecoic and pentadecoic acids obtained by the oxidation of sphingosine and dihydrosphingosine respectively, and their amides, are identical with the corresponding normal acids and amides prepared synthetically (see this vol., i, 1122). The carbon atoms in the sphingosine molecule are therefore united in a normal chain. The cleavage products of the ozonide of sphingosine are tridecoic acid and a substance which gives some of the reactions of an amino-tetrose.

H. W. B.

**Pyrrole Group. XI. Action of Tertiary Pyrroles on Organo-magnesium Compounds.** BERNARDO ODDO (*Gazzetta*, 1914, **44**, i, 706—713).—The author has repeated some of the work of Hess and Wissing (this vol., i, 725) and finds that pure methylpyrrole has no action on magnesium ethyl bromide. When acetyl chloride is added to the mixture, 2-acetyl-1-methylpyrrole is produced, but this substance is also formed in these circumstances by the direct action of acetyl chloride on the pyrrole alone. Similar results are also obtained with 1-benzylpyrrole. The contradictory observations of Hess and Wissing are to be ascribed to the presence of free pyrrole in the 1-methylpyrrole used by them.

R. V. S.

**Pyrrole Group. XII. Alkylation of Pyrroles. II.** BERNARDO ODDO and ROMUALDO MAMELI (*Gazzetta*, 1914, **44**, ii, 162—174).—The formation of 2- and 3-methylpyrroles by the action of methyl iodide on magnesium pyrrol bromide (this vol., i, 80) is confirmed by their conversion into pyrrole-2- and pyrrole-3-carboxylic acids by fusion with potassium hydroxide, and that of 3-methylpyrrole also by the formation of the corresponding acetylcinnamoyl derivatives. Further corroboration of the structures of these methylated pyrroles has been obtained by their reactions with hydroxylamine (compare Ciamician and Zanetti, A., 1891, 1502), which yields principally  $\beta$ -methylsuccindialdoxime, together with a small proportion of  $\alpha$ -methylsuccindialdoxime.

Application of these reactions to the products of the interaction of ethyl iodide and magnesium pyrrol bromide shows that these products consist of 3-ethylpyrrole, 2:5-diethylpyrrole and, if the reaction takes place in absence of solvent, also 2:3:4- or 2:3:5-triethylpyrrole,  $C_{10}H_{17}N$ , which is a pale yellow liquid, b. p. 200—205°.

Similarly, the action of propyl iodide on magnesium pyrrol bromide yields: (1) 3-propylpyrrole (?),  $C_7H_{11}N$ , b. p. 176—179°/753 mm., which is perhaps identical with that obtained by Zanetti (A., 1890, 65); (2) a dipropylpyrrole,  $C_{10}H_{17}N$ , b. p. 123—126°/15 mm., and (3) 2:3:4- or 2:3:5-tripropylpyrrole,  $C_{13}H_{23}N$ , b. p. 207—210° (decomp.), 150—160°/15 mm.

T. H. P.

**Indigotin. V. Halogenated Indigotins and Derivatives.** E. GRANDMOUGIN and P. SEYDER (*Ber.*, 1914, **47**, 2365—2373. Compare A., 1910, 74, 339).—An account is given of several halogenated indigotins, many of which are technical products, and of the isatins which they yield on oxidation. The positions of the absorption bands and the solubilities are the factors which receive most notice.

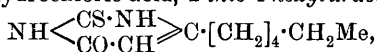
5:7:5':7'-Tetrachloroindigotin (brilliant indigo B) was oxidised to

5:7-dichloroisatin, and this converted into the  $\beta$ -phenylhydrazone,  $C_{14}H_9ON_3Cl_2$ , brilliant saffron-yellow crystals, m. p. 296—297°, and the  $\beta$ -oxime,  $C_8H_4O_2N_2$ , canary-yellow crystals, decomp. 255°. 4:4'-Dichloro-5:5'-dibromoindigotin (brilliant indigo 4G), yielded 4-chloro-5-bromoisatin,  $C_8H_3O_2NClBr$ , m. p. 273—274°, which sublimes with orange vapours and forms a phenylhydrazone, ochre-yellow crystals, m. p. 278°, and an oxime, m. p. 253—254° (decomp.). The constitution of the isatin was established by conversion into 3-chloro-4-bromoaniline on distillation with potassium hydroxide. 4:7:4':7'-Tetrachloroindigotin was converted into 4:7-dichloroisatin,  $C_8H_3O_2NCl_2$ , brilliant orange-yellow crystals, m. p. 252°, and this into the phenylhydrazone, m. p. 265°, and oxime, m. p. 245° (decomp.).

Octachloroindigotin (Orndorff and Nichols, A., 1913, i, 99) yielded 4:5:6:7-tetrachloroisatin,  $C_8HO_2NCl_4$ , an ochre-yellow substance, m. p. 294—295°, which was converted into tetrachloroaniline, and into a phenylhydrazone, m. p. 293°. 6:6'-Dibromoindigotin and 6:6'-diiodoindigotin were prepared from 6:6'-diaminoindigotin through the bis-diazonium sulphate. They crystallise from methyl benzoate, the latter in dark, bluish-violet crystals. 6:6'-Diaminoindigotin is valueless as a dye, but, on bromination, it yields a brown dye (ciba-brown R) (D.R.-P., 221531), which, as is now shown, consists chiefly of 5:7:5':7'-tetrabromo-6:6'-diaminoindigotin, for, on eliminating the amino-groups by diazotisation, it was converted into the blue 5:7:5':7'-tetrabromoindigotin, which was degraded to 5:7-dibromoisatin ( $\beta$ -phenylhydrazone, m. p. 297—298°,  $\beta$ -oxime, decomp. 272°), and finally to 2:4-dibromoaniline. J. C. W.

**Pyrimidines. LXXII. Synthesis of 4-Hexyluracil and its Relationship to Uracil-glucoside.** TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1914, 36, 1891—1899).—In earlier papers (Johnson and Chernoff, A., 1913, i, 656; this vol., i, 1091), the synthesis and properties of the simplest nucleosides of thymine and uracil have been described. The constitution of these compounds was established by their reduction with hydriodic acid to 4:5-dimethyluracil and 4-methyluracil respectively. As the higher homologues of these nucleosides ought theoretically to be capable of a similar interaction with hydriodic acid, it is desirable that the higher homologues of 4-methyluracil and the corresponding thymine compounds should be investigated. An account is now given of the synthesis of 4-hexyluracil, which may be regarded as the reduction-product of uracil-glucoside.

When ethyl heptoylacetate (Wahl and Doll, A., 1913, i, 532) is warmed with thiocarbamide in an alcoholic solution of sodium ethoxide, condensation takes place with formation of the sodium salt of 2-thio-4-hexyluracil. On acidifying an aqueous solution of the sodium salt with hydrochloric acid, 2-thio-4-hexyluracil,



m. p. 145°, is obtained, which crystallises in colourless needles. By digesting this compound with an aqueous solution of chloroacetic

acid, it is converted quantitatively into 4-hexyluracil (4-hexyltetrahydropyrimid-2:6-dione),  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{CH} \end{smallmatrix} \gg \text{C} \cdot [\text{CH}_2]_4 \cdot \text{CH}_2\text{Me}$ , m. p. 170°, which forms lustrous plates.

E. G.

**Allantoin.** MAURICE H. GIVENS (*J. Biol. Chem.*, 1914, 18, 417—424). Allantoin in aqueous solution undergoes slow decomposition. In distilled water the loss was found to be 6·3% in 620 days; in tap water, 6·4% in 24 days. The product gives off ammonia on distillation with magnesium oxide. Allantoin is also quickly destroyed by alkalis and by faecal bacteria. It disappears rapidly in alkaline urine, but is apparently stable if the urine is made acid.

In the estimation of allantoin in a series of samples by Wiechowski's method, the analyses must be carried out as quickly as possible to the point of precipitation of the allantoin by the mercuric acetate—sodium acetate reagent. They can then be set aside, if desired, as this compound is quite stable even in the presence of excess of the alkaline reagent.

H. W. B.

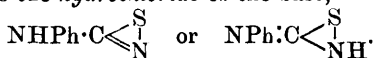
**Electrical Conductivity of Tetrazole and its Derivatives at Various Temperatures.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1914, 44, ii, 175—180).—The author has measured the conductivity of tetrazole, tetrazolamide, and bistetrazole at various temperatures. With rise of temperature, the temperature coefficient of the conductivity diminishes with bistetrazole, but increases with tetrazole and the amide. The value of the dissociation constant increases regularly with rise of temperature, the value at 35° being almost double (or treble) that at 0° in the case of tetrazole (or the amide). This increasing ionisation of tetrazole and its amide is interpreted on the basis of the tautomerism exhibited by the nucleus (compare A., 1913, i, 1398), an equilibrated mixture of the two forms probably existing in solution.

T. H. P.

**Constitution of Phenylsulphotetrazoline and of Triazosulphol.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1914, 44, i, 670—678).—Investigating the products described as thiophenyltetrazoline and triazosulphol by Freund and Hempel (A., 1895, i, 193) and Freund and Schwarz (1897, i, 125), the author finds that the chemical behaviour of the substances obtained by Freund by the action of nitrous acid on fatty derivatives of thiosemicarbazide is identical with that of the substances from aromatic derivatives, the difference being only one of stability. Azoidide acts on the esters of methylthiocarbimide and ethylthiocarbimide, yielding the same substances as Freund obtained from the corresponding thiosemicarbazides, whilst from aromatic thiocarbimides (*o*- and *p*-tolyl) similar compounds are formed. The chemical behaviour of all these substances shows them to be thiocarbamoylazoimides of the type  $\text{R} \cdot \text{NH} \cdot \text{CS} \cdot \text{N}_3$ , and by this formula all their reactions and decompositions may be explained.

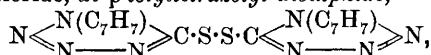
When phenylthiocarbamoylazoimide is boiled with concentrated hydrochloric acid, a substance crystallising in needles, m. p. 240—250°,

is obtained. It is the *hydrochloride* of the base,



The *base* forms lustrous leaflets, m. p. 121—123°.

*p*-Tolylthiocarbamoylazoimide,  $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CS} \cdot \text{N}_2$ , crystallises in needles, m. p. 140—144°. When it is treated with alkali carbonates, an isomeride, 5-thiol-1-*p*-tolyltetrazole,  $\text{N} \begin{array}{c} \text{N} \cdot \text{N} \cdot \text{C}_7\text{H}_7 \\ \diagup \diagdown \\ \text{N} : \text{C} \cdot \text{SH} \end{array}$ , is formed; it crystallises in needles, m. p. 150—151°. The *sodium* salt has the formula  $\text{C}_8\text{H}_7\text{N}_4\text{SNa}$ . When the mercaptan is oxidised with an alcoholic solution of ferric chloride, di-*p*-tolyltetrazolyl disulphide,



is obtained. When the oxidation is effected with alkaline permanganate in the cold, potassium *p*-tolyltetrazolesulphonate is formed, together with probably the potassium salt of hydroxytolyltetrazole. By oxidation of the mercaptan with alkaline permanganate in the warm,

5-hydroxytetrazole-1-benzoic acid,  $\text{N} \begin{array}{c} \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \\ \diagup \diagdown \\ \text{N} : \text{C} \cdot \text{OH} \end{array}$ , can be obtained.

Its *silver* salt has the formula  $\text{C}_8\text{H}_4\text{O}_3\text{N}_4\text{Ag}_2$ .

R. V. S.

**Apparent Formation of Euglobulin from  $\psi$ -Globulin and the Relationship between these two Proteins in Serum.** HARRIETTE CHICK (*Biochem. J.*, 1914, 8, 404—420).—Solutions of  $\psi$ -globulin from horse serum when subjected to dialysis deposit large quantities of a water-insoluble protein resembling euglobulin. The author brings forward evidence tending to show that this euglobulin is derived from the  $\psi$ -globulin by a gradual process of denaturation, which is accompanied by a disappearance from the solution of the small amount of phosphorus originally present in the  $\psi$ -globulin preparation. When all the phosphorus has disappeared from the solution, the precipitation of euglobulin ceases, but the denaturation process can be re-initiated by adding more phosphorus in the form of a watery emulsion of lecithin together with a trace of acid or alkali, or a little salt (for example, 1% of sodium chloride) to prevent the precipitation of the  $\psi$ -globulin.

The euglobulin thus artificially produced appears to be a mechanical complex resulting from the interaction and mutual precipitation of the two colloidal systems: (a) the solution of  $\psi$ -globulin and (b), the lipid emulsion, and it is suggested that the euglobulin in serum is a protein-lipoid complex of similar origin. This view is supported by (a) the inconstant phosphorus content of euglobulin; (b) the readiness with which phosphorus can be removed from euglobulin by extraction with acetone and ether, during which process the property of salt solubility is lost. This can, in some cases, be restored by the addition of the extracted fatty substance or of lecithin to the extracted euglobulin; (c) the similarity in chemical composition between  $\psi$ -globulin and euglobulin; (d) the want of accurate coincidence between the isoelectric point of euglobulin and the point of optimum flocculation, as pointed out by Walpole (this vol., ii, 547).

H. W. B.

**Action of Diazomethane on Caseinogen.** ARTHUR GEAKE and MAXIMILIAN NIERENSTEIN (*Biochem. J.*, 1914, 8, 287—292. Compare Krause and Skraup, A., 1909, i, 748, and Herzig and Landsteiner, this vol., i, 753).—Caseinogen on treatment with diazomethane in ethereal solution undergoes methylation, forming methylcaseinogen, which is a light colourless powder indistinguishable in appearance from caseinogen. It dissolves very slowly in dilute acids and alkalis and gives positive Millon's, Adamkiewicz's and the other protein reactions. This alkaline solution is optically active. The mean composition of the substance is C 55.31, H 7.32, N (by Kjeldahl) 14.84, N (by Dumas) 15.49, S 0.800, P 0.755 per cent. with 4.36 per cent. of methyl ( $\text{CH}_3$ ) as estimated by the Herzig and Meyer method. Caseinogen has been found to contain 0.88 per cent. of methyl. H. W. B.

**A Chemical Compound obtained from Wool and Indigotin.** M. FORT and L. L. LLOYD (*J. Soc. Dyers.*, 1914, 30, 297—298. Compare Green, Gardner, Lloyd and Frank, *ibid.*, 1913, 29, 227).—On extracting indigotin wrapped in flannel with boiling acetic acid and diluting the extract with water, a precipitate is formed which is fairly constant in composition and contains the whole of the original indigotin together with some of the wool products. This precipitate seems to be a chemical compound. On heating it with dilute sodium hydroxide, the wool substance is dissolved and the original weight of indigotin is left behind. Further, on boiling the precipitate with pyridine, reprecipitating by the addition of 50% alcohol, and boiling this second precipitate with formic acid and reprecipitating with water, the final precipitate was found to have practically the same weight and composition as the original precipitate. Solution in hot naphthalene followed by reprecipitation with alcohol does not affect the composition or weight of the precipitate. This chemical compound is also obtained by extracting indigotin wrapped in flannel with pyridine and adding 50% alcohol to the extract. Its formation helps to explain the superior fastness of indigotin dyed on wool to that dyed on cotton and also that in the former case stripping with solvents is more difficult. W. G.

**The Variations of Gluten.** MARCHADIER and GOUJON (*J. Pharm. Chim.*, 1914, [vii], 10, 191—202; compare Collin, *ibid.*, 1898, [vi], 8, 97, 150, 200; Baland, *ibid.*, 1899, [vi], 9, 239, 286; 1914, [vii], 9, 510).—The abnormal diminution in the percentage of coagulable gluten in wheat-flour produced by mixing with it flour from buckwheat, barley, rice, maize, etc., is also produced by the admixture of inorganic substances such as powdered talc, magnesia, or silica. This is not due to a variation in the ratio gliadin to glutenin, but to a variation in the sum of the gliadin and glutenin. Germination, milling, preservation of the flour either in a moist state or in a humid atmosphere, and unfavourable meteorological conditions during the growth of the corn produce a similar diminution in the percentage of coagulable gluten, due in this case to the conversion of gliadin into glutenin or vice versa, thus altering the ratio of these two closely allied substances. The authors suggest that the diminution in all these cases is due to a rise in the acidity of the flour under the

conditions named, the coagulation of gluten being known to be materially hindered by a very slight rise in the acidity. This rise in acidity has been found in flour after storing and after the addition of rye flour.

W. G.

**Sphingomyelin.** II. P. A. LEVENE (*J. Biol. Chem.*, 1914, 18, 453—462; compare A., 1913, i, 917).—Sphingomyelin has been prepared free from galactosides. It has the composition C=64, H=11, N=3.40, P=3.60, inorganic bases = 3 per cent. The ratio N:P=2:1 (approx.). It contains no free amino-nitrogen. There are three methyl groups to two atoms of nitrogen, indicating that one of the latter is in the form of choline. On hydrolysis the following substances were obtained:—phosphoric, lignoceric and cerebronic acids, choline, sphingosine and another base having the composition  $C_{17}H_{35}ON$ .

H. W. B.

**Specific Action of Enzymes considered from the Point of View of their Synthetic Power.** EM. BOURQUELOT (*J. Pharm. Chim.*, 1914, [vii], 9, 603—606).—A theoretical discussion in which the author points out the specific nature of various enzymes. Thus in an alcoholic solution of dextrose,  $\beta$ -alkylglucosides are alone formed under the influence of  $\beta$ -glucosidase, whilst  $\alpha$ -alkylglucosides result from the same solution if  $\alpha$ -glucosidase is employed. The mechanism of the change is discussed and the action contrasted with the action of hydrogen chloride on an alcoholic solution of dextrose or galactose.

The biochemical method is stated to be as advantageous as the ordinary chemical methods both in point of view of yield and purity of products.

H. W.

**Inversion of Sucrose by Invertase.** VIII. **An Improved Method for Preparing Strong Invertase Solutions from Top or Bottom Yeast.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1914, 36, 1566—1571).—The solution is prepared by well kneading yeast (10 kilos.) with tap water (10 litres) and toluene (500 c.c.). After three days, neutral lead acetate is added until precipitation is complete, the filtrate treated with hydrogen sulphide, filtered, and the filtrate at once thoroughly dialysed in collodion tubes, prepared from collodion solutions of Pharmacopœia strength in tubes 35 × 5 cm. The dialysed solutions are colourless and clear and show no loss in activity when kept, with toluene, for a month. At the end of a year the activity is reduced to about one-half. Both pressed top yeast and bottom fermentation (brewers') yeast were employed. The latter yields solutions about twice as strong as the former. Liquefaction occurs in a few hours and on the third day 5 c.c. of the filtered extract (from top yeast) was found to invert half the sucrose in 50 c.c. of a 9% solution, acidified with two drops of acetic acid and kept at 30°, in 5.9 minutes.

The solution is without action on  $\alpha$ -methylglucoside, maltose, and lactose. Whilst a solution prepared from top yeast changed the rotation of a solution of raffinose from +123° to +63.9°, a similar solution from bottom yeast changed the rotation from +123° to

+ 14.9°. This is attributed to the presence, in the solution from bottom yeast, of an enzyme (melibiase) which carried the hydrolysis of raffinose a step beyond that caused by invertase. N. H. J. M.

**Inversion of Sucrose by Invertase. IX. Is the Reaction Reversible?** C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1914, 36, 1571—1581).—From the results of experiments in which various degrees of slight alkalinity and acidity were maintained, the conclusion is drawn that invertase from yeast brings about the complete hydrolysis of sucrose to invert-sugar; that the reaction does not establish a mobile equilibrium, and is not a reversible reaction.

The results obtained by Osaka (A., 1908, i, 856) and by Visser (A., 1905, ii, 577) are attributed respectively to decomposition of lævulose by hydrochloric acid and the known effect of hydrochloric acid on the rotatory power of lævulose. The evidence afforded by the experiments of Kohl (A., 1910, i, 82) and of Pantanelli (A., 1906, ii, 623) on the synthesis of sucrose by the action of invertase on invert-sugar is considered to be doubtful. N. H. J. M.

**Specific Nature of  $\alpha$ -Glucosidase.** A. AUBRY (*J. Pharm. Chim.*, 1914, [vii], 10, 23—26).—The main source of  $\alpha$ -glucosidase is bottom yeast which contains also maltase, and several authors, therefore, appear to consider that these substances contain the same enzyme, although this conception is opposed to the work of Bourquelot and Hérissé (A., 1912, ii, 1104). The author has therefore investigated the question and is led to the conclusion that the two diastases are distinct.

Unsuccessful attempts to isolate maltase in the pure state from beer yeast are described; treatment of a maceration of yeast with 95% alcohol is found to destroy both maltase and  $\alpha$ -glucosidase. Experiments have therefore been performed to determine whether the hydrolysis of maltose and  $\alpha$ -methylglucoside occurs in a parallel manner, independently of the source of the maltase employed. Fresh human urine, after treatment with toluene, is found slowly to hydrolyse maltose but to be inactive towards  $\alpha$ -methyl-glucoside; the quantity of maltase contained in it is, however, very small, whilst  $\alpha$ -glucosidase appears to be completely absent.

A culture of *Aspergillus niger* on Raulin's liquid, after being washed with water, is known to yield a certain number of ferments, among which is maltase, on contact with distilled water. Such a solution is found to hydrolyse maltose rapidly, whilst it is without action on  $\alpha$ -methylglucoside. H. W.

**Hydrolysis of Glycogen by Diastatic Enzymes. III. Factors Influencing the End-point of the Hydrolysis.** ROLAND VICTOR NORRIS (*Biochem. J.*, 1914, 8, 421—433. Compare this vol., i, 215).—Glycogen is not completely hydrolysed to maltose by pancreatic diastase unless very high concentrations of enzyme are employed, although, even with low enzyme concentrations, the whole of the glycogen may be changed into compounds of smaller molecular weight. The most important factor in retarding hydrolysis is probably the



inhibiting influence of the products of the reaction other than maltose. Evidence is adduced to show that neither the resistance of the dextrins formed to further hydrolysis nor the destruction of enzyme can account for the marked retardation of hydrolysis observed in the experiments.

H. W. B.

**Constancy of the Optimum Temperature of an Enzyme under Varying Concentrations of Substrate and of Enzyme.** ARTHUR COMPTON (*Proc. Roy. Soc.*, 1914, [B], 88, 258—262. Compare this vol., i, 215).—The temperature of optimum action of the maltase of taka-diastrase is shown to be  $47^{\circ}$ , independent alike of the concentration of the substrate and that of the enzyme. E. F. A.

**A Modification of Amygdalinase and Amygdalase Due to Ageing.** GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1914, 159, 434—436. Compare A., 1911, i, 825).—Working with the same preparation of amygdalinase and amygdalase from almonds, obtained in 1910 and kept in the dark in a well-stoppered flask, and measuring its activity and the reaction of the medium for optimum activity in December, 1910, July, 1912, and July, 1914, the authors find that not only do these enzymes lose their activity very slowly indeed, but they require an increasing optimum concentration of hydrogen ions with passage of time. W. G.

**Enzyme Action. XXII. Lipase. IV.—Correlation of Synthetic and Hydrolytic Activity.** HENRY E. ARMSTRONG and H. W. GOSNEY (*Proc. Roy. Soc.*, 1914, [B], 88, 176—189. Compare A., 1913, i, 1120).—Parallel experiments have been made to ascertain the limits within which the opposing changes of hydrolysis and synthesis take place in presence of different proportions of the interacting substances and of water. Both in the case of the hydrolysis of triolein by lipase and of its synthesis from oleic acid and glycerol, the rate and extent of the change is retarded as the proportion of water present is increased. In the hydrolytic change the water interferes directly by preventing the enzyme and the oil from coming into direct contact. In the synthetic change the water acts by withdrawing glycerol from the system through its dissolution, though synthesis is not entirely prevented in quite dilute solutions of glycerol.

During hydrolysis mono- and di-glycerides are at first produced, the main synthetic product being a diglyceride. The maximum synthesis achieved was 40 per cent.

Bournot's observation (A., 1913, i, 920) as to the activity of the lipase of chelidonium seeds is confirmed. E. F. A.

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### Physiological Chemistry.

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**Respiratory Exchange in Fresh-water Fish. I. Brown Trout.** JOHN ADDYMAN GARDNER and CONSTANCE LEETHAM (*Biochem. J.*, 1914, 8, 374—390).—A new apparatus for determining the respiratory exchange of fishes is described and illustrated.

The oxygen absorbed by brown trout (*Salmo Fario*) appears to be proportional to the temperature of the water in which they are placed, and is approximately doubled for an increase of  $10^{\circ}$ . The average oxygen consumption is 102.5 c.c. per kilo. per hour at  $4-7^{\circ}$  and 206.5 c.c. per kilo. per hour at  $16-17^{\circ}$ . Large trout on being warmed in water up to  $25^{\circ}$  quickly die, although the water is thoroughly oxygenated.

The average value for the respiratory quotient of brown trout is 0.81, but below  $6^{\circ}$  it falls suddenly to about 0.18, indicating a state of hibernation.

H. W. B.

**The Blood in Acidosis from the Quantitative Point of View.** W. McKIM MARRIOTT (*J. Biol. Chem.*, 1914, 18, 507—517). Compare A., 1913, ii, 450).—By means of a method differing only slightly from that already described, the blood of normal human subjects, and of dogs, pigs, and cattle, has been found by the author to contain less than 1.5 mg. of acetone and acetoacetic acid, and less than 4 mg. of  $\beta$ -hydroxybutyric acid per 100 grams of blood, the results being expressed in terms of acetone. In acidosis, the acetone substances in the blood are higher than normal. The highest figures obtained were 28 mg. of acetone and acetoacetic acid, and 45 mg. of  $\beta$ -hydroxybutyric acid per 100 grams of blood, expressed as acetone.

H. W. B.

**The Behaviour of the Sugar and Lactic Acid in the Blood Flowing from the Liver, after Temporary Occlusion of the Hepatic Pedicle.** J. J. R. MACLEOD and A. M. WEDD (*J. Biol. Chem.*, 1914, 18, 447—452).—The temporary arrest of the blood flow through the liver has been found by the authors to lead to an increase in the amount of sugar and lactic acid in the blood subsequently obtained from the vena cava. The increased production of these substances continues for at least fifteen minutes after the blood flow has been re-established.

H. W. B.

**Effect of Hæmorrhage and Re-injection of Blood and Saline Solution on the Vasomotor Centre.** J. D. PILCHER and TORALD SOLLMANN (*Amer. J. Physiol.*, 1914, 25, 59—69).—Hæmorrhage progressively stimulates, depresses, and paralyzes the vasomotor centre. Re-injection of blood or saline solution before the onset of paralysis may restore the vasomotor tone. The low blood pressure (shock) level depends chiefly on the amount of blood lost, and not to an important degree on the rapidity of the hæmorrhage.

H. W. B.

**Effect of Intravenous Infusion of Normal Saline Solution on the Vasomotor Centre.** J. D. PILCHER and TORALD SOLLMANN (*Amer. J. Physiol.*, 1914, 25, 70—72. Compare preceding abstract).—In normal animals the intravenous infusion of 10—40 c.c. of saline solution per kilo. body-weight either slightly stimulates the vasomotor centre or leaves it altogether unaffected. In some animals there may be considerable stimulation observed, which is probably to be ascribed to a hypersensitive centre.

H. W. B.

**Viscosity of Laked Blood.** RUSSELL BURTON-OPITZ (*Amer. J. Physiol.*, 1914, 25, 51—58. Compare A., 1906, ii, 372).—By repeated freezing and thawing of defibrinated blood the viscosity is first slightly increased and then very considerably reduced. Expressed numerically, the viscous resistance changes from being, when freshly defibrinated, 5.3 times greater than that of water at 37° to 4.2 times greater after eight freezings and thawings. This is accounted for by the fact that after the blood has been frozen from five to eight times the erythrocytes agglutinate and collect on the bottom and sides of the receptacle. The present determinations were made only with the liquid portion of the blood which becomes relatively free from cells. H. W. B.

**The Clotting of Blood as Seen with the Ultramicroscope.** W. H. HOWELL (*Amer. J. Physiol.*, 1914, 25, 143—147).—The author gives a description with photomicrographs of the phenomena observed under the ultramicroscope when solutions of thrombin are added to oxalated blood-plasma or to solutions of fibrinogen. The essential point is that the fibrin formed is deposited, not as a network, but as separate well-formed needles of crystalline appearance, which are massed to produce a mesh. In certain circumstances the process is incomplete, giving rise to the production of threads or rods of different lengths in place of the needles.

H. W. B.

**Purine Metabolism of Rats.** HAROLD ACKROYD (*Biochem. J.*, 1914, 8, 434—437. Compare Folin and Morris, A., 1913, i, 925).—The experiments recorded by the author show that the large amount of uric acid excreted by rats is an expression of a very high rate of purine metabolism, the main end-product of which is allantoin, beside which the amount of uric acid is insignificant. Moreover, when hypoxanthine was given by the mouth to rats, about 60 per cent. of its nitrogen was excreted in the form of allantoin and only about 3 per cent. as purine nitrogen. The purine metabolism of rats is therefore like that of other lower animals, and unlike that of man.

H. W. B.

**Comparative Biochemistry of Purine Metabolism.** I. and II. **The Excretion of Purine Katabolites in the Urine of Marsupials, Rodents, Ungulates and Carnivora.** ANDREW HUNTER, MAURICE H. GIVENS, and CONNIE M. GUION (with REUBEN S. HILL and ALFRED OBERLE) (*J. Biol. Chem.*, 1914, 18, 387—401, 403—416. Compare A., 1913, i, 126, 558; this vol., i, 348, 354, 627, 898).—A detailed account of work the results of which have been already published (*loc. cit.*).

H. W. B.

**The Influence of Protein Intake on the Formation of Uric Acid.** A. E. TAYLOR and W. C. ROSE (*J. Biol. Chem.*, 1914, 18, 519—520).—By changing the nitrogen-free diet of a man fed for four days on starch and sugar to one of white of egg containing more than 40 grams of nitrogen per diem (but no purines), the uric

acid output was raised from about 0.3 gram to 0.8 gram per diem, the creatinine nitrogen remaining unaffected. The possible explanations of this formation of uric acid on the heavy purine-free protein diet are discussed.

H. W. B.

**Chemistry of Embryonic Growth. II. Comparative Analyses of the Eggs and of the Newly-hatched Larvæ of the Giant Salamander (*Cryptobranchus allegheniensis*).** ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1914, 36, 1556—1566. Compare A., 1913, i, 673).—The eggs of *Cryptobranchus* contain two yellow pigments soluble in ether and in alcohol respectively. During development the eggs lose 1.66% of the dry matter. The amount of fat increases 14%; there is also a gain in the nitrogen soluble in ether and in the nitrogen soluble in alcohol (insoluble in ether). The total nitrogen is unchanged, and there is a loss of nitrogen from the protein fraction. Carbamide and uric acid are not produced in appreciable amounts.

It is considered probable that the eggs contain a carbohydrate nucleus, either free or in the form of a glucoprotein, which is broken down to carbon dioxide and water in the process of embryonic growth; and that the process proceeds more rapidly than is required by the needs of growth, the surplus energy being stored as fat.

N. H. J. M.

**Comparison of the Carbon Dioxide Output of Nerve Fibres and Ganglia in *Limulus*.** SHIRO TASHIRO and H. S. ADAMS (*J. Biol. Chem.*, 1914, 18, 329—334. Compare this vol., i, 1018).—The authors have determined the rate of evolution of carbon dioxide from the dorso-median cord in the heart of the king-crab (*Limulus polyphemus*). It was found that about as much carbon dioxide was given off by this ganglionic nervous tissue as by the claw or optic nerves of the same animal. The absolute amounts were considerably smaller than those furnished by the corresponding nerves of the spider crab (*Libinia canaliculata*) or the frog (*Rana pipiens*), and this fact is correlated with the very sluggish behaviour of *Limulus* and its power of living for very long periods without food and with very little air. It is pointed out that the carbon dioxide output is directly proportional to the rate of propagation of the nerve impulse in these animals. The experiments so far recorded showing the influence of size and sex on the carbon dioxide output of nervous tissues do not allow of any definite conclusion being drawn.

H. W. B.

**The Effect of Acute Destructive Lesions of the Liver on its Efficiency in the Reduction of the Ammonia Content of the Blood.** CYRUS H. FISKE and HOWARD T. KARSNER (*J. Biol. Chem.*, 1914, 18, 381—385. Compare this vol., i, 110).—The livers of animals which have been treated with chloroform, phosphorus, phloridzin, hydrazine, and hæmolytic immune serum have been perfused with normal blood containing known amounts of ammonia. In each case the liver cells were able to remove practi-

cally the whole of the ammonia, showing that the pathological changes induced did not interfere with the normal capacity of the liver to deal with ammonia.

During the progress of the work it was found that oxygenation of the perfusing fluid by pure oxygen instead of air brings about an almost complete reduction of the ammonia content of the fluid as it passes through the liver.

H. W. B.

**Ovarian Extirpation and Vasomotor Irritability.** R. G. HOSKINS and HOMER WHEELON (*Amer. J. Physiol.*, 1914, 25, 119—123. Compare this vol., i, 900).—Ovarian extirpation in dogs results within six to eight weeks in a marked augmentation in the vasomotor reaction to nicotine, but not to adrenaline. These results, which are in conformity with clinical evidence, indicate that the operation causes a heightened irritability in the sympathetic nervous system.

H. W. B.

**The Vapour Pressure Hypothesis of Contraction of Striated Muscle.** H. E. ROAF (*Proc. Roy. Soc.*, 1914, [B], 88, 139—150).—Starting with the commonly accepted structure for striated muscle, it is shown that it is possible to explain the phenomena associated with contraction on the hypothesis that lactic acid is set free in the muscle fibre, and that this combines with protein to form a salt with a consequent rise of osmotic pressure. As a result of this increased osmotic pressure the anisotropic bands swell and the muscle is thereby shortened.

By various calculations, controlled by suitable experiments, it is shown that muscle can shorten by osmotic processes until its length is somewhere between 37% and 3% of its original length. From measurements of the elements of the sartorius muscle of the frog it is calculated that the amount of lactic acid formed during contraction of muscle can cause sufficient rise in osmotic pressure to account for the force exerted by the muscle and that the osmotic process can be completed in less than 0.04 of a second. The electrical changes are also accounted for on the assumption of the formation of a protein salt of lactic acid.

H. W. B.

**Creatine and Creatinine.** PHILIP A. SHAFFER (*J. Biol. Chem.*, 1914, 18, 525—540. Compare Shaffer and Reinoso, A., 1910, ii, 731).—A detailed description of work the results of which have already been published (*loc. cit.*).

H. W. B.

**Relations of Vitamine to Lipoids.** EVELYN ASHLEY COOPER (*Biochem. J.*, 1914, 8, 347—354).—A method is described for the preparation from cardiac muscle of a substance small amounts of which cure polyneuritis in pigeons. The substance is extremely unstable, and loses its activity in a few days. As in the case of voluntary muscle (A., 1913, i, 928), the bulk of the anti-neuritic substance contained in the fats and lipoids (alcoholic extract) of cardiac muscle can be separated therefrom by means of ether. In the case of the brain, separation of the anti-neuritic substance is

effected only by the addition of acetone as well as ether to the alcoholic extract.

Purified brain phosphatides, protagon, kephalin, cholesterol, and cerebron possess no curative power over polyneuritis. This is not due to failure to become digested, because hydrolysed protagon and brain phosphatides are still quite inactive.

The conclusion is drawn that vitamine is not a lipid, and although it may be adsorbed in the lipoids of the brain and muscle, it does not enter into their constitution, but is only stored until required by the organism. H. W. B.

**Colouring Matters in the Compound Ascidian *Diazona violacea*.** ALFRED HOLT (*Proc. Roy. Soc.*, 1914, [B], 88, 227—236).—The Ascidian *Diazona violacea* obtained by dredging near the Outer Hebrides is green while alive, but changes to violet when placed in alcohol, whilst the alcohol acquires the green colour. The spectrum of the green colour resembles that of ordinary plant chlorophyll, and separable green and yellow pigments are associated in the alcoholic solution.

The violet substance, purified by solution in hot *s*-tetrachloroethane, formed a purple powder with a coppery lustre. In general behaviour it resembled the dibromindigotin shown by Friedländer to be present in *Murex brandaris*. The same 6:6'-dibromindigotin has now been isolated from the British mollusc, *Purpura lapillus*.

It is considered that in the healthy animal the purple pigment is present in its reduced condition as a colourless chromogen, and is physiologically active as an oxygen carrier. On death, oxidation is complete, and the violet pigment persists. E. F. A.

**The Validity of the Microchemical Test for the Oxygen Place in Tissues.** A. N. DRURY (*Proc. Roy. Soc.*, 1914, [B], 88, 166—176).—Experiments have been made by the author which prove that the results obtained by Unna with rongalite-white [a solution of the leuco-base of methylene-blue kept in a state of reduction by excess of rongalite (formaldehydesulphoxylate)] do not justify his assumption that it is a specific stain for the oxygen place in tissues; consequently, his theory of staining by oxidation and reduction is not proven. Experiments were also performed which showed that the gas condensed on the surface is a great factor in determining the depth to which staining takes place. Altering a surface by preliminary treatment with various chemical substances also has a marked effect on the subsequent condensation of methylene-blue. H. W. B.

**Biochemistry of Iodine. I. The Distribution of Iodine in Plant and Animal Tissues.** A. T. CAMERON (*J. Biol. Chem.*, 1914, 18, 335—380).—The author has estimated the amount of iodine present in various animal and vegetable tissues by a modification of Hunter's method (A., 1910, ii, 650). The results are compared with those obtained by other workers.

Iodine has been found in the great majority of plants, the exact amount present being largely dependent on the amount of iodine in the environment. Marine algæ usually contain more than 0.001% of iodine, whereas in fresh-water algæ and vegetables the quantity is generally less than 0.0001%. Nevertheless, distinct variation of iodine content can occur in the same species growing under apparently the same conditions. A possible explanation is based on Allary's statement (which is confirmed) that when a leaf of one of the marine algæ ceases to grow and commences to lose its vitality, it gives up iodine to the surrounding medium.

Among the lower animals, sponges were found to contain about 0.01% iodine (calculated on the dried material), whilst worms contained up to 0.4%. In all the lower animals the iodine is dispersed throughout the various tissues of the organism, but in the higher animals it becomes concentrated in the thyroid, so that in vertebrates this gland is the only tissue containing more than a trace of it. In thyroid tissue marked variations of iodine content occur both in individuals of the same species and in different species. Such variations are all traceable to differences in diet. In vertebrates the amount of iodine in the dried thyroid varies from 0.01 to 1.16%.

Iodine is present in the thyroids of the young of sheep, swine, and cattle to a rather greater extent than in the adult animal. The iodine content of the parathyroids is of an altogether lower order than that of the thyroid. The remaining tissues, including thymus and pituitary, of the cat, dog, and rabbit do not contain more than a trace of iodine (less than 0.001% calculated on the dried material).

H. W. B.

**Relative Amounts of  $\beta$ -Hydroxybutyric Acid and Acetoacetic Acid Excreted in Acetonuria.** ERNEST LAURENCE KENNAWAY (*Biochem. J.*, 1914, 8, 355—365).—The author has estimated the relative amounts of  $\beta$ -hydroxybutyric acid and acetoacetic acid in the urine in conditions of acidosis. In diabetes the ratio of  $\beta$ -hydroxybutyric acid to acetoacetic acid remains fairly constant; in carbohydrate starvation, the proportion of  $\beta$ -hydroxybutyric acid rises with the increasing formation of acetone substances. In cases where two and a-half grams or more of the two acids were being daily excreted, the estimation of the separate acids indicated that from two to five molecules of  $\beta$ -hydroxybutyric acid were eliminated for one molecule of acetoacetic acid.

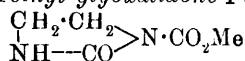
H. W. B.

**The Behaviour of Asparagine, Phenyl Carbamate and Methyl Ethyleneallophanate [Methyl Glyoxalidone-1-carboxylate] in Phloridzin Diabetes.** OTTO NITSCHKE (*Chem. Zentr.*, 1914, ii, 60; from *Beitr. Phys.*, 1914, 1, 53—89).—The author records the effects on the urinary sugar of the administration of *l*-asparagine, phenyl carbamate, and methyl glyoxalidone-1-carboxylate to phloridzinised dogs. From the quantity of "extra" sugar (Lusk) obtained after the ingestion of asparagine, the author infers that



three of the carbon atoms in asparagine become transformed into dextrose. The administration of 3 grams of phenyl carbamate in one dose to a phloridzinised dog caused the death of the animal; whilst a dose of 1 gram resulted in a diminished elimination of sugar.

[With NUSSHAG.]—*Methyl glyoxalidone-1-carboxylate*,



has been prepared from ethylenedicarbimide and methyl alcohol in crystalline form, soluble in water and alcohol. A 10-gram dose did not produce narcosis. Administration to a phloridzinised dog led to an increase in the urinary dextrose. H. W. B.

**Formation of Dextrose from Glutamic Acid in Phloridzin Diabetes.** BRUNO WARKALLA (*Chem. Zentr.*, 1914, ii, 60—61; from *Beitr. Phys.*, 1914, 1, 91—112. Compare Lusk, A., 1908, ii, 612).—The administration of glutamic acid, obtained from the gliadin of wheat, to phloridzinised dogs leads to an increased elimination of dextrose in the urine. The calculation of the “extra” sugar from the D : N ratio does not enable it to be decided whether the intermediate compound formed during the transformation of the glutamic acid into sugar possesses three or only two carbon atoms.

H. W. B.

**The Behaviour of Certain Amido-compounds in Phloridzin Diabetes.** KARL STEINHAUSEN (*Chem. Zentr.*, 1914, ii, 61; from *Beitr. Phys.*, 1914, 1, 113—142).—The author has determined the influence of the administration of succinimide, succinamide, and acetamide to phloridzinised dogs on the elimination of sugar in the urine. The experiments carried out on a fasting rabbit with succinimide did not give a conclusive result, but those on a fasting dog showed unmistakably that what Lusk has termed “extra” sugar was eliminated. After the ingestion of 40 grams of acetamide, about 30 grams were obtained during the next three days unchanged from the urine, leaving only 10 grams to take part in metabolism. The author does not come to any conclusion as to whether the “extra” sugar formed in this experiment arose by gluconeogenesis from the ingested acetamide. The administration of succinamide interrupts the normal course of phloridzin diabetes so that no statement as to its capacity for being utilised to form sugar can be given. H. W. B.

**The Behaviour of Acrylic Acid in Phloridzin Diabetes.** FRIEDRICH SCHWENKEN (*Chem. Zentr.*, 1914, ii, 254; from *Beitr. Phys.*, 1914, 1, 143—177).—The author advances the hypothesis that acrylic acid may be an intermediate product between lactic acid or alanine on the one hand and dextrose on the other. The administration of acrylic acid to phloridzinised dogs led to an increase in the amount of dextrose eliminated in the urine. The increase of urinary dextrose over that occurring in the urine before the acrylic acid was given to the animal was such as to lead the author

to infer that all the acrylic acid administered had been converted into dextrose. The formation of dextrose in the body from lactic acid or alanine may therefore occur with acrylic acid as the intermediate product.

H. W. B.

**Magnesium Narcosis.** I. E. STARKENSTEIN (*Chem. Zentr.*, 1914, ii, 59; from *Zentr. Physiol.*, 1914, 28, 63—70).—In order to determine whether the point of attack of magnesium salts is in the central or peripheral nervous system, the author has carried out a number of "combination" and "antagonistic" experiments on rabbits. Camphor, which has an antagonistic action on the central paraldehyde and chloral narcosis, has no action on magnesium narcosis. Eserine has a stimulating action on magnesium narcosis similar to that exerted on the peripheral paralysis brought about by curare; the paracetaldehyde and chloral narcosis of central nature remain unaffected. Eserine calls forth muscular tremor in normal and curarised rabbits, but not in animals narcotised by magnesium, paracetaldehyde, or chloral. Phenol in small doses behaves in the same way as eserine.

Ineffective doses of curare and ether when combined may bring about complete narcosis. Magnesium and ether have similar additive effects.

In view of these results, magnesium narcosis cannot be said to indicate either a purely central or a purely peripheral paralysis. It appears, rather, that all parts of the nervous system are rendered less excitable by the magnesium ions. The experiments also show that the action of the other drugs is not confined exclusively to the central or the peripheral nervous system, and that even when there is a pronounced peripheral action (as with curare), there may also be a considerable central paralysis.

The intensifying action of oxalates on magnesium narcosis noted by Gates and Meltzer (this vol., i, 459) has already been described by the author (*Wien. klin. Woch.*, July, 1913).

H. W. B.

**The Parenteral Utilisation of Disaccharide Sugars.** ALBERT G. HOGAN (*J. Biol. Chem.*, 1914, 18, 485—496).—Repeated injections of lactose and sucrose have been made into the intraperitoneal cavity of dogs. Most of the injected sugar has been regained from the urine. Greater utilisation of these sugars could not be attained by repeated injections. These experiments, therefore, do not yield any confirmation of Abderhalden's work showing the development of enzymes by the organism capable of hydrolysing these sugars when parenterally introduced.

H. W. B.

**Action of Tissues on Methyl-glucosides, Tetramethyl-glucosides and Natural Disaccharides.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1914, 18, 469—475).—An attempt has been made by the authors to trace the changes undergone by the dextrose molecule during its oxidation in the body by studying the action of the tissues, taken post-mortem, on derivatives of dextrose. Sliced rabbit's kidneys were incubated for thirty-six hours with solutions

of  $\alpha$ -methyl-glucose, tetramethyl-glucose, sucrose, lactose, *d*-glucose-phosphoric acid, maltose, and  $\beta$ -methyl-glucose. In all except the last two, no change in the reducing power of the solution, taken before and after hydrolysis, was observed. With maltose and  $\beta$ -methylglucose a slight change occurred, due doubtless to the preliminary cleavage of these substances into their components by the tissue enzymes. The conclusion drawn is that only free dextrose undergoes oxidation in the body, ester and ether derivatives of dextrose being unaffected. H. W. B.

**The Changes Undergone by Salicylic Acid in the Animal Organism.** ALESSANDRO BALDONI (*Chem. Zentr.*, 1914, i, 2066; from *Arch. Farm. speriment.*, 1914, 17, 241—247. Compare A., 1908, ii, 1060).—A critical consideration of the method of isolation and the properties of the hydroxysalicylic acid obtained by Neuberg (*Berl. klin. Woch.*, 1914, 48, 798) leads the author to the conclusion that it is possible that this substance is identical with the *salicyluric acid* which he prepared from human urine after administration of sodium salicylate (*loc. cit.*). H. W. B.

**Uricolysis.** A. E. TAYLOR and W. H. ADOLPH (*J. Biol. Chem.*, 1914, 18, 521—523).—A large quantity of allantoin was injected into the femoral vein of a dog and recovered almost quantitatively from the urine with no concurrent increase in the elimination of urea. In the dog, allantoin is not converted into urea, and therefore it is probable that in man the corresponding conversion of uric acid into urea does not take place. H. W. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Mechanism of Agglutination of Bacteria by Specific Sera.** WILLIAM JOHN TULLOCH (*Biochem. J.*, 1914, 8, 293—319).—The author has investigated the factors determining the flocculation of sensitised bacteria, and expresses the view that whereas unsensitised organisms exhibit characters that are similar to those of fresh protein, sensitised organisms recall in their properties the characteristic features of denaturated protein.

Specific agglutination is markedly affected by the presence of salts, hydrogen- and hydroxyl-ions. In the presence of salts with mono- and bi-valent cations, unsensitised bacteria behave like non-rigid colloids, such as egg-albumin, but after they have been sensitised they resemble rigid colloids (denaturated egg-white). The flocculation appears to be due to a direct interaction of the anti-substance-antigen complex with the electrolyte. Both hydrogen- and hydroxyl-ions inhibit agglutination by interfering with the

union of antigen with anti-substance as well as by preventing flocculation.

The agglutinating activity of an electrolyte depends on the valency of its cation when the bacteria are suspended in saline solution, and on the valency of the anion when suspended in an acid medium. Salts with multivalent cations are peculiar in their action in that they are as active in the precipitation of sensitised as of unsensitised organisms. Since flocculation takes place in the presence of fluorides, agglutination is independent of the calcium ions in the serum.

The general conclusion arrived at is that the process of sensitisation is akin to denaturation. H. W. B.

**Studies in Bacterial Metabolism. XXXI—XXXVII.** ARTHUR I. KENDALL, ALEXANDER A. DAY, and ARTHUR W. WALKER (*J. Amer. Chem. Soc.*, 1914, **36**, 1937—1962).—An investigation of the effect of various important types of bacteria on milk. Estimations were made of the free ammonia, total nitrogen, and the acidity or alkalinity as indicated by alizarin, neutral-red, and phenolphthalein. As certain changes, particularly increases in acidity, were observed which could not be adequately explained, experiments were undertaken with a view to determine the effect of butter-fat on the bacterial metabolism. For this purpose, skimmed milk (containing 0.15% of butter-fat), whole milk (containing 3.6% of butter-fat), and cream (containing 40% of butter-fat) were inoculated with certain organisms and studied under parallel conditions. The results of all these experiments are tabulated. E. G.

**Studies in Bacterial Metabolism. XXXVIII.** ARTHUR I. KENDALL, ALEXANDER A. DAY, and ARTHUR W. WALKER (*J. Amer. Chem. Soc.*, 1914, **36**, 1962—1966).—A study of bacterial metabolism in milk (preceding abstract) showed the occurrence of certain changes, chiefly in relation to acidity, which could not be explained by the information hitherto available. In seeking an explanation for these changes, experiments have been carried out to ascertain whether the organisms secrete lipases which effect the hydrolysis of the fatty constituents of the milk. The results show that the sterile filtrates of broth cultures of certain bacteria are capable of hydrolysing butter-fat, ethyl butyrate, and triacetin. E. G.

**Action of Stimulants on Nitrifying Bacteria.** C. MONTANARI (*Chem. Zentr.*, 1914, ii, 342; from *Staz. sper. agrar. ital.*, **47**, 441—448).—The results of experiments with manganese dioxide, carbonate, and sulphate showed that manganese dioxide and carbonate rendered nitrification more vigorous. N. H. J. M.

**Action of Organic Substances on Nitrification and Denitrification in Soils.** ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1914, ii, 260—261; from *Zeitsch. Gärungsphysiol.*, 1914, **4**, 1—48).—The results of experiments on nitrification in a soil rich in humus showed that straw only had a retarding action when employed in

very large amounts, and that straw plus peptone had less effect than peptone alone.

Denitrification is greatly accelerated by straw. Straw plus peptone acts similarly. This is followed by a vigorous nitrification of the ammonia produced from the peptone.

The retarding effect of the following substances on nitrification decreases in the following order: peptone, asparagine, acetamide, ammonium acetate, and carbamide. When peptone is added, nitrification and denitrification only commence when all the nitrogen of the peptone is converted into ammonia; production of nitrite and of nitrate nearly always begin simultaneously. The effect of dextrose is similar. In presence of soluble organic compounds nitrification does not proceed until they are completely mineralised.

N. H. J. M.

**Chemical Nature of a Bacterial Hæmolysin.** ERIC EDWIN ATKIN (*Biochem. J.*, 1914, 8, 328—346).—The velocity of destruction of nasik hæmolysin, prepared from *Vibrio nasik*, at 46° is at a minimum slightly on the acid side of the neutral point. This favours the view that the lysin is an ampholyte (amphoteric electrolyte) with its acid dissociation constant greater than its basic, and the point of minimum destruction is the isoelectric point. The anion and cation are therefore thermolabile, and the undissociated molecules thermostable. Kataphoresis experiments at 10° confirm this view. The approximate values for the isoelectric points are  $p_H$  at 10° = 3·3;  $p_H$  at 46° = 6·1. This decrease of acidity with rising temperature is also found in the case of simple ampholytes, but to a smaller extent.

A criterion is also given incidentally for the anomalous heat destruction of certain hæmolysins, for instance, megatheriolysin, namely, that the process is not unimolecular at temperatures where the velocity of destruction decreases with rising temperature, but it can be shown to be so at temperatures considerably removed where the velocity of destruction follows the more ordinary course of increase with rise of temperature.

H. W. B.

**Combination of Metallic Salts by Yeast; their Detection by Chemical Reactions.** TH. BOKORNY (*Chem. Zentr.*, 1914, i, 2195—2196; from *Allgem. Brauer-Hopfenzeit.*, 1914, 54, 1155—1158).—Pressed yeast (20 grams) fixes 0·25 gram of copper sulphate in two weeks from a 1% solution; the yeast gives a positive reaction with potassium ferrocyanide. Yeast-ferrous sulphate only reacts with potassium sulphide and potassium ferro- and ferri-cyanides after being boiled with hydrochloric acid. Yeast-ferric chloride also gives mostly negative reactions, except with ammonium sulphide. The compound with cobalt nitrate gives mostly negative reactions, whilst nickel sulphate seems to be incompletely fixed, and manganese sulphate not at all. The compounds with mercury salts only give positive reactions with ammonium sulphide, whilst the compound with lead acetate gives a negative reaction with potassium chromate. Sodium hydrogen sulphite enters into com-

bination with the aldehyde of the active protein; when treated with dilute sulphuric acid, it liberates sulphur dioxide.

N. H. J. M.

**Yeast Fermentation and Hydrogen.** SERGIUS LVOV (*Chem. Zentr.*, 1914, i, 2194—2195; from *Zeitsch. Gärungsphysiol.*, 1913, 3, 289—320).—Experiments on the action of chromogens, the fermentation of sugar, and the autofermentation of yeast. The vegetable pigments examined probably contain a double linking, and can unite with two atoms of hydrogen, with production of leuco-compounds. The process proceeds readily in presence of yeast reductase, for example. In leuco-compounds the hydrogen is in loose combination, and is oxidised to water by molecular oxygen. One gram-mol. of methylene-blue withdraws from the fermenting medium 1 gram-mol. of hydrogen, and renders 1 gram-mol. of hexose inactive, and thus prevents the further decomposition into alcohol and carbon dioxide.

As regards the autofermentation of yeast, 1 gram-mol. of methylene-blue causes the production of an excess of carbon dioxide (1 gram-mol.); that is to say, the fermenting medium contains a substance which, in absence of sugar, gives up 1 mol. of carbon dioxide, two hydrogen atoms being removed from the substance. This is an enzymatic process which does not take place if the ferment is destroyed by heat. The carbon dioxide presumably results from the fermentation of amino-acids, with production of aldehydes.

Reductase has the most important share in the fermentation processes by activating hydrogen.

N. H. J. M.

**Assimilation of Nitrites by Moulds.** ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1914, i, 2192; from *Zeitsch. Gärungsphysiol.*, 1913, 3, 321—326. Compare 1913, i, 571).—Whilst it is shown that moulds can assimilate nitrites directly, without previously converting the nitrite into ammonia, some moulds, when well developed, produce ammonia in solutions of nitrites. The production of ammonia in such cases is attributed partly to the reducing power of the mature moulds and partly to the decomposition of nitrogenous organic constituents of the moulds.

N. H. J. M.

**Germination and Growth of Some Plants and Nitrification in Presence of Naphthalene.** P. CACCIARI (*Chem. Zentr.*, 1914, ii, 53—54; from *Staz. sper. agrar. ital.*, 47, 347—367).—Considerable amounts of naphthalene are without effect on the germinating power of seeds; the energy of germination is, however, somewhat affected, and growth is retarded. Naphthalene is unfavourable to nitrification.

N. H. J. M.

**Photosynthetic Processes in Green Plants.** E. SERNAGIOTTO (*Gazzetta*, 1914, 44, i, 628—631. Compare this vol., i, 1121).—As described in the paper referred to, the author's efforts to obtain free methylene yielded, instead, unsaturated and cyclic polymerides

of it. He suggests that the initial reaction in the photosynthetic processes of green plants may be  $\text{CO}_2 + \text{H}_2\text{O} = \text{O}_2 + \text{CH}\cdot\text{OH}$ , and that the hydroxymethylene so formed then polymerises. A typical cyclic polymeride would be  $(\text{CH}\cdot\text{OH})_6$ , which is inositol, and is widely distributed in plants. Schemes are given showing the formation of other products from the original polymerides by changes identical with, or similar to, reactions which have been observed under laboratory conditions.

R. V. S.

**Partition of the Nitrogen of Plant, Yeast and Meat Extracts.** F. C. Cook (*J. Amer. Chem. Soc.*, 1914, 36, 1551—1556).—Comparing the amounts of nitrogen precipitated by different reagents in the various extracts, it was found that phosphotungstic acid precipitated the highest, tannin-salt the next highest, and acid-alcohol the lowest percentage of nitrogen. Sørensen's formaldehyde titration method gave lower results for amino-nitrogen than the Van Slyke method.

The results showed that more of the nitrogen is present in a more completely hydrolysed state in plant extracts than in yeast and meat extracts. Plant and yeast extracts were found to contain no creatine and creatinine; the former contains very little nitrogen as purine, whilst the latter showed high purine nitrogen. Only meat extracts showed the biuret reaction.

The nitrogen of plant extracts consists chiefly of monoaminoacids and ammonia, none of it being precipitated by acid-alcohol. In the case of meat and yeast extracts, about 25% of the nitrogen is precipitated by acid-alcohol.

N. H. J. M.

**Colouring Matter contained in the Seed-coats of *Abrus precatorius*.** SARASI LAL SARKAR (*Biochem. J.*, 1914, 8, 281—286).—The outer layer of cells of the seed-coats of *Abrus precatorius* is impermeable to water and other solvents, so that if a handful of seeds is thrown into water, the colouring matter is dissolved only out of those which may have become ruptured, the entire seeds retaining their colour.

On soaking the crushed seed-coats in water, two colouring matters, yellow and scarlet, are extracted, and can be separated by shaking with ether. The scarlet colouring matter, which is the chief one present, remains dissolved in the water, and can be purified by means of its insoluble copper salt. Its reactions with ferric chloride, gelatin, ammonium ferricyanide, etc., indicate that it is a tannin substance.

Observation of microscopical sections of the seed-coats of *Abrus precatorius* treated with the above reagents showed that the scarlet colouring matter is located in the outermost layer of cells, whilst the yellow pigment is contained in a layer of cells situated at some distance from the surface of the seed-coat.

H. W. B.

**Anatomy and Microchemistry of *Anacardium occidentale*.** ERNST KRATZMANN (*Chem. Zentr.*, 1914, ii, 244; from *Pharm. Post*, 1914, 47, 375—378).—Cardol and anacardic acid, an oily substance



and crystals, m. p. about  $117^{\circ}$ , were separated. The seeds contain considerable amounts of fat, besides much starch. N. H. J. M.

**Chemical Examination of Cotton-root Bark.** FREDERICK B. POWER and HENRY BROWNING, jun. (*Pharm. J.*, 1914, **93**, 420—423).—On distilling an alcoholic extract of cotton-root (*Gossypium herbaceum*) bark with steam, a very small amount of a pale yellow, essential oil is obtained. The product gives the colour reaction of furfuraldehyde, and, by keeping, deposits a few crystals, m. p.  $112$ — $114^{\circ}$ , which appear to consist of acetovanillone. The other constituents of the bark are found to comprise: (1) a phenolic acid, m. p.  $196$ — $199^{\circ}$ , which is probably 2:3-dihydroxybenzoic acid; (2) salicylic acid; (3) a colourless, phenolic substance,  $C_9H_{10}O_3$ , m. p.  $258$ — $260^{\circ}$  (acetyl derivative, m. p.  $152^{\circ}$ ), which forms yellow solutions in aqueous alkalis, and develops a purple coloration with ferric chloride; (4) a yellow, phenolic substance,  $C_{13}H_{18}O_5$  (?), m. p.  $210$ — $212^{\circ}$  (acetyl derivative, m. p.  $147$ — $149^{\circ}$ ), which develops a deep purple coloration with aqueous alkalis and with concentrated sulphuric acid, and a brown coloration with ferric chloride; (5) betaine; (6) a fatty alcohol,  $C_{20}H_{42}O$ , m. p.  $77.5$ — $78.5^{\circ}$ ; (7) a phytosterol,  $C_{27}H_{46}O$ , m. p.  $130^{\circ}$ ; (8) a small amount of a hydrocarbon (triacontane ?), m. p.  $60$ — $61^{\circ}$ ; (9) ceryl alcohol; (10) a mixture of fatty acids, consisting chiefly of oleic and palmitic acids; and (11) a considerable proportion of sugar, from which *d*-phenylglucosazone and penta-acetyldextrose have been prepared.

The bark does not contain any alkaloid or tannin. The resinous component, from which some of the substances mentioned above are isolated, has a deep purple colour, and amounts to 10.6% of the weight of the air-dried bark employed. C. S.

**Presence of Gentiopicroin and Gentianose in the Fresh Roots of *Gentiana purpurea*, L.** MARC BRIDEL (*J. Pharm. Chim.*, 1914, [vii], **10**, 62—66. Compare A., 1913, i, 149, 150, 434, 690, 806, 1212).—The author has previously examined a cultivated specimen of *Gentiana purpurea*, L., and now gives the results of his investigation of the wild plant, which is found to contain about twice as great a quantity of substances hydrolysable by invertin and emulsin as the cultivated specimen. Further evidence of the presence of an unknown sugar, hydrolysable by invertin, is also obtained. The roots of *Gentiana purpurea*, L., appear to be very similar in composition to those of other gentians previously studied, and, on extraction, yield crystallised gentiopicroin,  $[\alpha]_D -196.6^{\circ}$ , and gentianose,  $[\alpha]_D +31.43^{\circ}$ , the proportion of the former being identical with that contained in the yellow gentian. H. W.

**Biochemical Investigation of the Glucosides, Hydrolysable by Emulsin, in Indigenous Orchidaceæ.** EM. BOURQUELOT and M. BRIDEL (*J. Pharm. Chim.*, 1914, [vii], **10**, 14—18, 66—72).—The method is as follows. The fresh plant is introduced in portions

into boiling 85% alcohol, and ebullition continued for fifteen to twenty minutes to ensure the destruction of all ferments. After cooling, the extract is decanted, and the residue again heated with alcohol. The united alcoholic liquors are filtered and evaporated, and the residue dissolved in water containing thymol. The rotation of the liquid is determined, reducing sugar is estimated, and invertase added. Sucrose, if present, is thereby hydrolysed, and the rotation changes towards the lævo-direction. When no further change in rotation is observed, the liquid is heated at 100°. After cooling, emulsin is added. Should the plant contain a hydrolysable glucoside, the rotation returns towards the right, the extent being proportional to the amount of glucoside in solution.

The orchidaceæ examined are divisible into two groups. Those belonging to the series *Aceras*, *Loroglossum*, *Orchis*, *Ophrys*, and *Platanthera* yield dextrorotatory extracts; the others, comprising the species *Limodorum*, *Cephalanthia*, *Epipactis*, and *Neottia*, give lævorotatory extracts. All species contain a sugar hydrolysable by invertase. In most cases, sucrose is in all probability present, the most marked exception being presented by *N. Nidus-avis*. All the plants contain one or more glucosidic substances hydrolysable by emulsin, which possibly vary in the different cases. Nevertheless, for the majority of species, the indices observed lie within moderately close limits, which points to the presence of the same glucosidic principle in each, and the fact that a precipitate always separates during the action of emulsin lends support to this supposition.

H. W.

**Occurrence of Manganese in Kentucky Soils and its Possible Significance.** O. M. SHEDD (*J. Ind. Eng. Chem.*, 1914, **6**, 660—664).

—Although manganese is universally present in soils and plants, there are large differences in the manganese content of the soils of different geological areas, and sometimes in those from the same area. The amounts found in the surface soils examined varied from 0.005 to 0.331% (MnO), and in the subsoils from 0.002 to 0.264%. Usually, the surface soils contain the larger amount, but less manganese is found in cultivated soils than in the corresponding virgin soils; the same holds good in the case of the subsoils. Most soils contain considerably more manganese than phosphorus, but the loss of manganese from cultivated soils is greater than that of phosphorus. The application of certain manganese salts, particularly the sulphate, to soils is beneficial to the crops; the quantity applied must, however, be small, as large quantities are harmful.

W. P. S.

## Organic Chemistry.

**Isoprene from Commercial Turpentines.** CHAS. H. HERTY and J. O. GRAHAM (*J. Ind. Eng. Chem.*, 1914, 6, 803—804).—Ordinary oil of turpentine yielded 5.5% of isoprene when submitted to distillation in the "isoprene lamp" apparatus described by Harries and Gottlob (A., 1911, i, 798); the fraction of oil of turpentine, b. p. 155—156°, yielded 8.0% of isoprene, and the fraction b. p. 169—175°, 0.5%. No isoprene was obtained from the fraction b. p. above 175°. It is evident that the isoprene is derived from the pinene present. Oil of *Pinus serotina* yielded 12% of isoprene; pine oil, 4%; and refined spruce pine turpentine, none.  
W. P. S.

**Ethyl Ester of Linolic Acid Tetrabromide as a Product in the Analysis of Cotton-seed Oil.** LEROY S. PALMER and PHILIP A. WRIGHT (*J. Ind. Eng. Chem.*, 1914, 6, 822—823).—During an investigation regarding the composition of cotton-seed oil, in which the unsaturated fatty acids were isolated by making use of their solubility in ether, the authors obtained a crystalline compound, in place of linolic acid tetrabromide, when an attempt was made to form the latter substance. The crystals had m. p. 58—58.5°, and consisted of ethyl linolate tetrabromide. The cause of the formation of this ethyl ester has not been definitely ascertained, but it appears to take place during the time the lead soaps are in contact with ether.  
W. P. S.

**Humic Acid.** SVEN ODÉN (*Arkiv. Kem. Min. Geol.*, 1914, 5, No. 15. Compare A., 1912, i, 336; this vol., i, 500).—When suspensions of *Sphagnum*, *Sphagnum* peat and leaf humus are treated with ammonia, an adsorption of ammonia takes place, and, coincidentally, salts are formed in considerable amounts from the peat and humus, whilst the *Sphagnum* itself gives only a relatively insignificant amount of salt. These results are opposed to the view of Baumann and Gully, who consider that the adsorption of bases by peat is mainly due to the presence of *Sphagnum* cells. The effect on conductivity of the production of salts exceeds that of adsorption even in concentrations of  $N/0.01$ . Humates are extracted by ammonia in concentrations as low as  $N/0.005$ , so that the suggestion that humates are decomposition products of the action of ammonia on humus is improbable.

With reference to the criticisms of Ehrenberg and Bahr (this vol., i, 50) it is pointed out that filtration through collodion can only be depended on when not less than 10% collodion is employed. It is also considered possible that as Ehrenberg and Bahr omitted to extract their humic acid with alcohol, it may have contained a considerable amount of hymatomelanic acid which might account for the different value obtained for the mol. weight.  
N. H. J. M.

**Isolation of Crystalline *dl*-Glyceraldehyde from a Syrup Obtained by the Oxidation of Glycerol.** EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1914, 36, 2223—2234).—The syrupy product

obtained by the oxidation of glycerol with hydrogen peroxide in presence of ferrous sulphate (Fenton and Jackson, T., 1899, 75, 4) contains *dl*-glyceraldehyde. This was established by converting the aldehyde into the diethylacetal and recovering pure *dl*-glyceraldehyde from the latter by hydrolysis with 0.1*N*-sulphuric acid. E. G.

**Crystallised *l*-Mannose.** W. ALBERDA VAN EKENSTEIN and J. J. BLANKSMA (*Chem. Weekblad*, 1914, 11, 902).—A yield of 12.5% of *l*-mannose can be obtained by hydrolysis of the cyanhydrin of *l*-arabinose, isolation of mannonolactone from the mixture of *l*-mannonic acid and *l*-gluconic acid, and reduction with sodium amalgam. To crystallise the sugar, it is converted into the phenylhydrazone, and then regenerated by the action of benzaldehyde. After several days, the resulting syrup crystallises, and on recrystallisation from alcohol forms colourless crystals, m. p. 132°. It exhibits mutarotation, the initial rotation being  $[\alpha]_D + 14^\circ$ , and the final rotation  $[\alpha]_D - 14^\circ$ , in complete agreement with the corresponding constants for *d*-mannose.

A. J. W.

**Preparation of Raffinose.** C. S. HUDSON and T. S. HARDING (*J. Amer. Chem. Soc.*, 1914, 36, 2110—2114).—During a study of the hydrolysis of raffinose by enzymes, a large quantity of the sugar was required. A method for its preparation was therefore devised which is superior to any of those hitherto recorded.

Cotton-seed meal is extracted with water, the aqueous solution treated with basic lead acetate and filtered, and the filtrate treated with hydrogen sulphide to remove excess of lead, and again filtered. A little sodium hyposulphite is added to prevent development of colour, and the solution is boiled under reduced pressure until it becomes a syrup containing about 25% of water. Barium hydroxide is now added, and the barium raffinosate is powdered and washed with methyl alcohol. The barium compound is suspended in water and carefully decomposed with 50% phosphoric acid, so that the solution is exactly neutral at the end of this process. After filtration, a little sulphuric acid is added to remove the last traces of barium, and the solution is again filtered, treated for a few minutes with eponite (a form of vegetable charcoal), filtered, and concentrated in a vacuum to a syrup containing 20—25% of water. A small quantity of alcohol containing 0.3% of nitric acid is added, and the mixture is seeded with crystals of raffinose hydrate and left at 0° to crystallise. The crystalline mass is triturated with 75% alcohol, filtered, and washed with alcohol of the same strength until the washings are colourless. A yield of 4—5% of the weight of cotton-seed meal employed may thus be obtained of colourless raffinose crystals. The product may be further purified by recrystallisation. E. G.

**The Solubility of Nitrocellulose in Mixtures of Ether and Alcohol.** A. MATTEOSCHAT (*Chem. Zentr.*, 1914, i, 2095; from *Zeitsch. ges. Schiess-Sprengstoffwesen*, 1914, 9, 105—106).—The author has measured the solubility of a sample of gun-cotton in mixtures of ether and dry or dilute alcohol. Absolute alcohol and ether in the

proportion 1 : 1 make a useful mixture, but with the common diluted alcohols the proportion should be, ether to alcohol as 2 : 1 or 3 : 1.

J. C. W.

**The Plurality of Amyloses.** CH. TANRET (*Compt. rend.*, 1914, 159, 530—532).—The author has determined the absolute and relative percentages of amyloses dissolved by water at different temperatures in 16 different kinds of starch. For the starches used, water, at the same temperature, dissolves very different amounts of amylose. The results are a further proof of the plurality of amyloses as suggested by Maquenne and Roux.

W. G.

**Metallic Compounds of Glycine.** A. BERNARDI (*Gazzetta*, 1914, 44, ii, 257—260).—The author has investigated the compound prepared by Dessaigne (*Annalen*, 1852, 82, 365), examined later by Ley and Kissel (A., 1899, ii, 485), and known as mercury glycine,  $(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Hg}$ . It is found that the action of alkali on this compound results in no precipitation of mercuric oxide, but in the formation of the compound  $\text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{NH} \cdot \text{Hg}$ . It is suggested that the latter compound be termed mercuriglycine, and that the former be named mercury aminoacetate.

Mercury aminoacetate,  $(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Hg}$ , forms tufts of white needles, m. p. 110—111°. *Mercuriglycine*,  $\text{C}_2\text{H}_3\text{O}_2\text{NHg}$ , obtained by the action of the calculated proportion of calcium hydroxide solution on mercury aminoacetate, has m. p. 155° (decomp.), and when treated with sodium thiosulphate liberates sodium hydroxide quantitatively according to the equation:

$\text{C}_2\text{H}_3\text{O}_2\text{NHg} + \text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O} = \text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{NH}_2 + \text{HgS}_2\text{O}_3 + 2\text{NaOH}$ . With mercuric sulphate, mercury aminoacetate forms the double salt,  $\text{Hg}(\cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_2, \text{HgSO}_4, 3\text{H}_2\text{O}$ , decomp. 102°.

*Calciglycine*,  $\text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{NH} \cdot \text{Ca}$ , was also prepared.

T. H. P.

**Three Isomeric Ethyl-sec.-butylhydroxylamines.** LAUDER WILLIAM JONES and LEONORA NEUFFER (*J. Amer. Chem. Soc.*, 1914, 36, 2202—2208).—Jones (A., 1907, i, 897) has described two isomeric  $\alpha\beta$ -hydroxylamines, namely,  $\beta$ -methyl- $\alpha$ -ethyl- and  $\alpha$ -methyl- $\beta$ -ethyl-hydroxylamine. In the present paper, an account is given of  $\alpha$ -ethyl- $\beta$ -sec.-butyl- and  $\beta$ -ethyl- $\alpha$ -sec.-butyl-hydroxylamines which are isomeric with  $\beta$ -ethyl- $\beta$ -sec.-butylhydroxylamine (Bewad, A., 1900, i, 630; Dunstan and Goulding, T., 1901, 79, 641).

When hydroxyurethane (carbethoxyhydroxamic) ethyl ether (Jones, A., 1898, i, 174) is treated with sec.-butyl iodide and sodium ethoxide, it is converted into carbethoxy- $\alpha$ -ethyl- $\beta$ -sec.-butylhydroxylamine (hydroxy-sec.-butylurethane ethyl ether),  $\text{C}_4\text{H}_9 \cdot \text{N}(\text{OEt}) \cdot \text{CO}_2\text{Et}$ , b. p. 105—106.4°/55 mm. On hydrolysing this compound with potassium hydroxide, it yields  $\alpha$ -ethyl- $\beta$ -sec.-butylhydroxylamine,  $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{OEt}$ , b. p. 88.4—89°; its hydrochloride has m. p. 94°; the platinichloride was prepared and analysed.

By the action of sec.-butyl iodide on hydroxyurethane in presence of

potassium hydroxide, *carbethoxy- $\alpha$ -sec.-butylhydroxylamine (hydroxyurethane sec.-butyl ether)*,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{O}\cdot\text{C}_4\text{H}_9$ , b. p. 116—116.6°/27 mm., is produced, and this, on being treated with ethyl iodide and sodium ethoxide, is converted into *carbethoxy- $\beta$ -ethyl- $\alpha$ -sec.-butylhydroxylamine (hydroxyethylurethane sec.-butyl ether)*,  
 $\text{C}_4\text{H}_9\cdot\text{O}\cdot\text{NEt}\cdot\text{CO}_2\text{Et}$ ,

b. p. 86.5—87°/30 mm. The latter compound, on hydrolysis, furnishes  *$\beta$ -ethyl- $\alpha$ -sec.-butylhydroxylamine*,  $\text{NHEt}\cdot\text{OC}_4\text{H}_9$ , b. p. 93.5—94°; its *hydrochloride* is deliquescent; the *platinichloride* forms deep yellow crystals.

When *carbethoxy- $\alpha$ -sec.-butylhydroxylamine* is heated with potassium hydroxide, it is converted into  *$\alpha$ -sec.-butylhydroxylamine*,  $\text{NH}_2\cdot\text{O}\cdot\text{C}_4\text{H}_9$ , b. p. 85.5°; its *hydrochloride* has m. p. 54.7—55°, and the *platinichloride* forms deep yellow crystals.

The carbethoxyhydroxylamines described in this paper are oily liquids with a characteristic odour; they do not reduce ammoniacal silver nitrate or Fehling's solution.  *$\alpha$ -sec.-Butylhydroxylamine* and the *ethyl-sec.-butylhydroxylamines* have a characteristic ammoniacal odour; they reduce ammoniacal silver nitrate in the cold and Fehling's solution when heated.

E. G.

**Some New Hydroxyurethanes and Chromoisomeric Silver Salts of Their Acyl Derivatives.** LAUDER WILLIAM JONES and RALPH OESPER (*J. Amer. Chem. Soc.*, 1914, **36**, 2208—2223).—The experiments described in this paper were undertaken with a view to the preparation of mixed oximinocarbonic esters,  $\text{OR}\cdot\text{C}(\text{NOH})\cdot\text{OR}'$ . Several new carbalkyloxyhydroxamic acids (hydroxyurethanes) have been obtained and their benzoyl esters studied. The silver salts of some of these benzoyl esters were obtained in two isomeric modifications, white and yellow, which are mutually transformable. The methyl, ethyl, and isopropyl compounds yield only yellow salts, but the isobutyl, isoamyl, and benzyl compounds furnish both modifications. When treated with alkyl haloids, these silver salts yield derivatives in which the alkyl groups are attached to nitrogen instead of to oxygen, and for this reason the desired acyl derivatives of mixed oximinocarbonic esters could not be obtained.

*Carbomethoxyhydroxamic acid*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ , was obtained as a thick, yellow oil by the interaction of methyl chloroformate, hydroxylamine hydrochloride, and potassium carbonate. The *benzoyl* ester,  $\text{OBz}\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ , m. p. 82°, forms white needles; its *silver* salt,  $\text{OBz}\cdot\text{NAg}\cdot\text{CO}_2\text{Me}$ , has m. p. 149—150°.

When the silver salt of the benzoyl ester of carbethoxyhydroxamic acid (Jones, A., 1898, i, 174) is heated, it becomes white at 156—157°, then darkens rapidly, and melts at 174° (decomp.). The action of ethyl iodide and isoamyl iodide on this salt has already been described (this vol., i, 505). By the action of benzoyl chloride on the silver salt of carbethoxyhydroxamic acid or by the action of ethyl chlorocarbonate on the silver salt of dibenzhydroxamic acid, the dibenzoyl derivative of carbethoxyhydroxamic acid (A., 1898, i, 174) is produced.

*Carbopropoxyhydroxamic acid*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\text{Pr}$ , was obtained as a thick, colourless oil. The *benzoyl* ester yields a *silver* salt, m. p.

144—145°, forming yellow needles which do not become white when heated. By the action of benzoyl chloride on this silver salt, the *dibenzoyl* derivative,  $\text{OBz}\cdot\text{NBz}\cdot\text{CO}_2\text{Pr}$ , m. p. 78—89°, is produced, which crystallises in cubes. When the silver salt is treated with ethyl iodide, the *N-ethyl* derivative,  $\text{OBz}\cdot\text{NEt}\cdot\text{CO}_2\text{Pr}$ , is obtained as a pale yellow oil, and is hydrolysed by hydrochloric acid with formation of  $\beta$ -ethylhydroxylamine hydrochloride.

*Carbisobutoxyhydroxamic acid*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$ , is a colourless oil. The *benzoyl* ester, m. p. 43—44°, yields a yellow *silver* salt which, when heated at 80—82°, is converted into a white modification, and has m. p. 158°. The *N-ethyl* derivative,  $\text{OBz}\cdot\text{NEt}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$ , is a bright yellow oil.

*Carbisamyloxyhydroxamic acid*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11}$ , is a viscid, pale yellow oil. The *benzoyl* ester, a colourless oil, furnishes a yellow *silver* salt which becomes white at about 75° and melts at 141—142°. When this salt is treated with benzoyl chloride, the *dibenzoyl* derivative,  $\text{OBz}\cdot\text{NBz}\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11}$ , m. p. 69—70°, is produced. The *N-ethyl* derivative,  $\text{OBz}\cdot\text{NEt}\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11}$ , is a pale yellow oil which yields  $\beta$ -ethylhydroxylamine on hydrolysis.

*Carbobenzoyloxyhydroxamic acid*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}$ , has m. p. 65°. The *benzoyl* ester, m. p. 109—110°, yields a *silver* salt, m. p. 150—151°, which exists in yellow and white modifications. The *N-ethyl* derivative,  $\text{OBz}\cdot\text{NEt}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}$ , is a pale yellow oil.

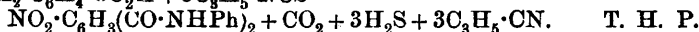
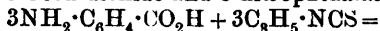
E. G.

**Syntheses in the Fluorene and Bisdiphenylene-ethylene Series.** GONZALO GALLAS (*Anal. Fis. Quim.*, 1914, 12, 112—131).—2 : 7-Dinitrofluorenone condenses with 2 : 7-dinitrofluorene at 160° in the presence of zinc chloride to form 2 : 7 : 2' : 7'-tetranitrobisdiphenylene-ethylene, which on reduction by means of tin and hydrochloric acid yields the corresponding *tetra-amino*-compound, colourless, silky needles, m. p. 250° (decomp.). The acid solution develops a blue coloration with oxidising agents.

G. D. L.

**Action of Allylthiocarbimide on Various Amino-organic Compounds.** G. ROSSI (*Gazzetta*, 1914, 44, ii, 264—268).—In the absence of a solvent, the interaction of *o*-toluidine and allylthiocarbimide at the boiling point of the latter yields, not *s-o*-tolylallylthiocarbimide, but *s*-di-*o*-tolylthiocarbimide and allylamine.

The action of allylthiocarbimide on *o*-aminobenzoic acid is of a more complicated character and yields allyl cyanide, hydrogen sulphide, carbon dioxide and 3-nitrophthalanilide :



T. H. P.

**Benzoylations in Ether Solution.** WILLIAM M. DEHN and ALICE A. BALL (*J. Amer. Chem. Soc.*, 1914, 36, 2091—2101).—In an earlier paper (Dehn, A., 1912, i, 833) an account was given of the action of acetyl chloride on various bases in solution in dry ether. Similar experiments have now been carried out with benzoyl chloride and it has been found that, as with acetyl chloride, a mixture of the hydrochloride and acyl chloride additive compound of the base is pre-

cipitated. In some cases, these precipitates are contaminated with the original bases or with their benzoyl derivatives. All the benzoyl chloride additive compounds are dissociated by water and many of them are unstable towards heat. The additive compounds of the primary and secondary bases can generally be prepared by adding hydrogen chloride in ether or toluene solution to solutions of the benzoyl derivatives; the hydrochlorides of benzanilide, *o*- and *p*-tolylbenzamide, and  $\alpha$ -naphthylbenzamide, however, could not be obtained in this way.

*iso*Butylamine yields a mixture of its hydrochloride with that of *isobutylbenzamide*. The precipitate obtained with *iso*amylamine has m. p. 201° and consists of *isoamylbenzamide hydrochloride*; *isoamylbenzamide* is an oil, b. p. 310—315°. Aniline gives a precipitate containing benzanilide and benzanilide hydrochloride. *p*-Toluidine yields *p*-tolylbenzamide and *p*-tolylbenzamide hydrochloride, whilst *o*- and *m*-toluidine and  $\alpha$ -naphthylamine afford mixtures of the hydrochloride of the base, the benzamide, and the additive compound. Phenylhydrazine gives a precipitate consisting of phenylhydrazine hydrochloride, and benzoylphenylhydrazine and its hydrochloride. Carbamide furnishes the additive compound,  $\text{CO}(\text{NH}_2)_2 \cdot \text{BzCl}$ , m. p. 209° (decomp.).

Diethylamine and methylaniline yield precipitates containing diethylbenzamide hydrochloride and phenylmethylbenzamide hydrochloride respectively. Piperidine furnishes benzoylpiperidine hydrochloride, which forms white, hygroscopic needles. Benzylethylamine gives benzylethylbenzamide hydrochloride; benzylethylbenzamide has b. p. 218°/29 mm.

Additive compounds were also obtained with triethylamine, tri-*iso*amylamine, dimethylaniline, diethylaniline, antipyrine, quinoline, pyridine, and  $\alpha$ -picoline.

E. G.

**Copper Lakes of Eosin.** HARVEY NICHOLAS GILBERT (*J. Physical Chem.*, 1914, 18, 586—618).—An investigation has been made of the eosin copper lake with the object of ascertaining whether the substance is a definite compound or merely an adsorption complex consisting of copper hydroxide with the eosin adsorbed in approximately equivalent amount. It is shown that copper hydroxide, when treated with ether solutions of eosin in varying quantities, exhibits the typical adsorption curve, and there is no indication of a chemical compound. The total amount of eosin taken up is about one-tenth of the amount required to form copper eosinate. Similar adsorption curves were obtained when magnesium oxide was shaken up with various eosin solutions. The composition of the copper lake produced by the interaction of copper sulphate and sodium eosinate was studied, and it was found that the precipitate contained an excess of copper in the cases where an excess of copper salt was employed. It was found possible to synthesise lakes from copper hydroxide and eosin which behaved like the original lake. These lakes could be brought into colloidal solution, and all behaved similarly, although the ratio of copper to eosin varied from two molecules of copper to one of eosin, to one molecule of copper to two of eosin. The amorphous lake has been



transformed into crystalline copper eosinate. The properties of the colloidal lake differed entirely from those of the crystalline substance. The decomposition of the lake in aqueous suspension by means of ether showed that the eosin was set free from the lake by the greater attraction of the copper hydroxide for the anions of certain salts. These anions are adsorbed by the copper hydroxide setting free the adsorbed eosin. The order of the decomposition, due to these adsorbed anions, is the same as is found for other cases of adsorption:  $\text{SO}_4^{2-} > \text{Br}^- > \text{Cl}^- > \text{NO}_3^-$ . The decomposition of the lake by aqueous alcohol and aqueous acetone is similar to that of ether and may be explained in the same way as due to the preferential adsorption of anions. The results obtained indicate that the lake, produced by the action of an aqueous solution of sodium eosinate on a solution of copper sulphate, does not consist of copper eosinate, although the copper and eosin are present in equivalent quantities. The lake consists of copper hydroxide, which from the method of formation contains an equivalent amount of adsorbed eosin. A colorimetric method for the estimation of eosin is devised, which consists in preparing a solution of cobalt nitrate of exactly the same tint as a solution of eosin containing 0.00125 gram per litre. Such a cobalt solution contains 17.84 grams of the nitrate per litre. The method of estimation consists in diluting the given eosin solution until it has exactly the same tint as the cobalt standard.

J. F. S.

*p*-Aminobenzaldehyde and Aniline. G. Rossi (*Gazzetta*, 1914, 44, ii, 261—263).—The interaction of *p*-aminobenzaldehyde and boiling aniline yields *p*-aminobenzylideneaniline, which crystallises in microscopic, canary-yellow needles, and forms a *picrate*, brick-red needles exploding violently at 150°, and, when treated with ethyl iodide, *p*-ethyl aminobenzylideneaniline,  $\text{NHEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{NPh}$ , red needles, decomp. 150°.

T. H. P.

Oxidation of the Nopinine of Spanish Oil of Turpentine. ANTONIO MADINAVEITIA (*Anal. Fis. Quim.*, 1914, 12, 259—264).—This oil on oxidation with potassium permanganate in alkaline solution yields nopic acid in conformity with the observations of Baeyer and of Wallach (A., 1907, i, 936), and in opposition to the statements of Dorrnsoro and Fernández (this vol., ii, 78).

G. D. L.

Volatile Oil of *Calycanthus floridus*. EMERSON R. MILLER, G. W. TAYLOR, and M. H. ESKEW (*J. Amer. Chem. Soc.*, 1914, 36, 2182—2187).—The material used for this investigation consisted of the shrubs of *Calycanthus floridus*, collected after the leaves had fallen. They were cut off just above the ground, freed from any remaining leaves, allowed to dry in the air, and submitted to distillation with steam.

Three samples of oil were obtained at different times in yields of 0.53%, 0.25%, and 0.39%; the small, young plants gave the best yield. The samples were pale yellow, soluble in all proportions in 90% alcohol, and furnished the following constants:  $D_{25}^{25}$  0.9209, 0.9161, 0.9136;  $n_D^{25}$  (in a 100 mm. tube), +2.85°, +2.84°, +6.6°;  $n_D^{25}$  1.4675, 1.4713, 1.4753; saponification number, 12.5, 14.40, 16.6; saponification

number after acetylation, 75.1, —, 65.7. Calculating the alcohols and esters as borneol and bornyl acetate, the oils contained 4.37%, 5.04%, and 5.81% of bornyl acetate, and samples (1) and (3) contained 18.44% and 14.46% of borneol respectively. Samples (1) and (3) contained 35—36% and 69—71% of cineole. Besides borneol, bornyl acetate, and cineole, the oil contained *d*- and *l*- $\alpha$ -pinene, salicylic acid, one or more esters other than bornyl acetate, and probably linalool and sesquiterpenes. E. G.

**Oils of the Coniferæ. II. The Leaf and the Twig, and Bark Oils of White Fir.** A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1914, 6, 809—810. Compare this vol., i, 1134).—The leaves and twigs of white fir, *Abies concolor*, yield from 0.029 to 0.272% of oil having  $D^{15}_D$  0.8720—0.8777,  $n^{10}_D$  1.4786—1.4796,  $\alpha^{25}_D$   $-20.11^\circ$  to  $-27.94^\circ$ ; acid number, 1.01—1.81; ester number, 12.52—27.34. The bark yields 0.095% of oil having  $D^{15}_D$  0.8702—0.8767,  $n^{10}_D$  1.4809—1.4833,  $\alpha^{20}_D$   $-20.15^\circ$  to  $-20.95^\circ$ ; acid number, 0.87—1.22; ester number, 6.43—6.88. The composition of the oils was found to be as follows:

	Leaf and twig oil.	Bark oil.
Furfuraldehyde .....	trace	trace
<i>l</i> - $\alpha$ -Pinene.....	12	9
<i>l</i> -Camphene.....	8	—
<i>l</i> - $\beta$ -Pinene.....	42	60
<i>l</i> -Phellandrene.....	15	Dipentene 12
Ester, as bornyl acetate.....	6.5	2.5
Free borneol.....	9.5	4.5
"Green oil" .....	3	5
Loss .....	4	7

W. P. S.

**Oil of Black Sage.** CHARLES E. BURKE and CHARLES C. SCALIONE (*J. Ind. Eng. Chem.*, 1914, 6, 804—806).—Black sage (*Ramona Stachyoides*) from Southern California yielded 0.9% of oil having  $D^{15}_D$  0.8979,  $[\alpha]$   $24.4^\circ$ ,  $n_D$  1.4729; acid number, 2.2; ester number, 1.6. The oil had the following composition: pinene, 6.0%; cineole, 30.0%; dipentene, terpinene, etc., 25.0%; thujone, 8.0%; camphor, 25.0%; resinous substance, 5.0%. W. P. S.

**Essential Oil of Argentine Mint (*Bystropogon Mollis* Kth.).** ADOLFO DOERING (*Bol. Acad. Nac. Ciencias Cordoba*, 1913, 19, 379—391).—The essential oil forms about 0.4% of the plant, is clear, not depositing crystals of menthol at  $12^\circ$ , has  $D$  0.918—0.920, and distills chiefly at  $210^\circ$ . As much as 2.5% of furfuraldehyde may be present, and is removed by means of permanganate. Free acid amounts to about 0.7%, and phenols are present in traces. Menthol appears to be absent. The terpenes have not so far been characterised.

G. D. L.

**Optical Activity of Cinnamein.** L. ROSENTHALER (*Chem. Zentr.*, 1914, ii, 36—37; from *Schweiz. Apoth.-Zeit.*, 1914, 52, 273—275).—The rotations of the cinnameins isolated from genuine and false Peru balsams and from some artificial products have been measured, in alcoholic and ethereal solutions. The majority of the extracts from genuine balsams had a small dextrorotation. In addition, the

cinnamein content was determined, as well as the saponification number of each balsam and of the cinnamein which was isolated from it.

J. C. W.

**Synthetic Caoutchouc.** I. I. ANDRÉEV (*Chem. Zentr.*, 1914, ii, 325—326; from *Ber. St. Petersburg Polytech. Inst.*, 1913, 21, 313—368).—An apparatus is described, with diagrams, in which turpentine may be decomposed by means of an electrically heated platinum wire, and thus converted into isoprene. The addition of carvene, dipentene, or aromatic hydrocarbons is found to improve the yield of isoprene.

J. C. W.

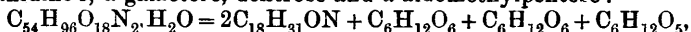
**The Gitalin Question.** L. ROSENTHALER (*Chem. Zentr.*, 1914, ii, 328; from *Schweiz. Apoth.-Zeit.*, 1914, 52, 349—350).—The author agrees with Kiliani (this vol., i, 857) that gitalin is a mixture. He has separated it into a fraction which forms a hydrate and one which does not, and has isolated a crystalline substance which is physiologically very active, and seems to differ from any known constituent of digitalis.

J. C. W.

**Dimethylpyrone Hydrochloride.** H. N. K. RØRDAM (*Oversigt. K. Danske Vidensk. Selskabs. Forhandl.*, 1914, 243—262).—The investigations which have hitherto been carried out have not made it certain whether dimethylpyrone hydrochloride acts as a true salt in aqueous solution, or whether it is resolved into the components dimethylpyrone and hydrochloric acid. In order to decide the question, the author has determined the concentration of the chloride ion in solutions of varying strength, by measuring the potential of the electrode:  $\text{Hg} \mid \text{solid Hg}_2\text{Cl}_2, \text{solution of dimethylpyrone hydrochloride}$ , against a *N*/10-calomel electrode; similar measurements were made with various solutions of hydrochloric acid. The equivalent conductivities of all the solutions were also measured, and on plotting the values of the chloride ion concentrations (abscissæ) against the equivalent conductivities (ordinates) it is found that the curve for dimethylpyrone hydrochloride lies below that for hydrochloric acid, both curves approaching the same value for infinite dilution. The conclusion is therefore that dimethylpyrone exists as a true salt in solution; it is hydrolysed to some extent, the hydrolysis constant being 0.63, and the dissociation constant of dimethylpyrone as base is calculated to be  $1.9 \times 10^{-14}$  (compare Walden, A., 1902, i, 168).

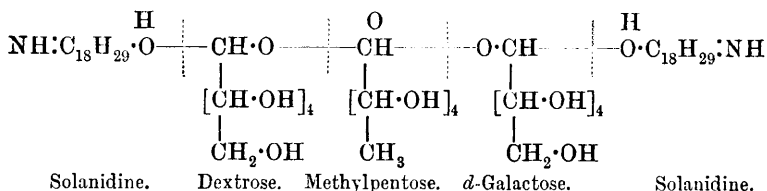
T. S. P.

**Solanine-s.** VIII. Nature of the Glucosidic Condensation of Solanine-s; Glucosides in General. GIUSEPPE ODDO and MARCELLO CESARIS (*Gazzetta*, 1914, 44, ii, 181—190. Compare this vol., i, 1141).—The hydrolysis of solanine-s from *Solanum sodomaeum* yields solanidine-s, *d*-galactose, dextrose and *d*-aldomethylpentose:



the molecule of water of crystallisation sufficing for the decomposition. Solanine-s does not react with phenylhydrazine or hydroxylamine; further, the only oxygen atom of solanidine-s is hydroxylic, and the nitrogen is present in the form of the imino-group in both compounds.

From these results, the structure of solanine-*s* and the manner in which water is added to it on hydrolysis are represented thus :



The results obtained by Oddo and Mameli (A., 1904, i, 280) with the acetals prepared from dichloroacetaldehyde hydrate are utilised in elaborating a theory to explain the synthesis of solanine from its constituents. T. H. P.

**Solanine-*s*. IX. Solandine sodomaeum and Some of its Products of Disintegration.** GIUSEPPE ODDO AND MARCELLO CESARIS (*Gazzetta*, 1914, 44, ii, 191—208).—*Solandine ether*,  $(\text{NH:C}_{18}\text{H}_{29})_2\text{O}$ , obtained by the action of hydrochloric acid on solandine-*s* in alcoholic solution, crystallises in needles, m. p. 176—177°,  $[\alpha]_D - 141.5'$  in benzene, and has the molecular weight 373—425 in freezing benzene and 248—259 in freezing acetic acid, the calculated value being 536.5. When its alcoholic solution is poured on to concentrated sulphuric acid, a yellow ring, changing to orange, forms at the surface of separation. When treated with nitrous acid, the ether yields the compound,  $[\text{N}(\text{OH})_2\cdot\text{C}_{18}\text{H}_{29}\text{N}\cdot\text{O}\cdot\text{C}_{18}\text{H}_{29}\text{N}]_2\text{N}\cdot\text{OH}$ , 2 mols. of the ether reacting with 3 mols. of the acid, with elimination of  $1\text{H}_2\text{O}$ . This compound forms pale reddish-yellow needles, m. p. 224—225° (decomp.). It gives neither a blue coloration with diphenylamine nor the characteristic reaction of nitroso-compounds with Liebermann's reagent. When treated with acid or alkali, it yields solandine ether.

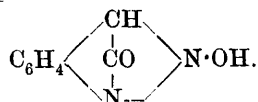
The compound described as azosolandine (A., 1911, i, 671) is found to have the composition  $\text{C}_{72}\text{H}_{116}\text{O}_9\text{N}_8$  [ $= 4(\text{C}_{18}\text{H}_{31}\text{ON}, \text{HNO}_2) - 3\text{H}_2\text{O} - 6\text{H}$ ]. When treated with hydrochloric acid it gives *dihydrosolanidyl chloride*,  $\text{C}_{18}\text{H}_{33}\text{Cl}$  (?), m. p. 113°, and another compound, m. p. 110—125°, which appears to be a chlorinated alcohol,  $\text{C}_{18}\text{H}_{33}\text{OCl}$ .

No definite compounds could be separated from the products of the action of energetic dehydrating or oxidising agents on solandine-*s*.

T. H. P.

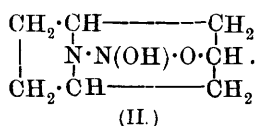
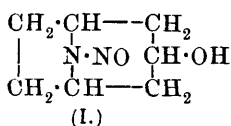
**Action of Nitrous Acid on Amines. Behaviour Towards Tropigenine and Granatoline. I.** GIUSEPPE ODDO AND MARCELLO CESARIS (*Gazzetta*, 1914, 44, ii, 209—227).—From the results of their investigations on the action of nitrous acid on solanine-*s* and solandine-*s* (compare preceding abstract), the authors draw the conclusion that the action of nitrous acid on a primary or secondary amine results in the formation of the corresponding nitrite,  $\text{NHR}^1\text{R}^2\cdot\text{HNO}_2$ , which then undergoes transformation into an *as*-dihydroxyhydrazine derivative,  $\text{NR}^1\text{R}^2\cdot\text{N}(\text{OH})_2$ . The further decomposition of the latter varies with the nature of the radicles present, and may follow one or other of three types, which have been named: (1) *Anazoic*. In this case, ammonium nitrite yields nitrogen and water; primary amines, nitrogen,

water and an alcohol, and secondary amines, nitrogen and either two alcohols, or, if  $R^1=R^2$ , a single alcohol. (2) *Diazoic*. Here, ammonium nitrite yields nitrosoamine,  $NH_2 \cdot NO$ , or *isonitrosoimide*,  $NH:NOH$ ; primary amines give nitrosoamines,  $NHR \cdot NO$ , or diazo-hydroxides,  $R \cdot N:N \cdot OH$ , and secondary amines, true nitroso-compounds,  $NR^1R^2 \cdot NO$ . (3) *Cyclazoic*, which either gives stable azocyclic compounds or  $\psi$ -nitroso-compounds, such as  $\begin{array}{c} C_8H_{14} \\ CO \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} C \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} N \cdot OH \\ NH \end{array}$ , from aminocamphor nitrite, or results in the opening of the nucleus and formation of *allonitroso*-compounds, for instance, *allonitroso*-oxindole  $C_6H_4 \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} CH(NO) \\ NH \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} CO$ , from  $\psi$ -nitroso-oxindole,



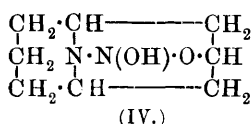
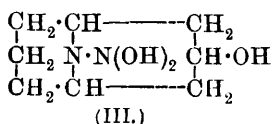
A true dihydroxyhydrazine derivative is obtained by the action of nitrous acid on the ether of solanidine-*s* (*loc. cit.*). With the compounds obtained from solanine-*s* and solauidine-*s*, the complete elimination of the nitrogen by the action of acids shows that in these cases the action of nitrous acid proceeds immediately to the cyclazoic stage.

Since the sole difference between solanidine-*s* and its ether consists in the presence of a hydroxyl group in the former, it has been thought advisable to study the action of nitrous acid on tropigenine and granatoline, which are saturated, alicyclic, iminic, alcoholic bases of simpler structure. In aqueous solution faintly acidified with acetic acid, tropigenine yields the corresponding nitrite at the ordinary temperature. At the temperature of a boiling-water bath, however, the reaction yields a compound which has the composition, but none of the properties of the true nitroso-compound (I) and is regarded as the azocyclic  $\psi$ -nitroso-compound (II):



This compound is accompanied by two others in small proportions, the more abundant having the properties of the hydrate of a true nitroso-compound, that is, of the intermediate dihydroxyhydrazine derivative.

The interaction of granatoline hydrochloride and silver nitrite gives the nitrite of the base, and this in aqueous solution is converted by acetic acid into the hydrate of the true nitroso-compound (III) (compare Ciamician and Silber, A., 1895, i, 160).



In a vacuum, this hydrate gradually loses  $1H_2O$ , with formation of the

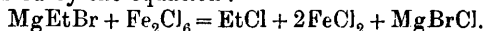
compound, m. p.  $125^{\circ}$ , which was obtained by Ciamician and Silber, and is the  $\psi$ -nitroso-compound (IV).

*Tropigenine nitrite*,  $C_7H_{13}ON, HNO_2$ , prepared by the action of silver nitrite on the hydrochloride of the base, forms a white, crystalline powder, which turns yellow at about  $100^{\circ}$ , and has m. p.  $160^{\circ}$ .

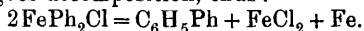
$\psi$ -Nitrosotropigenine (formula II) forms rosettes of white needles, m. p.  $195-196^{\circ}$ . Nitrosotropigenine hydrate has a structure analogous to that of the corresponding granatoline derivative (formula III), and forms white crystals, m. p. about  $160^{\circ}$  (decomp.).

*Granatoline nitrite*,  $C_{18}H_{15}ON, HNO_2$ , forms white needles, m. p.  $215-216^{\circ}$  (decomp.). Nitrosogranatoline hydrate (formula III) forms white leaflets, m. p.  $72-73^{\circ}$ .  $\psi$ -Nitroso ranatoline (formula IV), m. p.  $125^{\circ}$ , yields an ethyl ether,  $C_{10}H_{18}O_2N_2$ , white prisms, m. p.  $65-67^{\circ}$ .  
T. H. P.

**Direct Attempts to Prepare Ferropyrroles. I. BERNARDO ODDO** (*Gazzetta*, 1914, 44, ii, 268-278).—The author discusses the occurrence of iron and magnesium in hæmoglobin and chlorophyll respectively and their derivatives. It is not found possible to prepare organic ferro-compounds containing alkyl or aryl groups, the action of ferric chloride on magnesium ethyl bromide being a chlorinating action, expressed by the equation:



With magnesium phenyl bromide and magnesium benzyl bromide, the action of ferric chloride yields diphenyl and dibenzyl respectively, this result indicating the intermediate formation of an organo-ferrichloride, which then undergoes decomposition, thus:



With an organo-magnesium derivative containing a 2-methylindole residue, the action of ferric chloride gives, however, a more stable di-2-methylindolyl ferrichloride,  $CH \langle \begin{smallmatrix} C_6H_4 \\ CMe \end{smallmatrix} \rangle N \cdot FeCl \cdot N \langle \begin{smallmatrix} C_6H_4 \\ CMe \end{smallmatrix} \rangle CH$ , yellow solid, blackening and contracting at about  $130^{\circ}$ , and remaining unmelted at  $230^{\circ}$ .  
T. H. P.

**Salts of Acridine, Pyridine, and Quinoline. II. L. H. CONE** (*J. Amer. Chem. Soc.*, 1914, 36, 2101-2110).—It has been shown by the author (A., 1913, i, 92) that when diphenylacridyl chloride or 5-phenyl-10-methylacridyl chloride is shaken with nitrobenzene and molecular silver, a highly coloured solution is produced which absorbs oxygen. It was assumed that these coloured solutions contain free acridyl radicles analogous to triphenylmethyl. Evidence has now been obtained which proves the accuracy of this assumption, and several unsaturated acridyl radicles and their peroxides have been isolated. The free radicles are dark brownish-red, crystalline substances which in solution absorb oxygen from the air to form colourless peroxides, and also unite directly with halogens with production of the corresponding haloids. They are best prepared by shaking an aqueous solution of a salt, preferably the sulphate, with zinc dust. The zinc

becomes coated with the free radicle and the liquid becomes colourless. On decanting the colourless solution and adding benzene to the moist residue, the benzene dissolves the free radicle, forming a dark red solution. On shaking this benzene solution with air, its colour rapidly disappears and the colourless peroxide soon begins to separate.

*Diphenylacridyl*,  $C_{25}H_{19}N$ , can be prepared by the method already described or less satisfactorily by the electrolysis of its normal sulphate; it softens when heated and melts at about  $185-190^{\circ}$ . Molecular weight determinations have shown that it exists mainly in the unimolecular condition. The radicle unites instantly with chlorine to form yellow *diphenylacridyl chloride*, and also dissolves slowly in hydrochloric acid with production of the chloride. The *peroxide*,  $C_{50}H_{38}N_2O_2$ , crystallises in slender, pale yellow prisms, and when heated begins to darken at about  $190^{\circ}$  and melts at  $204-207^{\circ}$  according to the rate of heating; it dissolves slowly in mineral acids with formation of the corresponding acridyl salts. When an aqueous solution of diphenylacridyl chloride is treated with zinc dust, diphenylacridyl is produced together with a small quantity of *dihydrodiphenylacridine* ("diphenylacridane"),  $C_{25}H_{19}N$ , m. p.  $175^{\circ}$ , which crystallises in cubes; this substance can also be prepared by adding zinc dust to a boiling solution of diphenylacridol in acetic acid.

The following substances have also been prepared together with their salts, free radicles, and peroxides, and will be described subsequently: *p*-chlorophenyl-10-phenylacridol, *p*-methoxyphenyl-10-phenylacridol, 2:4-dimethoxyphenyl-10-phenylacridol, phenyl-10-methylacridol, and phenyl-10-ethylacridol. E. G.

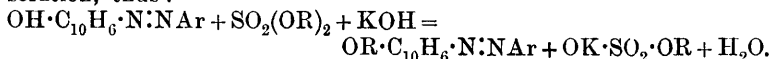
**Purines.** XV. 5-Amino-6-ethylamino-2:3-dihydro-2-pyrimidone and 2:8-Dioxy-9-ethyl-2:3:8:9-tetrahydropurine. CARL O. JOHNS and BYRON M. HENDRIX (*J. Biol. Chem.*, 1914, 19, 25-30. Compare this vol., i, 440).—2:8-Dioxy-9-ethyl-2:3:8:9-tetrahydropurine has been prepared for the purpose of comparing its properties with those of the methylated compounds, 2:8-dioxy-6-methyl-9-ethyl-2:3:8:9-tetrahydropurine (A., 1913, i, 1000) and 2-oxy-6-methyl-9-ethyl-2:3-dihydropurine (*ibid.*, i, 1397).

2-Ethylthiol-6-ethylaminopyrimidine,  $NH\text{Et}\cdot C \begin{smallmatrix} \nearrow N\cdot C(SeEt) \\ \searrow CH=CH \end{smallmatrix} N$ , b. p.  $199.5^{\circ}/11\text{ mm.}$ , obtained in almost quantitative yield by heating 6-chloro-2-ethylthiopyrimidine and 33% aqueous ethylamine at  $100^{\circ}$  in a sealed tube, is converted by boiling with concentrated hydrochloric acid and subsequent evaporation to dryness with sodium hydroxide into 6-ethylamino-2:3-dihydro-2-pyrimidone,  $C_6H_9ON_3$ , bluntly pointed prisms, m. p.  $218^{\circ}$ . The latter, by nitration with concentrated sulphuric acid and nitric acid (D. 1.5) below  $70^{\circ}$ , yields quantitatively 5-nitro-6-ethylamino-2:3-dihydro-2-pyrimidone, acicular prisms, decomp.  $275^{\circ}$ , which is converted into 5-amino-6-ethylamino-2:3-dihydro-2-pyrimidone, stout prisms, decomp.  $240^{\circ}$ , by reduction with aqueous ammonia and ferrous sulphate at the ordinary temperature. The base develops in ammoniacal solution a deep blue coloration with phosphotungstic acid and reacts with powdered carbamide at  $170-180^{\circ}$  to form 2:8-dioxy-9-ethyl-2:3:8:9-

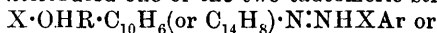
tetrahydropurine,  $\begin{array}{c} \text{N}=\text{CH}\cdot\text{C}\cdot\text{NH}- \\ \text{CO}\cdot\text{NH}\cdot\text{C}\cdot\text{NEt} \end{array} > \text{CO}$ , small prisms, decomp. above 300°.

C. S.

Etherification of *o*-Hydroxyazo-compounds. V. G. CHARRIER and G. FERRERI (*Gazzetta*, 1914, **44**, ii, 228—256. Compare this vol., i, 597, 599, 748).—The *o*-hydroxyazo-compounds derived from  $\alpha$ -naphthol and from 10-hydroxyphenanthrene, that is, the 2-aryldazo-1-naphthols and the 9-aryldazo-10-hydroxyphenanthrenes, react with methyl or ethyl sulphate in the presence of concentrated alkali solution, thus:



The ethers obtained in this way are well-crystallised, orange or bright red compounds, which are markedly more soluble in organic solvents, and melt, without decomposing, at lower temperatures than the corresponding *o*-hydroxyazo-compounds. They are also more decidedly basic than the latter, owing to the intensification of the basic properties of the oxygen consequent on etherification. All the salts isolated and analysed contain two equivalents of acid, and those of the 10-hydroxyphenanthrene series, which could not be isolated, react as though the base is diacid. To these salts, therefore, is attributed one of the two tautomeric structures:



where X represents a halogen atom or a univalent acid residue. Nascent hydrogen decomposes the ethers into a primary amine,  $\text{NH}_2\text{Ar}$ , and an ether of an aminophenol,  $\text{OR}\cdot\text{C}_{10}\text{H}_6(\text{or } \text{C}_{14}\text{H}_8)\cdot\text{NH}_2$ . These ethers are extremely resistant to the action of boiling concentrated alkali hydroxide solution, but towards acids their behaviour varies. The 2-aryldazo-1-naphthols are, with some exceptions, highly resistant to boiling dilute or concentrated acid, and, when heated, their hydrochlorides suffer loss of hydrogen chloride without decomposition of the ether; on the other hand, the 9-aryldazo-10-hydroxyphenanthrenes and also 2-*o*-methoxy- and 2-*o*-ethoxy-benzeneazo-1-naphthols are hydrolysed readily by dilute acid, their hydrochlorides being largely decomposed on heating into the corresponding hydroxyazo-compounds and the chlorides of the alkyl radicles of the ethers.

2-Benzeneazo-1-naphthyl methyl ether hydrochloride,  $\text{C}_{17}\text{H}_{14}\text{ON}_2\cdot 2\text{HCl}$ , forms dark red needles with metallic, green reflection (compare Noelting, Grandmougin, and Freimann, A., 1909, i, 442).

2-Benzeneazo-1-naphthyl ethyl ether has m. p. 46°; Noelting, Grandmougin, and Freimann (*loc. cit.*) gave 44°. Its hydrochloride,



forms dark garnet-red scales with metallic, golden reflection; its nitrate,  $\text{C}_{18}\text{H}_{16}\text{ON}_2\cdot 2\text{HNO}_3$ , loses nitrous vapours at 47—48°, the residue melting at 143—145°.

2-*o*-Tolueneazo-1-naphthyl methyl ether,  $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in mammillary masses of orange-yellow needles, m. p. 60—61°, and forms a red solution in concentrated sulphuric acid; its hydrochloride forms shining, cantharides-green scales. The corre-



sponding *ethyl ether*,  $C_{19}H_{18}ON_2$ , forms yellow, acicular crystals, m. p.  $51^\circ$  (*hydrochloride*, metallic golden scales).

*2-m-Tolueneazo-1-naphthol*,  $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4Me$ , prepared by the action of *m*-tolylhydrazine hydrochloride on  $\beta$ -naphthaquinone, forms mammillary aggregates of slender, bright red needles, m. p.  $117-118^\circ$ , and yields a ruby-red solution in concentrated sulphuric acid. The *methyl ether* forms chrome-yellow scales, m. p.  $49-50^\circ$ , and its *hydrochloride*, bronze needles. The *ethyl ether* forms orange-red prisms, m. p.  $22^\circ$ , and its *hydrochloride*, mammillary masses of garnet-red needles.

*2-p-Tolueneazo-1-naphthyl methyl ether* forms orange-red needles, m. p.  $77-78^\circ$ , and its *hydrochloride*, minute, brick-red needles. The *ethyl ether* forms slender, orange-yellow needles, m. p.  $51^\circ$ , and its *hydrochloride*, deep garnet needles.

*2-as-m-Xyleneazo-1-naphthol*,  $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_3Me_2$ , prepared by the action of *as-m*-xylylhydrazine hydrochloride on  $\beta$ -naphthaquinone, forms deep red scales or needles with metallic, golden reflection, m. p.  $186^\circ$ . The *methyl ether* forms slender, orange-yellow crystals, m. p.  $68^\circ$ , and its *hydrochloride*, metallic, green crystals. The *ethyl ether* forms bright red prisms, m. p.  $89^\circ$ , and its *hydrochloride*, golden scales.

*2-s- $\psi$ -Cumeneazo-1-naphthol*,  $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_2Me_3$ , crystallises in red leaflets or needles with faint golden reflection, m. p.  $194-195^\circ$ . The *methyl ether* forms orange-yellow prismatic needles, m. p.  $82-83^\circ$ , and its *hydrochloride*, golden-green leaflets. The *ethyl ether* forms red prisms, m. p.  $64^\circ$ , and its *hydrochloride*, cantharides-green needles.

*2-p-Chlorobenzeneazo-1-naphthol*,  $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4Cl$ , forms bright red, silky needles, m. p.  $187^\circ$ . The *methyl ether* crystallises in orange-yellow leaflets, m. p.  $111^\circ$ , and its *hydrochloride* in dark green, metallic needles. The *ethyl ether* forms orange-red, acicular crystals, m. p.  $84-85^\circ$ , and its *hydrochloride*, heavy, cantharides-green plates.

*2-o-Methoxybenzeneazo-1-naphthyl methyl ether*,  
 $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OMe$ ,  
 forms bright red prisms, m. p.  $90-91^\circ$ , and its *hydrochloride*, greenish-brown needles or leaflets with metallic reflection. The *ethyl ether* forms pale red prisms, m. p.  $88-89^\circ$ , and its *hydrochloride*, slender, cantharides-green needles.

*2-o-Ethoxybenzeneazo-1-naphthyl methyl ether*,  
 $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OEt$ ,  
 crystallises in brick-red needles, m. p.  $62^\circ$ , and its *hydrochloride*, in cantharides-green needles. The *ethyl ether* forms bright red needles, m. p.  $63^\circ$ , and its *hydrochloride*, slender, bronze-green needles.

*9-Benzeneazo-10-methoxyphenanthrene*,  $OMe \cdot C_{14}H_8 \cdot N:NPh$ , forms small, bright red prisms, m. p.  $88-89^\circ$ , and, on reduction by means of zinc dust and acetic acid, yields aniline and a basic compound, which is probably 9-amino-10-methoxyphenanthrene. The corresponding 10-ethoxy-derivative,  $C_{22}H_{18}ON_2$ , forms bright red, flattened needles, m. p.  $136^\circ$ , and on treatment with ethereal nitric acid yields benzenediazonium nitrate, 9-nitro-10-ethoxyphenanthrene, and a compound which crystallises in pale red needles, m. p.  $249-250^\circ$  (decomp.), and is probably a nitro-9-benzeneazo-10-hydroxyphenanthrene; its behaviour on reduction appears similar to that of the methoxy-compound.

The interaction of *as*-phenylmethylhydrazine hydrochloride (1 mol.) and phenanthraquinone in boiling acetic acid yields neither 9-benzene:10-10-hydroxyphenanthrene nor its methyl ether, but a compound which forms pale yellow leaflets, m. p. 221—222°, and is under investigation.

9-*o*-Toluenazo-10-10-hydroxyphenanthrene,  $\text{OH}\cdot\text{C}_{14}\text{H}_8\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , forms minute, orange-red scales with golden reflection, m. p. 222—223°, and the corresponding *ethyl ether*, flat, garnet-coloured needles, m. p. 109°.

9-*p*-Toluenazo-10-10-hydroxyphenanthrene,  $\text{C}_{21}\text{H}_{16}\text{ON}_2$ , forms lustrous, bright red needles, m. p. 169°; its *methyl ether*, dense, bright red needles, m. p. 117°, and its *ethyl ether*, lustrous, bright red plates, m. p. 158°.

9-*o*-Methoxybenzeneazo-10-10-hydroxyphenanthrene,  
 $\text{OH}\cdot\text{C}_{14}\text{H}_8\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ ,  
 forms red leaflets with golden reflection, m. p. 248—249°, and its *ethyl ether*, red needles, m. p. 140—141°. T. H. P.

**Aminoazo-compounds.** L. CASALE and MARIA CASALE-SACCHI (*Atti R. Accad. Sci. Torino*, 1914, 49, 1199—1209).—The authors have prepared a number of new aminoazo-compounds by coupling  $\alpha$ -naphthylamine with diazonium salts obtained from anilines substituted in the ortho-position. In the products obtained, which form well crystallised and moderately stable salts with acids, the azo-group occurs in the para-position to the amino-group of the naphthalene residue, since 4-*o*-toluenazo-1-naphthylamine, for example, yields naphthylene-1:4-diamine on reduction.

4-*o*-Toluenazo-1-naphthylamine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ , crystallises in bright red, silky needles, m. p. 95°, and yields blood-red solutions in chloroform, benzene or alcohol, and an intensely violet solution in acetic acid; it gives a red coloration with concentrated, and a violet one with dilute, sulphuric acid. Its *monoacetyl* derivative,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$ , orange-red needles, m. p. 215°; *diacetyl* derivative,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}(\text{Ac})_2$ , brick-red, prismatic plates, m. p. 136°, and *benzoyl* derivative,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHBz}$ , pale yellow needles, m. p. 200°, were prepared. When excess of sodium nitrite is used in the diazotisation of the *o*-toluidine, the above compound is accompanied by 4-*o*-toluenazo-1-naphthol.

4-*o*-Methoxybenzeneazo-1-naphthylamine,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ , forms tufts of crimson needles, m. p. 184—185°, and gives deep red solutions in chloroform, alcohol or ether, and an intensely violet one in acetic acid. Its *acetyl* derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$ , forms garnet-red needles, m. p. 203—204°, and its *benzoyl* derivative,  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}_3$ , orange-red needles, m. p. 182°. Here, too, the use of sodium nitrite in excess results in the formation of 4-*o*-methoxybenzeneazo-1-naphthol (compare Charrier and Casale, this vol., i, 748).

4-*o*-Ethoxybenzeneazo-1-naphthylamine,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ , forms groups of vermilion crystals, m. p. 169°; its *acetyl* derivative,  $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}_3$ , red, prismatic needles, m. p. 191°, and its *benzoyl* derivative,  $\text{C}_{25}\text{H}_{21}\text{O}_2\text{N}_3$ , tufts of green, silky needles, m. p. 180°.

4-*Nitrobenzeneazo*-1-*naphthylamine*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ , forms shining, emerald-green scales, m. p. 174—175°, and gives intensely red solutions in alcohol, benzene, chloroform or ether. Its *acetyl* derivative,  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_4$ , forms tufts of shining, pale green needles, m. p. 200°, and its *benzoyl* derivative,  $\text{C}_{23}\text{H}_{16}\text{O}_3\text{N}_4$ , shining, black needles with red reflection, m. p. 185°. T. H. P.

**Phosphorus Content of Caseinogen.** ALFRED W. BOSWORTH and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1914, 19, 67—71. Compare A., 1913, i, 659).—Additional evidence is adduced to show that caseinogen contains only about 0.7% of phosphorus (compare Harden and Macallum, this vol., i, 442). H. W. B.

**Mode of Action of Urease and of Enzymes in General.** DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1914, 19, 141—180. Compare this vol., i, 606).—The consideration of the results already published (*loc. cit.*), and now described in detail, leads to the conclusion that urease destroys urea by means of two successive reactions: (1) combination of enzyme and substrate; (2) disruption of the combination, the urea being freed as ammonia and carbon dioxide. This process is formulated in accordance with the law of mass action, and the equation  $t = 1/E[1/c \log a/(a-x) + x/d]$ , where  $a$  represents the amount of substrate (urea) present per unit volume at the beginning of the reaction,  $x$  the amount decomposed in time  $t$ ,  $E$  the enzyme concentration,  $c$  the velocity of combination of enzyme and substrate, and  $d$  the velocity at which the combination decomposes, yielding ammonium carbonate and free enzyme, is found accurately to express all the results thus far obtained. H. W. B.

**Effect of Hydrogen Ion Concentration and of Inhibiting Substances on Urease.** DONALD D. VAN SLYKE and GOTTHARD ZACHARIAS (*J. Biol. Chem.*, 1914, 19, 181—210. Compare Marshall, this vol., i, 606; Armstrong and Horton, A., 1912, i, 594; and the preceding abstract).—The authors have measured the rates of decomposition of urea by urease when the hydrogen ion concentration has been maintained at constant levels by Sørensen's method (A., 1909, i, 861).

Changes in the concentration of hydrogen ion have absolutely different and independent effects on the two successive reactions [(i) combination with substrate; (ii) decomposition of combined substrate] by which the enzyme destroys urea. Throughout the range of experimental observation ( $P_{\text{H}} = 5.9$  to 8.7), the combining velocity has been found to vary in inverse ratio to the hydrogen-ion concentration (the more alkaline the solution the more rapid the combination), whilst the decomposition by enzyme of the urea combined with it is most rapid in neutral solution and is retarded by either alkalinity or acidity.

In the absence of inhibiting substances such as salts and dextrose, and provided the concentration of urea lies between 0.08 and 10%, the combination of urease and urea is so quick that it consumes a hardly appreciable proportion of the total time, which is almost entirely taken up by the slower decomposition reaction. The maximum rate of

ammonia formation under these conditions is consequently fixed by that of the decomposition reaction, and takes place when the solution is maintained at the neutral point. When, however, the combining reaction is retarded by adding neutral salts or using dilute urea solutions, it becomes an appreciable factor in the total time consumption, and the optimum hydrogen ion concentration for the total enzyme action is therefore shifted towards the alkaline side. The effect of hydrogen ion concentration on invertase may also be accounted for as the sum of independent effects on the two separate phases of enzyme action.

The effect of the generated ammonium carbonate in retarding the action of urease is due chiefly to the alkalinity of the carbonate. When a phosphate mixture prevents the ammonium carbonate formed from affecting the hydrogen-ion concentration, it also prevents the effect on the velocity. Neutral salts retard the action of urease by interfering with the combination of enzyme with substrate. The effect is the greater the more dilute the urea solution, and consequently it is especially the decomposition of the last traces of urea that is retarded by neutral salts.

Dextrose retards the enzyme action in the same manner as neutral salts. Alcohol in 30% concentration depresses both phases of the enzyme's action. Both electrolytes and non-electrolytes in more than bimolecular concentration retard the enzyme action in its second phase, namely, the decomposition of urea after it has combined with urease. All these effects can be represented by the general mass action formula for enzyme action already set forth (*loc. cit.*). H. W. B.

**Enzyme Action. XI. Some Experiments with Castor Bean Urease.** K. GEORGE FALK and K. SUGIURA (*J. Amer. Chem. Soc.*, 1914, **36**, 2166—2170).—In an earlier paper (Falk, A., 1913, i, 433) it has been shown that castor beans contain a urease. Further experiments have now been made in comparison with the urease of soja beans. It has been found that, under comparable conditions, castor bean preparations hydrolyse much less urea than similar soja bean preparations. The action of acids, bases, and salts on the hydrolysis of urea by castor bean urease has been studied and relations have been found similar to those which have been observed in the case of soja bean urease. E. G.

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### Physiological Chemistry.

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**Influence of Pituitrin on Respiration.** L. B. NICE, J. L. ROCK and R. O. COURTRIGHT (*Amer. J. Physiol.*, 1914, **35**, 194—198).—The characteristic effect of pituitary extract on respiration is an increase in the depth, followed by a shallowness and a decrease in the rate of breathing. In some cases, however, the increase in the

depth of respiration is followed by shallowness and an increase in the rate of breathing. The effect of pituitrin on the respiratory mechanism occurs synchronously with that on the circulatory system. The effect on respiration, however, passes off sooner than that on circulation. After a few injections of pituitrin, the respiratory mechanism becomes immune and the characteristic responses are not elicited.

H. W. B.

**Normal Level of Blood-Sugar of the Dog.** PHILIP A. SHAFFER (*J. Biol. Chem.*, 1914, 19, 297—302).—The author finds that the concentration of dextrose in the blood of normal dogs, when the animals are free from excitement or pain, is in the neighbourhood of 0.05%, or about one-half to one-third the values usually accepted as normal. Higher figures are obtained after anaesthesia or when the animal is excited. These higher results are comparable with those hitherto regarded as normal, which really represent varying degrees of emotional hyperglycæmia brought about by the procedure of drawing the blood.

H. W. B.

**The Fat of Blood. I. Fat Content of the Blood under Approximately Normal Conditions.** W. R. BLOOR (*J. Biol. Chem.*, 1914, 19, 1—24).—The author has determined the fat content of dog's blood, in various circumstances, by his nephelometric method (this vol., ii, 392). In normal circumstances, the fat content of the blood is practically constant, both for the individual and the species, amounting to 0.59 gram per 100 grams of blood. After a fat meal, the fat in the blood increases gradually, reaching a maximum in about six hours. If the thoracic duct is tied, however, an increase in the fat does not occur after feeding with fat. Intravenously injected fat, in quantities up to 0.4 gram per kilo. of body-weight, disappears from the blood within five minutes. When larger amounts are injected, some of the fat persists in the blood for several hours. Apparently the liver is able to withdraw from the blood, and loosely store, a certain amount of fat, but the storage capacity is limited.

Fasting and the administration of chloroform produce an increase in the fat of blood only when the animal has previously been well supplied with fatty foods. Ether, however, regularly causes a rise in the fat content of the blood during the narcosis. The loosely stored fat may, therefore, be quickly released by certain stimuli, and the sudden flooding of the organism with fat may be a potential source of danger. In the animals that died under the anaesthetic there was observed a rapid and continuous rise in the fat content of the blood during the anaesthesia until death.

H. W. B.

**Urea and Total Non-Protein Nitrogen in Normal Human Blood: Relation of their Concentration to Rate of Elimination.** FRANKLIN C. MCLEAN and LAURENCE SELLING (*J. Biol. Chem.*, 1914, 19, 31—38).—The authors have determined by Folin's methods

the relation between the concentration of urea in the blood and its corresponding rate of elimination in the urine. The concentration of urea and of total non-protein nitrogen in normal human blood varies within wide limits according to various factors, such as diet, amount of fluid ingested, etc. There is, however, a close parallelism between the concentration of urea in the blood and the amount excreted in the urine in normal individuals under average conditions. The elimination of urea is retarded if insufficient water is taken, and the retention of urea is even more marked in cases of nephritis. A high concentration of urea in the blood is not necessarily a sign of pathological renal insufficiency unless associated with a relative decrease in the amount of urea eliminated in the urine.

H. W. B.

**Proteins of the Blood of *Limulus Polyphemus*, L.** CARL L. ALSBERG (*J. Biol. Chem.*, 1914, 19, 77—82).—The proteins of the blood of *Limulus* consist almost exclusively of the clot protein (which differs greatly from ordinary fibrinogen) and hæmocyanin. Hæmocyanin is several times as abundant as the clot protein. Other proteins occur only in minimal amounts. The blood also contains a small amount of nitrogen in non-coagulable form.

The quantity of protein in the blood seems to vary with the state of nutrition of the animal, diminishing in starvation. The blood of *Octopus* contains at least twice as much hæmocyanin as that of *Limulus*. The hæmocyanin of *Limulus* coagulates at 67—68°.

H. W. B.

**Carbohydrate Metabolism. VII. Influence of Subcutaneous Injections of Dextrose and of Calcium Lactate on the Sugar in the Blood and on Tetany after Thyreoparathyroidectomy.** FRANK P. UNDERHILL and NORMAN R. BLATHERWICK (*J. Biol. Chem.*, 1914, 19, 119—126. Compare this vol., i, 897).—The hypoglycæmia resulting from thyreoparathyroidectomy seems to be neither the cause nor the effect of the accompanying tetany, for although injections of dextrose raise the sugar in the blood to the normal amount, such injections have little influence on tetany. Moreover, the condition of hypoglycæmia precedes that of tetany. The authors therefore suggest that the removal of the thyroids and parathyroids gives rise to two distinct effects, one affecting the mechanism concerned in the maintenance of the sugar content of the blood at its normal level, thereby causing hypoglycæmia, and the other acting on the nervous system, producing tetany. Calcium appears to be intimately associated with both effects, for injections of calcium lactate will temporarily restore the normal sugar content of the blood and also abolish tetany.

H. W. B.

**Basal Metabolism and Creatinine Elimination.** WALTER W. PALMER, JAMES H. MEANS, and JAMES L. GAMBLE (*J. Biol. Chem.*, 1914, 19, 239—244).—The authors have determined the relationship between basal metabolism (minimum heat production of an

individual at rest, at least twelve hours after food, and surrounded by a temperature of 30°) and the total mass of active protoplasm the metabolism of which is represented by the urinary creatinine eliminated on a creatine-creatinine-free diet. The number of calories per mg. of creatinine varied in eight men from 0.89 to 1.04, average 0.98, whilst in nine women the number ranged from 1.17 to 1.37, average 1.26. Definite conclusions as to the value and significance of these results are deferred until further observations have been made.

H. W. B.

**Gaseous Exchange in Decerebrate Animals.** CHARLES G. L. WOLF and T. S. HELE (*J. Physiol.*, 1914, 48, 428—442).—The decerebrate animal responds to carbohydrates and proteins in the same way as the intact animal. The rise in the total metabolism following administration of protein is accompanied by a rise in the non-protein nitrogen of the blood. The decerebrate animal responds to small amounts of amino-acids, such as glycine, which cause a very considerable rise in the protein metabolism. Glycine when injected into the blood-stream, causes a greater rise in metabolism than was found by Lusk (*A.*, 1913, i, 123), who administered this substance *per os*.

S. B. S.

**Inhibition of Autolysis [of Liver] by Alcohol.** H. GIDEON WELLS and GEORGE T. CALDWELL (*J. Biol. Chem.*, 1914, 19, 57—65).—These experiments were performed primarily to ascertain what strength of alcohol is necessary to preserve specimens of tissue intended for histological purposes. The results show that for the complete suppression of autolytic disintegration of liver tissue by alcohol, the actual strength of alcohol present cannot be safely less than 90%; between 80 and 90% a slight autolysis may take place, and below 80% alcohol concentration, autolysis is certain to take place at either room or incubator temperature. Small blocks of tissue not greater than 5 × 1 × 1 cm. must therefore be placed directly in at least 50 c.c. of 96% alcohol to prevent autolytic changes.

When experimenting with finely minced tissues, at least 10 c.c. or, better, 15 c.c., of 96% alcohol must be added for each gram of tissue to ensure effective preservation. When not contra-indicated, it is best to boil the tissues a short time in the alcohol to destroy the enzymes.

H. W. B.

**Metabolic Changes in Muscular Tissue. I. The Fate of Mixtures of Amino-acids.** S. A. MATTHEWS and C. FERDINAND NELSON (*J. Biol. Chem.*, 1914, 19, 229—234. Compare Fiske and Sumner, this vol., i, 1019).—After repeated injections of a diuretic salt solution into (1) dogs with an Eck-fistula, and (2) eviscerated dogs, the urine becomes practically free from ammonia, and contains only a small amount of nitrogenous substances. If, now, a solution of mixed amino-acids is injected subcutaneously, ammonia appears in the urine, followed usually by an increase in the amount of urea. The conclusion drawn by the authors is that the first



action of the tissues on amino-acids is the formation of ammonia and then the production of urea. The latter change is considered to be capable of being brought about by the tissues without the assistance of the liver.

H. W. B.

**Reversibility of the Geotropism of *Arenicola* Larvæ by Salts.** SAKYO KANDA (*Amer. J. Physiol.*, 1914, 35, 162—176).—The addition of calcium and magnesium salts in isotonic solution to sea-water containing the larvæ of *Arenicola cristata* reverses the normal negative geotropism of these organisms without affecting the normal positive heliotropism. Sodium and potassium salts, as well as acids and alkalis, have no action on the negative geotropism, but prevent the appearance of positive heliotropism. The reversal of the negative geotropism of the larvæ is not an osmotic effect, but is due to the specific action of the calcium and magnesium ions.

H. W. B.

**Purine Enzymes of the Opossum (*Didelphis Virginiana*).** GEORGE T. CALDWELL and H. GIDEON WELLS (*J. Biol. Chem.*, 1914, 19, 279—283. Compare Hunter and Givens, A., 1913, i, 558).—In the tissues of the opossum, enzymes acting on free purines *in vitro* were found distributed as follows: uricase (uricolytic enzyme), present only in the liver; xantho-oxydase, present in the liver and probably in the kidney; guanase, present in all tissues; adenase, probably not present in any of the tissues, except possibly in the liver.

H. W. B.

**Excretion of Creatinine by Normal Women.** MARTHA TRACY and ELIZABETH E. CLARK (*J. Biol. Chem.*, 1914, 19, 115—117).—The analysis of the urines of twenty-six women students on a creatine- and creatinine-free diet gave the following average figures for daily urinary creatinine: absolute amount eliminated, 0.90 gram, varying from 1.71 to 0.53; gram per kilo. of body-weight, 0.015, varying from 0.023 to 0.010; creatinine coefficient (mg. of creatinine nitrogen per kilo. of body-weight), 5.8, varying from 9.8 to 3.5. These figures are considerably smaller than the corresponding figures for normal men.

H. W. B.

**Some Observations on the Excretion of Creatinine by Women.** MARY HULL (*J. Amer. Chem. Soc.*, 1914, 36, 2146—2151).—The urine of several women in normal health has been analysed. The creatinine output was the chief factor considered, but the nitrogen excretion in other forms was also determined, and the results are tabulated. The creatinine varied between 6.91 and 14.97 mg. daily per kilo. of body-weight, the lowest value being obtained in the case of a corpulent woman who lacked proper physical exercise. These figures are very much lower than the corresponding values found for men by Long and Gephart (A., 1912, ii, 961), which ranged from 21.5 to 27.8 mg. per kilo. of body-weight. It is suggested that this difference may perhaps be explained by the lower muscular structure and lower muscular tone of women.

E. G.

**Creatine and Creatinine in Starvation.** G. GRAHAM and E. P. POULTON (*Proc. Physiol. Soc.*, 1914, lii—liv; *J. Physiol.*, 48. Compare this vol., i, 228).—The results suggest that traces of creatine only are excreted in starvation of the human subject which has lasted over three days. The excretion did not begin until forty-eight to fifty-eight hours after the last meal. Complications due to the excretion of acetoacetic acid were avoided. S. B. S.

**Elimination of Phenolsulphonephthalein in Acute and Chronic Tartrate Nephritis.** FRANK P. UNDERHILL and NORMAN R. BLATHERWICK (*J. Biol. Chem.*, 1914, 19, 39—56).—The rate of elimination of phenolsulphonephthalein after ingestion may be markedly diminished during the acute stage of nephritis produced in rabbits by the subcutaneous injection of tartrates (A., 1912, ii, 787). In the chronic condition, the excretion of the dye is more rapid, but does not reach the rapidity associated with the normal state. When excretion by the kidney is prevented, the dye is eliminated in the fæces through the bile.

The injection of tartrates does not reduce the excretion of nitrogenous substances in the urine. Although the rate of elimination is undoubtedly diminished, the total amount of waste material excreted is unchanged. A reduced rate of elimination does not necessarily mean that the kidney is not efficient.

It has been observed in these experiments that, contrary to what was previously noted (*loc. cit.*), the glomerulus has been injured as well as the renal tubules. H. W. B.

**Volatile Substances of Urine.** WILLIAM M. DEHN and FRANK A. HARTMAN (*J. Amer. Chem. Soc.*, 1914, 36, 2118—2136).—The characteristic odour of urine cannot be attributed to any of the volatile substances hitherto detected in it, and it is evident that other compounds must be present. As this subject has not been investigated systematically, the present work was undertaken.

Vapour-pressure determinations of samples of urine, from a few minutes to three weeks old, have shown that the variations of the vapour pressure with age are not large, but that in all cases the vapour pressures are lower than those of water at the same temperature.

The largest yields of volatile substances were obtained from urine by treating it with dilute sulphuric acid, leaving it for several days, and then distilling it. The distillates furnished products which were separated into four fractions, namely, acids, phenols, bases, and neutral substances. Of the acids, the principal is benzoic acid, formed by the hydrolysis of hippuric acid; the others comprise hydrogen sulphide, fatty acids up to heptioic acid, and possibly cyclohexanecarboxylic acid. The phenols include phenol, *p*-cresol, and some higher compounds. The chief bases are methylamine and indole; traces of these occur in fresh urine and large quantities in fermented urine. The neutral substances contribute most largely to the characteristic odour; indications were obtained of the presence of at least four new compounds, including urinod (see following abstract). E. G.

**Urinod, the Cause of the Characteristic Odour of Urine.** WILLIAM M. DEHN and FRANK A. HARTMAN (*J. Amer. Chem. Soc.*, 1914, **36**, 2136—2146. Compare preceding abstract).—The characteristic odour of urine has been found to be due to the presence of *urinod*,  $C_6H_8O$ , b. p.  $108^\circ/28$  mm., a pale yellow oil, slightly heavier than water, and possessing a very penetrating, persistent, nauseating odour. This substance is readily volatile with steam, reduces potassium permanganate and ammoniacal silver nitrate in the cold, and reacts with Millon's reagent, but not with Fehling's solution or solution of alkali picrate. The *dinitro*-derivative, m. p.  $78^\circ$ , forms golden needles. *Urinod* reacts with semicarbazide with production of a *compound*, m. p.  $254^\circ$ , which crystallises in thin, hexagonal leaflets. When *urinod* is treated with bromine, two compounds are produced; one of these has m. p. about  $110^\circ$ , whilst the other is not melted at  $250^\circ$ . The compound probably has the structure of *cyclohexene*-4-one,  $CO<\begin{smallmatrix} CH_2-CH \\ CH_2 \cdot CH_2 \end{smallmatrix}>CH$ , or the quinonoid constitution  $CO<\begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix}>C:$ . *Urinod* does not occur in the free state in urine, but exists in a conjugated form, and is liberated by fermentation or by the action of dilute sulphuric acid. It is very toxic, and may have some connexion with uræmia.

E. G.

**The Isolation of the Substance in Butter Fat which Exerts a Stimulating Influence on Growth.** E. V. MCCOLLUM and MARGUERITE DAVIS (*J. Biol. Chem.*, 1914, **19**, 245—250. Compare Osborne and Mendel, A., 1913, i, 1128).—The growth-stimulating substance present in butter-fat has been isolated by saponifying the fat and extracting the soaps formed with a mixture of olive oil and ether. After removal of the ether, the olive oil was found to have acquired growth-stimulating properties which were previously absent. Rats which had ceased to grow on a diet of casein, dextrin, lactose, agar-agar, and salts, with the addition of ordinary olive oil or of cotton-seed oil, began to grow again when the above olive-oil extract of butter soaps was added to the diet.

H. W. B.

**Pharmacological Action of Tetra-alkylammonium Compounds. I. The Action of Tetramethylammonium Chloride.** C. R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1914, **50**, 17—40).—A detailed account of work published previously (A., 1911, ii, 754).

**Metabolism of an Isomeride of Xanthine and of some Isomerides of the Methylxanthines.** SAMUEL GOLDSCHMIDT (*J. Biol. Chem.*, 1914, **19**, 83—104).—The author has studied the behaviour of various purine derivatives closely related to xanthine and uric acid when injected subcutaneously into rabbits. 2: 8-Dioxytetrahydropurine, an isomeride of xanthine, is excreted unchanged in the urine, whereas xanthine itself forms allantoin and uric acid. Uric acid, when injected subcutaneously, is eliminated chiefly as allantoin. 2: 8-Dioxy-6-methyl-2: 8-dioxy-

9-methyl- and 2:8-dioxy-6:9-dimethyl-tetrahydropurines do not lead to an increase of urinary allantoin when injected subcutaneously into rabbits, which is in accordance with the view that demethylation is effected only with great difficulty in the body. The above methylated purines do not produce diuresis.

H. W. B.

**Toxicity of Sodium Tartrate.** WILLIAM SALANT and C. S. SMITH (*Amer. J. Physiol.*, 1914, **35**, 239—264).—The toxic action of sodium tartrate has been observed in rabbits, cats, fowls, and frogs after intravenous and subcutaneous injection and administration by the mouth. Comparatively large doses, up to 4 grams per kilo., may be given with the food to rabbits and fowls without producing any toxic effect. Larger quantities cause death often within a few hours. Sub-acute intoxication is produced by subcutaneous or intravenous injection of small doses, the effects being injury to the kidney and symptoms of muscular and nervous disturbance.

The state of nutrition of the animal plays a considerable rôle in determining the extent of intoxication produced by a given dose of sodium tartrate. Rabbits fed on carrots are much more resistant than those fed on oats and cabbage or on a milk diet. The fatal dose for fasting animals may be barely toxic for those in a well-fed state. Resistance seems to decrease with age.

*d*- and *l*-Tartrates are found to be equally toxic. H. W. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Chemical Changes in Vegetable Organisms Undergoing Fermentation.** MARIN MOLLIARD (*Compt. rend.*, 1914, 159, 512—514).—Experiments were made on the changes in the sugars and nitrogenous compounds in the pericarp of *Cucurbita maxima* kept in open and in closed tubes for periods of 30, 75, and 150 days.

Both the loss of total substance and of reducing sugars soluble in alcohol was greatest in the open tubes, whilst the non-reducing sugar soluble in alcohol first disappeared in the closed tube; the sugars insoluble in alcohol remained almost the same in the open tube, and were only considerably reduced in quantity in the closed tube during the last period of the experiment.

Whilst the total nitrogen remained about the same, the protein nitrogen decreased to rather more than half in the open tube and to less than half in the closed tube. The soluble nitrogen (especially ammonia) increased under both conditions, the increase being greater in the closed tube. The amino-nitrogen remained constant in the open tube, and was doubled in the closed tube, and the amide nitrogen disappeared altogether, first in the closed tube.

N. H. J. M.

**Relation of Bacterial Transformations of Soil Nitrogen to Nutrition of Citrous Plants.** KARL P. KELLERMAN (*J. Agric. Research*, 1914, 2, 101—113).—The results of pot experiments in which soils from typical orange-growing areas in California were employed showed that an excess of nitrogen as nitrates produces the same symptoms of malnutrition as have been observed in small areas throughout the orange belt in California. An examination of samples of soil from California showed that samples from the vicinity of deteriorating trees are richer in nitrates than elsewhere.

Both the poor and good soils usually contain rather large amounts of insoluble nitrogen, the difference being in the rate of nitrification. In pot experiments it was found that a normal rate of nitrification is obtained by mixing a green crop with the soil. Large amounts of mature straw are to be avoided; small amounts of straw may, however, be applied with advantage to fields too high in nitrates. Ground limestone, in addition, will probably be beneficial.  
N. H. J. M.

**The Soluble Polysaccharides of Lower Fungi. II. Mycogalactan, a New Polysaccharide in *Aspergillus niger*.** ARTHUR W. DOX and RAY E. NEIDIG (*J. Biol. Chem.*, 1914, 19, 235—237. Compare this vol., i, 1038).—*Mycogalactan*,  $C_6H_{10}O_5$ , is obtained from hot aqueous extracts of immature cultures of *Aspergillus niger* by treatment with alcohol. The dried material dissolves in cold water at the ordinary temperature, and when the solution is immersed in a freezing mixture a transparent jelly is formed. It gives a faint blue colour with iodine, which may be due, however, to a trace of impurity. It has  $[\alpha]_D^{20} + 284^\circ$ . Galactose is produced by hydrolysis with dilute acid. H. W. B.

**Formation of Hexone and Purine Bases in the Autolysis of *Glomerella*.** HOWARD S. REED (*J. Biol. Chem.*, 1914, 19, 257—262. Compare A., 1911, ii, 916).—Autolytic changes occurring in cultures of *Glomerella rufomaculans* result in the production of ammonia, histidine, lysine, xanthine, and hypoxanthine. No indication of the formation of amines could be detected. The dried fungous mycelium when incubated with gelatin solution liberated lysine.  
H. W. B.

**$\beta$ -*p*-Hydroxyphenylethylamine, a Pressor Compound in an American Mistletoe.** ALBERT C. CRAWFORD and WALTER K. WATANABE (*J. Biol. Chem.*, 1914, 19, 303—304).—The base  $C_7H_{11}N$  previously isolated by the authors (*Jour. Amer. Med. Assoc.*, 1911, 57, 865) from *Phoradendron flavescens* (mistletoe) has been identified by them as  $\beta$ -*p*-hydroxyphenylethylamine. H. W. B.

**Proximate Analysis of Wheat.** A. BARBIERI (*Compt. rend.*, 1914, 159, 431—434).—Twenty kilos. of wheat were washed with distilled water, and the residue submitted first to maceration with cold water, then extraction with warm water ( $50$ — $60^\circ$ ), and finally with boiling water. The residue from this treatment was sieved.

and the portion passing through was treated with absolute alcohol, a finely granular, homogeneous, white flour (*M*) being obtained on filtration. The portion remaining on the sieve was similarly treated with alcohol, filtered, and the filtrate kept. The aqueous extracts obtained with boiling and warm water were separately concentrated on a water-bath, and then alcohol was added, the precipitates,  $\alpha$  and  $\beta$ , being filtered off. These two filtrates were mixed with those from *M*, and from the residue on the sieve, the alcohol was distilled off, and the aqueous residue (*C*) shaken with chloroform. The filtrates from the first two treatments with water were also shaken with chloroform after concentration. The three separate chloroform extracts so obtained were mixed, and on distilling off the chloroform, the residue, after treatment first with ether, and then with alcohol, yielded from the second solvent 2 grams of a yellow colouring matter, which was probably a physiological transformation product of chlorophyll. It did not give either the biuret reaction or the reaction for acraldehyde, was insoluble in water, but soluble in benzene, carbon disulphide, or light petroleum. The aqueous layer from *C* was treated with alcohol until a slight precipitate appeared, and then dialysed, and from the dialysed liquid monopotassium phosphate and potassium sulphate were obtained, but no monocalcium phosphate.

The flour *M*, together with the precipitates  $\alpha$  and  $\beta$ , on extraction with ether, gave an oil, of which the major portion was insoluble in acetone, and contained no phosphorus, sulphur, or nitrogen, and the smaller, soluble portion, 8 grams, contained 0.221 gram of phosphorus, thus proving the non-existence of lecithins in the wheat. By incinerating the flour *M*, and also the residue on the sieve, they were found to contain, respectively, 0.30 and 0.62% of insoluble salts, consisting chiefly of calcium sulphate and tricalcium phosphate, but no carbonates.

W. G.

#### The Organic Phosphoric Acid Compound of Wheat Bran.

II. R. J. ANDERSON (*J. Biol. Chem.*, 1914, 18, 425—440. Compare A., 1912, ii, 1205).—The author shows that the organic phosphoric acid compounds obtained from wheat bran by the usual methods are contaminated with oxalates and inorganic phosphates. Purer preparations have now been obtained by precipitation from very dilute hydrochloric acid with alcohol. Several amorphous barium salts have been prepared; also an amorphous silver salt, which darkens very rapidly, and finally turns quite black. These compounds are quite different from the corresponding phytates. Evidence is adduced to show that wheat bran contains several organic phosphoric acids differing so slightly from one another that their separation is very difficult.

H. W. B.

#### The Organic Phosphoric Acid Compound of Wheat Bran.

III. Inositol Monophosphate, a New Organic Phosphoric Acid Occurring in Wheat Bran. R. J. ANDERSON (*J. Biol. Chem.*, 1914, 18, 441—446. Compare preceding abstract).—Inositol monophosphate is prepared from the hydrochloric acid extract of

wheat bran by treatment with barium hydroxide, filtering off the precipitate, and, after removing excess of barium, concentrating in a vacuum and precipitating with alcohol. The substance was purified by means of its insoluble lead salt. After recrystallisation from water, with the addition of alcohol, it was obtained in colourless, star-shaped aggregates of plates or prisms.

Inositol monophosphate,  $C_6H_6(OH)_5 \cdot O \cdot PO(OH)_2$ , when heated rapidly in a capillary tube, softens at  $200^\circ$ , and decomposes at  $201\text{--}202^\circ$ . When slowly heated, it softens at  $188^\circ$ , and melts at  $190\text{--}191^\circ$  (decomp.). It is optically inactive. It is very soluble in water, giving an acid solution, but is insoluble in alcohol and the usual organic solvents. In the cold, no precipitate is produced with copper acetate, but on warming the solution, a bluish-white precipitate separates, which again dissolves completely on cooling. After hydrolysis with sulphuric acid or ammonia in a sealed tube, inositol and phosphoric acid were isolated and identified.

H. W. B.

### Is Silica an Indispensable Constituent of Plant Food?

MARSHALL LUNDIE (*S. African J. Sci.*, 9, No. 10; *Chem. News*, 1914, 110, 200—202).—Water culture experiments with wheat, supplied with the usual nutrients, but without silica. The dried leaves and stems contained, respectively, 1.212 and 0.449% of silica.

Reference is made to a previous experiment, by Hahn, in which wheat grown under similar conditions was attacked by rust, every plant being overrun with the fungus in two days.

It is suggested that whilst silica is not an essential plant food for cereals, it may be of use in enabling the plants to resist attacks of fungoid growth. If this is correct, cereals grown on dolerite and basalt soils should suffer less from fungoid attacks than cereals grown on granite soils, climatic and weather conditions being the same (compare Hall and Morison, *Proc. Roy. Soc.*, 1906, [B], 77, 455).

N. H. J. M.

[Influence of Zinc, Copper, Manganese and Cerium on the Growth of Wheat.] J. A. VOELCKER (*J. Roy. Agric. Soc. Engl.*, 1913, 74, 411—427. Compare A., 1913, i, 1430).—Experiments with wheat grown in pots containing 40 lbs. of soil. Zinc was applied at the rate of 0.01, 0.02, and 0.03% in the forms of phosphate, nitrate, and carbonate; copper (0.0025, 0.005, 0.01, 0.025, 0.05, and 0.1%) as sulphate and carbonate; manganese as phosphate and carbonate, and cerium as oxide and sulphate (0.001, 0.025, and 0.005%).

As regards zinc, it was found that the larger amounts of nitrate retarded germination, whilst the other salts were almost without effect on germination and in the earlier stages of growth. Later, in June, a toxic effect was shown in the case of the larger amounts of carbonate and phosphate, and especially with nitrate, which caused the tops of the ears to be practically "blind." The final results showed a reduction in the yield of grain, except with 0.01%



of zinc as nitrate, and, coincidentally, a more or less considerable gain of straw (except with the largest amount of nitrate); with 0.01% of zinc as nitrate the yield of straw was nearly doubled, and the lowest gain, with 0.03% as carbonate, was 29%. Zinc phosphate and carbonate increased the root development, which was very stunted when nitrate was employed.

The conclusions drawn from the copper experiments are that stimulation occurs when the application is between 0.01 and 0.02%; that larger amounts are toxic, and that smaller amounts are without effect. The greatest gain (straw 79 and grain 62%) was obtained with 0.02% of copper as carbonate. With the beneficial amounts of copper, especially with the sulphate, the roots were very extensive and fibrous as compared with untreated plants.

The results obtained with manganese and cerium were negative, no indications of stimulation or of toxicity being obtained.

N. H. J. M.

**Occurrence of Hydrogen Cyanide in Millet and Guinea Corn.** J. R. FURLONG (*Analyst*, 1914, 39, 430—432).—See this vol., ii, 821.

**Occurrence of Methyl Alcohol in Maize Silage.** E. B. HART and A. R. LAMB (*J. Amer. Chem. Soc.*, 1914, 36, 2114—2118).—Hart and Willaman (A., 1912, ii, 1205) have found that maize silage contains a small amount (about 0.05%) of methyl alcohol, whereas Dox and Neidig (A., 1913, i, 236) have stated that this alcohol is absent.

Several samples of maize silage have now been examined, and in all cases the presence of methyl alcohol was detected. As a number of different tests were employed for identifying the methyl alcohol, the possibility is precluded of the reactions being due to some other substance.

E. G.

**Lucerne. V. Enzymes Present in Lucerne.** C. A. JACOBSON and AUGUST HOLMES (*J. Amer. Chem. Soc.*, 1914, 36, 2170—2182).—In an earlier paper (A., 1913, i, 151) an account was given of the enzymes present in the seeds of lucerne (*Medicago sativa*). A qualitative study has now been made of the enzymes in (a) the dried stems and leaves, (b) the fresh stems and leaves, and (c) the fresh roots. The following enzymes have been detected. In (a), emulsin and pectinase in large quantities, invertase and protease (peptolytic), and small quantities of amylase and peroxydase. In (b), emulsin and pectinase in large quantities, coagulase, peroxydase, and protease (peptolytic), and small quantities of lipase, amylase, and invertase. In (c), peroxydase in large amount, coagulase, invertase and pectinase, and small quantities of amylase and emulsin.

E. G.

**Experiments with Tomatoes.** J. A. VOELCKER (*J. Roy. Agric. Soc. Eng.*, 1913, 74, 419—422).—Pot experiments with tomatoes in an artificial soil consisting of rotted turf, sand, and limestone, both in its natural state and after being heated in a moist con-

dition at 80—100°. To some pots lithium phosphate ( $\text{Li} = 0.0025$  and  $0.005\%$ ) was added, whilst others received magnesia in such amounts that the total magnesia in the soil was raised from  $0.396$  to  $0.792$ ,  $1.188$  and  $1.584$  respectively. The highest amount of magnesia was practically equal to the lime present in the soil.

The effect of heating alone was to raise the yield of fruit  $73\%$ . Addition of  $0.002$  and  $0.005\%$  of lithium to the unheated soil reduced the yields to  $29$  and  $37\%$  respectively of the amounts obtained in soil alone. In the heated soils with lithium the yields were  $71$  and  $14\%$ . So that the toxic effect of the smaller amount of lithium was much reduced by heating the soil, whilst with the larger amount the toxic action was more marked in the heated soil.

As regards magnesia, the normal soil containing  $1.118\%$  showed an increase of  $13\%$  over the unmanured soil, whilst in those containing  $0.792$  and  $1.584\%$  the yields were respectively reduced to  $89$  and  $12\%$ . In the heated soils containing  $0.792\%$  of magnesia the yield was  $31\%$  over that of the unheated soil without added magnesia; with  $1.584\%$  of magnesia in the heated soil the yield was only  $22\%$ . Magnesium carbonate gave similar results to the oxide.

As compared with wheat, tomatoes are more affected by lithium and magnesium.

N. H. J. M.

**Comparative Efficiency for Milk Production of the Nitrogen of Lucerne Hay and the Maize Grain. Effect of Diuresis on Milk Secretion.** E. B. HART and G. C. HUMPHREY [with J. J. WILLAMAN and A. R. LAMB] (*J. Biol. Chem.*, 1914, **19**, 127—140. Compare A., 1913, i, 151).—Further experiments on heifers show that the nitrogen of lucerne hay is as effective as that of the maize kernel for the formation of the milk proteins.

Lucerne hay has specific diuretic properties. The increased renal activity observed when it is employed as a constituent of the food is associated with a corresponding diminution in the flow of milk. The diuretic stimulus causes in some cases a shrinkage in volume of  $2.5$ — $2.75$  kilos. of milk in a flow of  $11.5$  kilos. daily. It has not been ascertained whether salts or specific substances of organic nature in the hay are responsible for the diuretic action.

H. W. B.

**Flavour of Roquefort Cheese.** JAMES N. CURRIE (*J. Agric. Research*, 1914, **2**, 1—14).—During the ripening of Roquefort cheese a considerable amount of the fat is hydrolysed, the chief factor in the hydrolysis being a water-soluble lipase produced by *Penicillium roqueforti*. The result is an accumulation of the acids of milk fat, both free and combined.

The peppery flavour of the cheese is due to hexoic, octoic, and decolic acids, and their readily hydrolysable salts.

N. H. J. M.

**Humic Acids.** BR. TACKE, A. DENSCH, and TH. ARND (*Landw. Jahrb.*, 1914, **45**, 195—265).—A reply to Gully (*Mitt. k. bayr. Moorkulturanst.*, No. 5), in which the behaviour of peat towards tricalcium

phosphate, sodium acetate and other salts, calcium oxalate, aluminium and ferric chlorides, and colloidal ferric hydroxide, the extraction by water of absorbed bases from *Sphagnum* and peat, the electric conductivity, the iodine reaction, the inversion of sucrose by peat, and the liberation of hydrogen in presence of iron and peat, are discussed. The results are opposed to the view that reactions are due to colloid adsorption, and not to the presence of acids.  
N. H. J. M.

**Selective Adsorption (by Soils).** E. G. PARKER (*J. Ind. Eng. Chem.*, 1914, 6, 831—835).—Soils have not only the power of adsorbing dissolved salts from solution, but also of adsorbing one ion at a greater rate than the other; the nature of the surface of the constituents of a soil is such that the cation is adsorbed at a much greater rate than the anion. The presence of bases (calcium, magnesium, etc.) in solution, after contact of certain salt solutions with a soil, is not due to direct chemical reaction of the salt with the silicates of the soil, but to a secondary reaction of the free acid, resulting from the selective adsorption of the cation, with the mineral constituents of the soil. Generally, the smaller the soil particles, the greater the selective adsorption of the cation. The adsorption of the cation increases with the concentration of the solution up to a certain point, and then remains practically constant. At very low concentrations the adsorption of the cation is complete. The presence of other substances may or may not affect selective adsorption by a soil.  
W. P. S.

**Occurrence of Aldehydes in Garden and Field Soils.** OSWALD SCHREINER and J. J. SKINNER (*J. Franklin Inst.*, 1914, 178, 329—343).—Experiments in which a large number of soils were extracted with 3% sodium hydroxide, and the extracts, after being treated with acid to remove the humic acids, examined for aldehydes. Physiological tests were made with the aldehydes by means of wheat seedlings, and when possible qualitative tests with ferric chloride and magenta reagent were made. The soils included fourteen garden and greenhouse soils which had failed to grow good crops, and sixty field soils.

Of the unproductive garden soils, five contained aldehydes; out of thirty unproductive field soils, nine contained aldehydes; and out of the same number of productive soils, three contained aldehydes.

Aldehydes were found in neutral, acid, and alkaline soils, mostly in acid soils. No relation seems to exist between the crop being grown or the type or texture of the soil and the presence of aldehydes. The presence of aldehyde is not confined to any locality, being found as far apart as New York and Mississippi.

The effect of the extracted aldehyde material on the growth of wheat varied from slightly, to very, harmful. Of the extracts in which aldehydes were not found, nineteen were without effect, nineteen were injurious, and fourteen beneficial or slightly so.

N. H. J. M.

**Action of Manganese in Soil.** J. J. SKINNER and M. X. SULLIVAN (*U.S. Dept. Agric., Bull. No. 42, 1914*).—The results of pot experiments in which wheat was grown in an unproductive sandy loam, both without and with addition of manganese (as chloride, sulphate, nitrate, carbonate, and dioxide), showed a stimulating effect when the salt was applied in amounts from 5 to 50 per million. On a productive loam, manganese salts were without effect.

In further experiments on the action of manganese salts on the growth of wheat in aqueous extracts of soils, and on the oxidising power of the plants, it was again found that manganese increased growth and oxidation in unproductive soils; in productive soils there was increased oxidation, whilst the growth was decreased.

Finally, a field experiment is described in which wheat, rye, maize, cowpeas, and potatoes were manured with manganese sulphate (56 kilos. per hectare). It was found that manganese sulphate decreased both the crop and the oxidising power of the soil, which was an acid one.

The conclusion is drawn that the beneficial action of manganese may be due to increased oxidation, resulting in the destruction of injurious products in the soil, whilst the injurious action in the case of good soils may be due to excessive oxidation.

Acid soils, which are unfavourable to oxidation and catalysis, do not seem to be benefited by manganese. N. H. J. M.

**Sulphur as a Fertiliser.** J. A. VOELCKER (*J. Roy. Agric. Soc. Engl., 1913, 74, 419*).—Applications of flowers of sulphur, at the rate of 3.36, 6.72, and 13.44 kilos. per hectare, were without effect on mustard, rape, and clover grown in pots. The sulphur was mixed with the last portion of the soil used to fill the pots.

N. H. J. M.

**Influence of Sulphur on Soil Acidity.** H. CLAY LINT (*J. Ind. Eng. Chem., 1914, 6, 747—748*).—In order to ascertain the rate of oxidation of sulphur in soils, 100-gram portions of soil were treated with 33 mg. of sulphur (equivalent to 1000 lb. of sulphur per acre foot), and the moisture content was adjusted at 20%. The acidity of the soils increased gradually, as shown by the Jones calcium acetate method, up to the eighth week, when all the sulphur was oxidised. Sulphur is oxidised more rapidly in heavy clay loam soils than in sandy loam soils (compare A., 1913, i, 811).

W. P. S.

## Organic Chemistry.

**Composition of Mid-Continental (American) Petroleum.** F. W. BUSHONG (*J. Ind. Eng. Chem.*, 1914, 6, 888—890).—Crude oil from the wells of the Alluwe Oil Co., Oklahoma, was submitted to fractional distillation, the fractions being collected separately for each difference of 2° in the boiling point between 60° and 300°; the physical constants of these fractions are recorded. The total gasolene fraction, b. p. 40° to 150°, amounted to 13·77%, and the kerosene fraction, b. p. 150° to 300°, to 28·80%. Ozonides were separated from some of the fractions similar to those obtained by Molinari and Fenaroli from Russian and Roumanian petroleum (A., 1908, i, 933). W. P. S.

**A Crystalline Compound of Isoprene with Sulphur Dioxide.** G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 585—586).—When isoprene is mixed with an equal volume of liquid sulphur dioxide, a crystalline substance of the composition  $C_5H_8SO_2$  separates after one or two days. It may be purified by recrystallisation from ethyl ether and melts without decomposition at 62·5°. According to freezing point measurements, it dissolves unchanged in benzene. When dissolved in carbon tetrachloride or ethyl ether, it is only slowly acted on by bromine, but reacts quickly with alkaline potassium permanganate. H. M. D.

**The So-called "Acetone-soluble Phosphatides."** HUGH MACLEAN (*Biochem. J.*, 1914, 8, 453—459. Compare Fränkel and Pari, A., 1909, i, 620).—The author shows that the so-called acetone-soluble phosphatide obtained from the heart of the ox is impure lecithin. The lecithin can be separated from the accompanying fats and fatty acids by the addition of a small amount of an electrolyte such as calcium chloride to the acetone solution. The precipitate, when purified, has all the reactions of lecithin and is insoluble in acetone. The author considers it probable that all the acetone-soluble phosphatides described in the literature consist of lecithin contaminated with a nitrogenous impurity. H. W. B.

**Brain Kephalin. I. Distribution of the Nitrogenous Hydrolysis Products of Kephalin.** C. G. MACARTHUR (*J. Amer. Chem. Soc.*, 1914, 36, 2397—2401).—An account is given of a method of extracting kephalin from sheep's brains and the hydrolysis of the product.

The hydrolysis was effected by boiling the kephalin with 1% hydrochloric acid for twenty hours. The nitrogen in the residue was estimated and is referred to as "residual nitrogen." The ammonia nitrogen was estimated in the usual way, the total amino-nitrogen by means of the amino-apparatus described by van Slyke (A., 1912, ii, 1008), and the amino-acid nitrogen by Kober's copper method (A., 1913, ii, 990). The results were as follows: residual nitrogen, about 0·20%

ammonia nitrogen, about 0.20%; amino-alcohol nitrogen (difference between the total amino-nitrogen and the amino-acid nitrogen), 0.80%; and amino-acid nitrogen, 0.40%.

Kephalin contains neither choline nor neurine. Ordinary kephalin consists of at least two kephalins which contain the larger proportion of their nitrogen in the form of amino-alcohol and amino-acid respectively. E. G.

**Action of Selenium Bromide on Magnesium Alkyl Compounds.** A. PIERONI and C. COLI (*Gazzetta*, 1914, 44, ii, 349—353).—Attempts to introduce selenium into hydroxybenzonitrile and hydroxynaphthonitrile, etc., by treatment with hydrogen selenide, and into oxanilide, by heating with phosphorus pentaselenide, were unsuccessful, but it was found that selenium bromide reacts with organo-magnesium derivatives.

With dimagnesium acetylene dibromide (compare Iocitsch, this vol., i, 405), the reaction does not follow the normal course, but seems to proceed according to the equation:  $3\text{MgBr}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr} + 4\text{Se}_2\text{Br}_2 + 2\text{H}_2\text{O} = \text{OH}\cdot\text{Se}\cdot\text{C}\equiv\text{C}\cdot\text{Se}\cdot\text{C}\equiv\text{C}\cdot\text{Se}\cdot\text{C}\equiv\text{C}\cdot\text{Se}\cdot\text{OH} + 6\text{MgBr}_2 + \text{Se}_4 + 2\text{HBr}$ . The compound thus formed was obtained only in an impure condition as a brown powder.

With magnesium ethyl bromide, the reaction takes place as follows: (1)  $\text{Se}_2\text{Br}_2 + 2\text{MgEtBr} = \text{Se}_2\text{Et}_2 + 2\text{MgBr}_2$ ; (2)  $\text{Se}_2\text{Et}_2 + \text{EtBr} =$

$\text{SeEt}_2\text{Br}\cdot\text{SeEt}$

and (3) the latter  $+ \text{MgEtBr} + \text{H}_2\text{O} = \text{SeEt}_3\cdot\text{SeH} + \text{MgBr}_2 + \text{EtOH}$ . *Triethylselenitine hydroselenide*,  $\text{SeEt}_3\cdot\text{SeH}$ , thus obtained, is a dense, yellow oil of disagreeable odour; with alcoholic silver nitrate it gives up part of its selenium as silver selenide, and with hydrochloroplatinic acid it forms a crystalline product, which has been obtained only in small amount and has not been purified. T. H. P.

**Equilibrium in the System, Lead Acetate, Lead Oxide, Water, at 25°.** RICHARD F. JACKSON (*J. Amer. Chem. Soc.*, 1914, 36, 2346—2357).—In view of the fact that comparatively little modern work has been done on the basic lead acetates, an investigation has been carried out on the basis of the phase rule in order to ascertain the compounds capable of existence and their relative stability.

Mixtures of lead acetate, lead oxide, and water were shaken in flasks kept in a thermostat at 25° for at least forty-eight hours. After equilibrium had been attained, the solid phase was removed and the composition and density of the solution were determined. The results show that three solid phases are capable of existence. Normal lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 3\text{H}_2\text{O}$ , forms brilliant, monoclinic crystals, and is soluble in water to the extent of 35.50% at 25°. The compound,  $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot \text{PbO}\cdot 3\text{H}_2\text{O}$ , crystallises in needles and is exceedingly soluble in water, yielding solutions with  $D_4^{25}$  1.93—2.28; it is unstable and can only exist in presence of excess of dissolved basic lead acetate. The compound,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 2\text{PbO}\cdot 4\text{H}_2\text{O}$ , forms minute needles, and is stable in contact with solutions of itself, but under such conditions has a solubility of only 13.3%. Saturation curves

have been constructed and a new theory of the course of such curves is put forward. E. G.

**Structure of Maltose and its Oxidation Products with Alkaline Hydrogen Peroxide.** W. LEE LEWIS and SIEGEL A. BUCKBOROUGH (*J. Amer. Chem. Soc.*, 1914, 36, 2385—2397).—Lewis (A., 1909, i, 767) investigated the action of Fehling's solution on maltose, but the results failed to elucidate the constitution of the sugar as the oxidation did not proceed far enough.

The present work was undertaken in the hope that alkaline hydrogen peroxide might effect a more complete destruction of the maltose molecule and permit a better quantitative separation of the products. It has been found that the formation of saccharinic acid does not take place under these conditions. The ratio and nature of the oxidation products are quite different from those of dextrose with the same reagent, this difference being due to the effect of the glucoside bond. About half the maltose is oxidised as such, whilst the remainder seems to be hydrolysed before being oxidised.

From 100 grams of anhydrous maltose there were obtained 22.97 grams of hydrolysed dextrose, 0.16 gram of mannonolactone, 16.04 grams of glycollic acid, 0.11 gram of oxalic acid, 55.37 grams of formic acid, and 4.44 grams of carbon dioxide, together with 1.18 grams of other substances, which probably included erythronic and *l*-threonic acids.

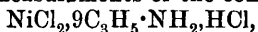
The formation of glucosido-acids in the oxidation of maltose affords an explanation of the fact that a molecule of dextrose requires 2.48 atoms of oxygen by Fehling's solution whilst the large maltose molecule requires only 2.86 atoms. The formation of  $\alpha$ - and  $\beta$ -isosaccharinic acids from maltose under the influence of alkali hydroxide involves the three hydroxyl groups attached to the first, second, and third carbon atoms from the free aldehyde group, and these carbon atoms must be present in the original maltose molecule, and their participation in the glucoside union is therefore precluded. The formation, in the oxidation of maltose, of relatively large amounts of  $\gamma$ -*d*-glucosidoglycollic acid, rather than  $\gamma$ -*d*-glucosidoglyceric acid, indicates that the terminal or primary alcohol carbon atom functions in the glucoside union of the two dextrose molecules. Maltose, therefore, is a  $\gamma$ -*d*-glucosidodextrose with the glucoside union on the primary alcohol carbon atom. It is probable that, under the influence of alkali hydroxide, maltose enters into an equilibrium of the six glucosido-hexoses of the dextrose series, and that the various oxidation products found result from the dissociation and oxidation of the intermediate hexose-dienols. E. G.

**Effect of Pressure on Yields of Products in the Destructive Distillation of Hardwood.** R. C. PALMER (*J. Ind. Eng. Chem.*, 1914, 6, 890—893).—Destructive distillations of birch and maple woods under increasing pressure result in a slight increase in the yield of alcohol, charcoal, and gas, whilst the quantities of acetic acid, pyroligneous liquor, and tar are decreased. The maximum effect on all the products is obtained with a pressure of 60 lbs. per square

inch, the most decided effect being noticed in the tar, which is diminished to the extent of 60 to 65%. Distillations were also made at pressures as high as 450 lbs. per square inch, but the exothermic reaction was so violent that the experiments were discontinued. At this pressure, the concentration of the dissolved tar in the pyroligneous liquor was so low that redistillation was not necessary in order to titrate the acidity; in practical operation, the first distillation of the primary liquor would not be necessary in order to make grey acetate of lime. It is possible, therefore, that pyroligneous acid, free from soluble tar, might be obtained by subjecting the distillate to a high pressure during the vapour stage.

W. P. S.

**Compounds of Salts of Nickel and of Allylamine.** A. PIERONI and A. PINOTTI (*Gazzetta*, 1914, 44, ii, 366—373).—The authors have endeavoured to ascertain the influence of aliphatic double linkings on the co-ordination numbers of complex salts by investigating double salts of nickel and allylamine. In no case, however, do these salts contain latent nickel in complex union; they decompose in aqueous solution, and the ions of the component salts are revealed by their reagents. Cryoscopic measurements of the compound,



in water indicate a molecular weight of 46.29 instead of the calculated value, 972.73, so that the compound forms twenty-one ions. The other compounds described undergo hydrolysis in aqueous solution with formation of nickelous hydroxide.

The compound,  $\text{NiCl}_2 \cdot 9\text{C}_3\text{H}_5 \cdot \text{NH}_2 \cdot \text{HCl}$ , obtained by saturating allylamine with nickel chloride previously dried at  $140^\circ$ , forms extremely deliquescent, square plates of an intense red colour, which is changed to yellow by traces of moisture. It has a neutral reaction and a strong taste, and exhibits marked chromoisomerism, becoming blue when heated and resuming its red colour when cool.

The compound,  $\text{NiCl}_2 \cdot 7\text{C}_3\text{H}_5 \cdot \text{NH}_2$ , or  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_4]_2\text{Cl}_2 + 3\text{C}_3\text{H}_5 \cdot \text{NH}_2$ , obtained by saturating allylamine with nickel chloride dried at  $140^\circ$ , the mass being kept cool, forms square, blue plates and loses  $3\text{C}_3\text{H}_5 \cdot \text{NH}_2$  in a vacuum over sulphuric acid, the resultant green compound,  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_4]_2\text{Cl}_2$ , resembling nickelous hydroxide in appearance.

The compound,  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_3]_2\text{SO}_4$ , prepared by the interaction of nickel sulphate and allylamine in presence of water, forms square, blue plates and effloresces and loses  $2\text{C}_3\text{H}_5 \cdot \text{NH}_2$  in the air; the residual compound,  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_3]_2\text{SO}_4$ , is an almost odourless, green powder, which is decomposed by water. Treatment of the compound,  $\text{NiSO}_4 \cdot 5\text{C}_3\text{H}_5 \cdot \text{NH}_2$ , with concentrated hydrochloric acid yields the compound,  $\text{NiCl}_2 \cdot 9\text{C}_3\text{H}_5 \cdot \text{NH}_2 \cdot \text{HCl}$  (see above). T. H. P.

**Organic Fluorine Derivatives.** I. J. RINKES (*Chem. Weekblad*, 1914, 11, 952—956. Compare this vol., i, 679).—Chlorination of *p*-fluoronitrobenzene in the presence of ferric chloride yields 4-fluoro-3-chloro-1-nitrobenzene, b. p.  $227\text{--}232^\circ$ , m. p.  $41^\circ$ , which is volatile with steam. Reduction with tin and hydrochloric acid



converts it into 4-fluoro-3-chloroaniline, plates, m. p.  $43.9^{\circ}$ , which decomposes on distillation. Diazotisation converts this product into o-fluorochlorobenzene, b. p.  $138.5^{\circ}/774$  mm., m. p.  $-42.5^{\circ}$ , which is volatile with steam.

*p*-Fluoroanisole, prepared from diazotised *p*-anisidine, cannot be readily purified; however, by heating with aluminium chloride at  $130^{\circ}$ , it yields *p*-fluorophenol, m. p.  $46.5^{\circ}$  (compare Swarts, A., 1913, i, 841), which in alkaline solution is re-converted by methyl sulphate into *p*-fluoroanisole, b. p.  $157.1^{\circ}/767$  mm., m. p.  $-43.5^{\circ}$ .

Sodium persulphate oxidises *p*-fluoroaniline to *p*-fluoronitrosobenzene, m. p.  $35.2^{\circ}$ , which is volatile with steam. This substance reacts with *p*-fluoroaniline in solution in glacial acetic acid to form 4:4'-difluoroazobenzene, orange-red needles, m. p.  $101.1^{\circ}$ . A. J. W.

**Action of Nitric Acid on the Three Isomeric Fluorotoluenes.** I. J. H. SLOTHOUWER (*Chem. Weekblad*, 1914, 11, 956—958).—Nitration of *p*-fluorotoluene yields a very small proportion of two fluoronitrotoluenes, one having m. p.  $27^{\circ}$  and b. p.  $138-139^{\circ}/83$  mm., and the other b. p.  $134-135^{\circ}/83$  mm. The main product is 3-nitro-*p*-cresol, m. p.  $32^{\circ}$ , proving that the oxidation detaches fluorine from the nucleus. A. J. W.

**Aldehyde- and Acetone-bisulphites of Organic Bases as Photographic Developers.** GUIDO PELLIZZARI (*Ann. Chim. Applicata*, 1914, 2, 129—132).—*p*-Aminophenol in the presence of sulphurous acid forms hydrogen sulphite derivatives with acetone, ethyl acetoacetate, formaldehyde and acetaldehyde, and *p*-methylaminophenol (metol) yields such derivatives with acetone, formaldehyde, and acetaldehyde. Glycine is more acidic than basic and does not form hydrogen sulphite compounds. The compounds formed by acetone with *p*-aminophenol hydrogen sulphite,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{H}_2\text{SO}_3\cdot\text{C}(\text{Me})_2$ , and with *p*-methylaminophenol hydrogen sulphite,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}\cdot\text{H}_2\text{SO}_3\cdot\text{C}(\text{Me})_2$ ,

act as photographic developers in the presence of sodium carbonate, which liberates the amino-compound and the acetone and converts the sulphurous acid into sodium sulphite; the presence of an aldehyde or ketone enhances the reducing power of the developer. T. H. P.

**Sulphonation of Benzoic Acid.** J. MAARSE (*Rec. trav. chim.*, 1914, 33, 207—238).—A determination of the relative proportions of the isomeric sulphobenzoic acids obtained on sulphonating benzoic acid under varying conditions. For the quantitative estimation, the products of sulphonation are converted into the corresponding sulphonyl chlorides by the action of phosphorus pentachloride on the potassium salts, and the solidification points of the resulting mixtures determined. The author has prepared the pure potassium salts of *o*-, *m*-, and *p*-sulphobenzoic acids, and the corresponding acid chlorides and amides. With these substances, solidification curves were obtained for mixtures of the *m*- and *p*-sulphonyl chlorides, and mixtures of the two isomeric ortho-acid chlorides. To detect the presence of small amounts of *o*-sulphobenzoyl dichloride in a mixture of the meta- and para-isomerides, the mixture was submitted to the action of ammonia,

the ortho-compound being thereby converted into the compound,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{smallmatrix} N \cdot NH_4$ . The liquid was exactly neutralised with hydrochloric acid and filtered, and from the filtrate the "saccharin" was set free by the addition of sulphuric acid and extracted with ether. After evaporating the ether, the residue was dissolved in a few drops of water, a sweet taste at this stage indicating the presence of the ortho-isomeride in the original mixture of acid chlorides. This test is sensitive to considerably less than 1% of the ortho-isomeride in the mixture.

The sulphonations were carried out in the apparatus described by Polak (A., 1911, i, 30), a study being made of the influence of temperature, duration of heating, concentration of the sulphuric acid, relative molecular proportion of sulphuric and benzoic acids, and the presence of a catalyst on the composition of the mixture of sulphobenzoic acids obtained. The presence of *o*-sulphobenzoic acid could only be detected in the one case where mercuric sulphate was used as a catalyst. The main product of the sulphonation was, in all cases, *m*-sulphobenzoic acid to the extent of well over 90%. Variation in temperature, increase in the duration of heating, variation in the concentration of the sulphuric acid (from 100 to 93%), and variations in the molecular proportions of sulphuric and benzoic acids used, had hardly any appreciable effect on the composition of the product. Of the three catalysts tried, potassium sulphate and silver sulphate had little or no influence on the composition of the product, whilst with mercuric sulphate *o*-sulphobenzoic acid was produced to the extent of 0.7% of the total product, as estimated by conversion into salicylic acid and weighing as such after extracting it with chloroform.

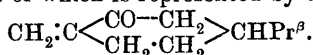
In the latter part of the paper the author discusses the results obtained by various workers on the sulphonation of other benzene derivatives.

W. G.

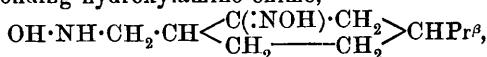
**Calcium *o*-Acetoxybenzoate.** L. VAN ITALLIE and A. P. OLIVIER (*Pharm. Weekblad*, 1914, 51, 1361—1366).—Calcium *o*-acetoxybenzoate is best prepared by passing ammonia into an alcoholic solution containing calcium chloride and *o*-acetoxybenzoic acid in molecular proportions, care being taken to maintain an acid reaction. The salt separates in colourless crystals.

A. J. W.

**$\alpha$ -Santolinenone, its Formula and Optical Inactivity. Resolution of the Hydroxylamino-oxime Compounds.** L. FRANCESCONI, N. GRANATA and A. SANNA (*Gazzetta*, 1914, 44, ii, 354—366).—The authors discuss the evidence in support of the racemic character of the optically inactive  $\alpha$ -santolinenone (this vol., i, 1134), the most probable constitution of which is represented by the formula,



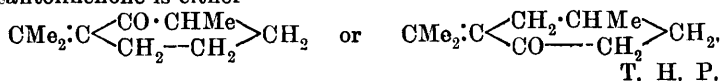
The corresponding hydroxylamino-oxime,



should be capable of existing in a *cis*- and a *trans*- modification for

each form of the ketone, the *d-cis*-compound being enantiomorphous with the *l-cis*-compound, and the *d-trans*- with the *l-trans*-isomeride. As with a number of the ketones of similar structure, it is, however, found that the rupture of the double linking accompanying the formation of the hydroxylamino-oxime can occur only in one way, so that only one pair of enantiomorphous compounds results. Fractionation of the hydroxylamino-oxime *d*-camphorsulphonate gives salts for which the value of  $[\alpha]_D$  in aqueous solution varies between  $-20.35^\circ$  and  $+21.9^\circ$ , the values for the corresponding bases in alcoholic solution ranging from  $-103^\circ$  to  $+16.7^\circ$ .

As will be shown in a subsequent communication, the structure of  $\beta$ -santolinenone is either



Oils of the Coniferae. III. The Leaf and Twig and the Cone Oils of Western Yellow Pine and Sugar Pine. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1914, 6, 893—895. Compare this vol., i, 1134, 1172).—The leaves and twigs of western yellow pine (*Pinus ponderosa*) yield from 0.04 to 0.126% of oil having  $D^{15}$  0.8718 to 0.8849;  $n_D^{15}$  1.4793 to 1.4838;  $a_D^{20}$   $-15.73^\circ$  to  $-19.59^\circ$ ; acid number, 0.67 to 2.36; ester number, 3.88 to 8.10. The cones of the tree yield 0.063% of oil, having  $D^{15}$  0.8757;  $n_D^{15}$  1.4789;  $a_D^{20}$   $-11.48^\circ$ ; acid number, 1.27; ester number, 7.20. The leaves and twigs of the sugar pine, *Pinus lambertiana*, give from 0.45 to 0.12% of oil, having  $D^{15}$  0.8676 to 0.8738;  $n_D^{15}$  1.4777 to 1.4795;  $a_D^{20}$   $-11.07^\circ$  to  $-16.50^\circ$ ; acid number, 0.68 to 2.38; ester number, 2.22 to 5.91. The cones of this tree yield 0.318% of oil, having  $D^{15}$  0.8692;  $n_D^{15}$  1.4771;  $a_D^{20}$   $-23.18^\circ$ ; acid number, 0.63; ester number, 3.75. The percentage composition of the oils was found to be:

	Western yellow pine.		Sugar pine.	
	Leaf and twig oil.	Cone oil.	Leaf and twig oil.	Cone oil.
Furfuraldehyde .....	—	trace	trace	trace
<i>l</i> - $\alpha$ -Pinene .....	2	6	21	22
<i>l</i> -Camphene .....	—	—	—	21
<i>l</i> - $\beta$ -Pinene.....	75	60	51	39—40
Dipentene.....	6	12—13	12	4—5
Bornyl ester (as acetate) .....	2	2.5	1.5	1.5
Free alcohol ( <i>l</i> -borneol) .....	7	4	8	3.5
"Green oil" .....	3	3—4	1	—
Sesquiterpene (?) .....	—	—	—	1
Loss, etc. ....	5	10	7	7

W. P. S.

Gentiaacaulin. MARC BRIDEL (*J. Pharm. Chim.*, 1914, [vii], 10, 329—335).—The author has isolated a large amount of the glucoside gentiaacaulin, from *Gentiana acaulis*, by the biochemical method already described (A., 1913, i, 1212), and has made a closer study of its chemical and physical properties. The roots of the plant contain more of the

glucoside than the leafy stem, fresh roots yielding about 2% and the stems about 1%, these values diminishing slightly towards the end of the plant growth. The glucoside, when thoroughly purified, is found to have  $[\alpha]_D - 64.42^\circ$  instead of  $-63.84^\circ$ , as previously given (*loc. cit.*). Dextrose has now been isolated, in addition to xylose, from the products of hydrolysis with boiling 2% sulphuric acid, the proportion of dextrose to xylose being about 55 : 45. W. G.

**Andrographolide.** K. GORTER (*Rec. trav. chim.*, 1914, 33, 239—243. Compare *ibid.*, 1911, 30, 151).—An attempt to determine whether andrographolide (the bitter principle of *Andrographis paniculata*) contains more than the one double linking already proved to be present (*loc. cit.*). Triacetylandrographolide, dissolved in ether saturated with water, reacts with aluminium amalgam, acetic acid being eliminated and diacetyldeoxyandrographolide,  $C_{20}H_{28}O_2(OAc)_2$ , colourless needles, m. p.  $121^\circ$ , formed. This substance combines only with two atoms of bromine, giving a dibromide, small plates, m. p.  $168^\circ$ , which is still unsaturated since it decolorises potassium permanganate in acid solution. This is confirmed by the fact that diacetyldeoxyandrographolide in acetic acid solution under the influence of platinum black absorbs two molecules of hydrogen, giving diacetyltetrahydroandrographolide,  $C_{20}H_{32}O_2(OAc)_2$ , prisms, m. p.  $90-91^\circ$ . This substance does not decolorise potassium permanganate, and on hydrolysis with alcoholic potassium hydroxide, followed by treatment with dilute sulphuric acid, yields the corresponding lactone, small needles, m. p.  $172-173^\circ$ .

Andrographolide, on boiling with concentrated formic acid for five minutes, followed by the immediate addition of water, yields a compound, small needles, m. p.  $215^\circ$ , which cannot be analysed, owing to the fact that in the combustion tube it decomposes into very difficultly combustible hydrocarbons. This substance cannot be acetylated.

These results show that andrographolide has two double linkings, only one of which can be saturated by bromine, that one of its three hydroxyl groups seems to be tertiary, and that the molecule probably contains two carbocyclic nuclei in addition to the lactonic ring.

W. G.

**Black Pigment in the Skin of an Australian Black.** WILLIAM JOHN YOUNG (*Biochem. J.*, 1914, 8, 460—462).—The pigment was prepared by dissolving the skin of the Australian Black in 5% potassium hydroxide solution and then acidifying with hydrochloric acid, when the melanin was precipitated as a dark brown powder. It was purified by repeated precipitation from its alkaline solution. It contains C 60.12, H 6.70, N 11.89, Fe 0.21%, and some sulphur (unestimated). A solution of the pigment in 5% potassium hydroxide or in concentrated sulphuric acid absorbs all the rays in the violet, the blue and, in part, the green of the spectrum to a wave-length of about  $515 \mu$ . Beyond this point there is slight blurring of the green and orange, whilst the red is practically unaffected. H. W. B.

**Transformation of Glutamic Acid into *l*-Pyrrolidonecarboxylic Acid in Aqueous Solution.** FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1914, 8, 481—493. Compare Abderhalden and Kautzsch, A., 1910, i, 768; 1912, i, 492).—When an aqueous solution of glutamic acid is heated above 80°, a certain proportion of it is converted into *l*-pyrrolidonecarboxylic acid, and the same change occurs with an acid salt of glutamic acid, but to a smaller extent. Mineral acids exert an inhibitory action to an extent proportional to their strength and to the amount present. The presence of more than 8% of sulphuric acid or about 3% of hydrochloric acid inhibit the change altogether.

The reverse change, namely of *l*-pyrrolidonecarboxylic acid into glutamic acid, occurs on boiling with concentrated hydrochloric acid.

It appears that the occurrence of pyrrolidonecarboxylic acid among the products of protein hydrolysis is often due to this secondary change.

H. W. B.

**Diketotriazines.** J. BOUGAULT (*Compt. rend.*, 1914, 159, 631—633. Compare this vol., i, 1004).—Diketotriazines can be prepared quite well by the action of cold dilute alkali on the semicarbazones of the corresponding  $\alpha$ -ketonic acids, the yield being better than on heating owing to the elimination of a secondary action, but the process requires several months under these conditions. With sodium hypobromite, diketotriazines give bromo-acid amides and nitrogen is evolved. Thus 4:6-diketo-3-benzyltriazine yields *aa*-dibromo- $\beta$ -phenylpropionamide,  $\text{CH}_2\text{Ph}\cdot\text{CBr}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 138°, which is reduced by zinc in acetic acid to phenylpropionamide, m. p. 105°. 4:6-Diketo-3-phenylethyltriazine similarly yields *aa*-dibromo- $\gamma$ -phenylbutyramide,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CBr}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 139°, yielding on reduction phenylbutyramide. This behaviour on oxidation with sodium hypobromite is a further proof of the constitution of the diketotriazines.

W. G.

**Gelatinisation of Pectin in Solutions of the Alkalis and the Alkaline Earths.** DOROTHY HAYNES (*Biochem. J.*, 1914, 8, 553—583).—The rate of gelatinisation of pectin is not determined by the rate of diffusion or by the rate of adsorption of the alkali or alkaline earths producing gelatinisation, but by the rate of a chemical reaction involving the replacement of hydrogen by potassium, barium, strontium, or calcium and hydroxyl ions. That a reaction of this kind takes place is supported by the facts that it can be expressed by a velocity equation involving the concentrations of the reacting substances, and that the constitution deduced for compounds of the alkalis and alkaline earths with pectin is strictly analogous to that of the corresponding compounds of the mono- and di-saccharides. Similar molecular compounds with salts are probably also formed. Gelatinised pectin forms solid solutions with the alkaline earths which may be compared with the solid solutions of lime and sucrose.

H. W. B.

**Activation of Trypsinogen.** HORACE MIDDLETON VERNON (*Biochem. J.*, 1914, 8, 494—529. Compare this vol., i, 214).—The author describes experiments from the results of which he draws the

conclusion that in the activation of trypsinogen by enterokinase, the trypsin liberated in the earlier stages by the direct action of the enterokinase gradually sets free an enzyme (termed *deuterase*, to indicate that it acts secondarily to enterokinase) from a precursor, and that this deuterase is mainly responsible for the later stages of the activation process. It is found that the rate of activation of the trypsinogen during the last half of the process (when deuterase is acting) may be one thousand times more rapid than the initial rate, and it is independent of the amount of enterokinase used.

Deuterase has a temperature coefficient of 1.00 to 1.22 and is further distinguished from enterokinase by the fact that the former is relatively much more retarded in its action by glycerol, and the latter by Witte's peptone.

There is no relationship between the amounts of deuterase and trypsin present in pancreatic extracts prepared from various animals. A glycerol extract of monkey's pancreas contained only a fourth as much trypsin as a glycerol extract of pig's pancreas, but two-thirds as much deuterase. Some extracts of ox pancreas did not seem to contain any deuterase, but this was shown to be due to the masking action of an anti-substance. Deuterase is extremely unstable, except in the presence of glycerol, and therefore, aqueous pancreatic extracts have relatively little activating power; freshly activated pancreatic juice was observed to lose most of its activating power in two hours at 37°, owing probably to destruction of the deuterase by trypsin. Both trypsin and trypsinogen appear to exist in various degrees of stability.

The activating power of deuterase may be nearly doubled by the addition of small quantities of intestinal extract which themselves do not possess any appreciable activating power. Deuterase is not, however, regarded as a co-enzyme of enterokinase. H. W. B.

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### Physiological Chemistry.

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**Determination of the Composition of the Different Proteins of Ox and Horse Serum by the Method of Van Slyke.** PERCIVAL HARTLEY (*Biochem. J.*, 1914, 8, 541—552).—The author has separated the proteins of ox and horse serum, and estimated the ammonia-, melanin-, cystine-, arginine-, histidine-, lysine-, and residual amino- and non-amino-nitrogen present in each compound by van Slyke's method (*A.*, 1911, ii, 944). The conspicuous differences existing between serum-albumin and serum-globulin with regard to their content of cystine, diamino-acids (particularly lysine), melanin and ammonia, are advanced by the author as additional evidence controverting Moll's statement of a transformation of serum-albumin into serum-globulin occurring in warmed blood serum (compare Bywaters and Tasker, *A.*, 1913, i, 1399). On the

other hand, the similarity of the figures obtained for the various globulins supports the views of Chick (this vol., i, 1145) regarding the close relationship existing between euglobulin and  $\psi$ -globulin.

H. W. B.

**Influence of Excessive Water Ingestion on Protein Metabolism.** JOHN BOYD ORR (*Biochem. J.*, 1914, 8, 530—540. Compare Fowler and Hawk, A., 1910, ii, 625).—A series of experiments carried out on men shows that the excessive ingestion of water produces an increased excretion of urinary nitrogen, due chiefly to an increase in the elimination of ammonia and urea. The action is not, however, to be regarded as a mere flushing out of waste products from the system, because it is found that the most marked rise in the urinary nitrogen after water drinking occurs on a low protein diet, whilst when the subject is on an excessively high protein diet, where a large amount of nitrogenous end-products would be present in the system, the smallest rise occurs in the total urinary nitrogen. In the latter case, although during the period of excessive water ingestion the total urinary nitrogen remains almost stationary, the absolute amount of urea, and the percentage of the total nitrogen excreted as urea, both increase. This result, which is obtained in all the experiments, shows that the main effect of excessive water drinking is a stimulation of the catabolic processes of metabolism. Since, on returning to a normal water consumption, a retention of nitrogen is observed, the period of excessive water ingestion is also attended by a stimulation of the anabolic phases of protein metabolism.

The appearance of creatine instead of creatinine in the urine during the period of excessive water drinking, as recorded by Fowler and Hawk (*loc. cit.*), was not observed. A decrease in the faecal nitrogen, indicating a more complete utilisation of the protein of the food, is another of the beneficial effects accompanying copious water drinking.

H. W. B.

**Physiology of Reproduction in the Domestic Fowl. IX. Effect of Corpus Luteum Substance on Ovulation in the Fowl.** RAYMOND PEARL and FRANK M. SURFACE (*J. Biol. Chem.*, 1914, 19, 263—278).—The desiccated fat-free substance of the corpus luteum of the cow, when injected in suspension, in proper dosage, into an actively laying fowl immediately inhibits ovulation. The duration of this effect varies with different birds from a few days to two to three weeks. After the bird begins ovulating again, the laying goes on unimpaired. The same effect is produced by the injection of extracts of the luteal substance, either intravenously or intra-abdominally. The active substance which produces the inhibition is inactivated by boiling.

H. W. B.



## Chemistry of Vegetable Physiology and Agriculture.

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**Significance of Certain Substances for Plant Growth.** W. B. BOTTOMLEY (*Ann. Bot.*, 1914, 28, 531—540).—Peat which was subjected to the action of certain aerobic soil organisms at 26°, and, after being sterilised, mixed with nine parts of soil and kept for seventeen days at 26°, induced a considerable fixation of nitrogen, amounting with two different soils to 77 and 54 mg. per 100 grams of soil.

Further experiments with various plants showed that aqueous extracts of the bacterised peat (1 part of peat to 200 of water) supplied all the plant food required, and that seedlings of *Primula malacoides* (in loam, leaf-mould, and sand) grew to twice the size when treated twice with an aqueous extract of 0.18 gram of the peat.

Stimulating effects were obtained by employing the residue of an alcoholic extract of peat, by the phosphotungstic acid precipitate from an aqueous extract of the same residue, and finally by the silver fraction, corresponding with Funk's "vitamine" fraction. The last substance added to a complete nutritive solution, at the rate of 0.35 per million, increased the growth of excised wheat seedlings grown for fifty days 59%. The plants showed a continuous growth, whilst those without the peat substance increased 14.7% in sixteen days, and then lost in weight, the final loss being 10.9%. It is suggested that during germination substances are formed which enable the embryo to utilise the food present in the seed, and that this substance can be wholly or partly replaced by the substance obtained from peat.

N. H. J. M.

**Injurious Root Secretions.** D. PRIANISCHNIKOV (*Rev. gen. Botan.* 1914, 25, 563—582).—The results of experiments in which etiolated wheat plants were grown successively in the same distilled water showed no reduction in the yield; under these conditions, no substance toxic to wheat seems to be secreted by the roots of wheat. In sand and soil-culture experiments it was found, however, that the yields of subsequent crops were considerably reduced, according to the plants grown, not only when the same plant was grown two or three times in succession, but with different plants. The reduction in yield was much greater when the roots of the first plant were left in than when they were removed.

Oats grown in an extract of black soil gave a very small yield, whilst normal growth was obtained when the extract was filtered through charcoal. When the extract was distilled, and both the distillate and the residue employed as culture solutions, the former produced a normal growth and the latter a much smaller yield; the difference was still more marked when the distillation was conducted under reduced pressure.

The conclusion is drawn that roots contain a substance which is

toxic both to the same and to other plants. It is suggested that one cause of the reduced yield of a second growth may be the increased alkalinity, which would be greater when the first crop is removed during early periods of growth, and varies according to the plant grown. On the other hand, alkalinity is not removed by charcoal, which in some cases raised the yield to its original amount.

The experiments referred to form part of a research by Péritourine (*Ann. Inst. agron. Moscow*, 1913, No. 4; in Russian).

N. H. J. M.

**Origin of Vanillin in Soils. Vanillin in Wheat and in the Water in which Wheat Seedlings have Grown.** M. X. SULLIVAN (*J. Ind. Eng. Chem.*, 1914, 6, 919—921).—Since vanillin, or a closely related parent substance, appears to be fairly widely distributed in the vegetable kingdom, the author has determined whether or not vanillin can be detected in wheat, as a type of field crop, and in the water in which wheat has grown. Ungerminated wheat was found to contain about three parts per million of vanillin; the quantity increases slightly during the early growth of the plant, and the substance can pass from the plant to the medium of growth either directly or, more probably, as a result of cell sloughing and disintegration. Treatment of the ground seeds with acids increases the yield of vanillin, this being due, apparently, to the hydrolysis of the parent substance; the latter is regarded as being coniferin. Vanillin is also found in rotten oak wood, pineapple pulp, and lawn grasses. Its presence in wood and various forms of vegetation would lead to the conclusion that the vanillin found in soil has its origin in vegetable débris and, to a minor extent, in direct excretion or cell sloughing by growing plants.

W. P. S.

**Analyses of Two Echinacea Roots.** F. W. HEYL and J. F. STALEY (*Amer. J. Pharm.*, 1914, 86, 450—455).—The following results were obtained on the analysis of the roots of two species of the genus *Brauneria* (*Echinacea*) obtained from Kansas and Missouri: *B. angustifolia*: moisture, 10·90%; starch, none; pentosans, 15·6%; "crude fibre," 24·77%; protein, 6·54%; ash, 7·76%; inulin, 5·9%; resin, 1·84%; sucrose, 6·92%; reducing sugars, 3·65%. *B. purpurea*: moisture, 10·18%; starch, none; pentosans, 15·6%; "crude fibre," 29·65%; protein, 5·31%; ash, 6·93%; inulin (not estimated); resin, 2·00%; sucrose, 3·40%; reducing sugars, 3·41%. *B. angustifolia* also yielded 0·04% of an amber-coloured, volatile oil, but did not contain any alkaloid sufficiently basic to be extracted by the ordinary methods; this does not exclude the possibility of the presence of choline and allied substances.

W. P. S.

**Plant Chemistry.** P. Q. KEEGAN (*Chem. News*, 1914, 110, 211—212).—Qualitative analyses of various plants. In *Parnassia palustris* a moderate amount of mucilage, a tannoid, and a catechol

tannin were found. *Pinguicula vulgaris* contains a good deal of mucilage, sucrose, and tannoid, but no tannin. Nitrates were not found in either plant. The golden saxifrage was found to produce much mucilage, with some gum, a little nitrate, some sucrose, a little tannin, but no tannoid. Holly-leaved barberry resembles ivy; both contain caffetannin and a tannoid, probably quercitagenin (the former containing more caffetannin and the latter more tannoid), and the aqueous extracts of the leaves show several reactions in common. *Mimulus luteus* contains nitrates and about 1% of caffetannin, but no tannoid. An examination of both leaves and roots of wild geranium showed that the leaves (in July) contained a little nitrate, much sucrose, considerable gallotannin and tannoid, but very little catechol-tannin; the roots contained no nitrates and no sucrose, but considerable amounts of starch and calcium oxalate.

The relation of assimilation and deassimilatory processes in plants to the reaction of the protoplasm is discussed.

N. H. J. M.

**Urease Content of Certain Indian Seeds.** HAROLD EDWARD ANNETT (*Biochem. J.*, 1914, 8, 449—452).—Urease has been detected in the following seeds: sword bean (*Canavalia ensiformis*), khultikalai (*Dolichos biflora*), *Urana lobata*, and six varieties of soja bean. The sword bean contains, weight for weight, several times as much urease as the soja bean, and may possibly be substituted for it in the estimation of urea (compare Plimmer and Skelton, this vol., ii, 306).

H. W. B.

**Investigation of the Diastase of Alfalfa [Lucerne] and the Effect of Rapid Curing on the Food Value of Alfalfa.** R. C. SHUEY (*J. Ind. Eng. Chem.*, 1914, 6, 910—919).—The diastatic activity of lucerne (*Medicago sativa*) is greater in the morning or after a period of darkness than after exposure to light. Much more diastase is present in the plants during the summer than in the spring and autumn, and the younger plants contain the larger quantity. Drying in a moist atmosphere at 50° decreases the diastatic activity, but it is considerably increased when the material is dried in a current of air with gradual increase of temperature. Light and weathering in the field tend to destroy the diastase, and the effect of rain during the curing is very injurious. Highly diastatic lucernes generally contain more water-soluble constituents than specimens low in diastase, but the water-soluble substances cannot be increased above a certain limit (about 40%). The loss of digestible constituents during handling and curing may vary from 20% under favourable conditions to as much as 50% under adverse weather conditions. Curing by artificial heat gives a hay of better colour, odour, and flavour than can be produced by other means, and the cost of artificial drying is estimated to be less than that due to losses sustained during curing in the field.

W. P. S.

**Chemical Changes during Silage Formation.** RAY E. NEIDIG (*J. Amer. Chem. Soc.*, 1914, 36, 2401—2413).—In earlier work (Dox and Neidig, A., 1913, i, 236), a study has been made of the acids and alcohols contained in maize silage. An account is now given of an investigation of the changes occurring during silage formation in silos of three different types: (1) a hollow clay tile silo; (2) a wooden silo; and (3) a concrete silo. The following changes were observed, but no differences were noticed which could be attributed to the materials of which the silos were constructed. Non-reducing sugar was rapidly changed to reducing sugar, and the amount of the latter subsequently decreased. The quantity of volatile acids and lactic acid increased daily. Small quantities of alcohol were produced. Carbon dioxide was formed with considerable rapidity after the silos had been filled, and free oxygen disappeared from the silos after the second or third day. The maximum temperature reached in any of the silos was 32·5°. E. G.

**Acid Mineral Soils.** G. DAIKUHARA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1914, 2, 1—40).—Results of pot experiments in which barley was manured with potassium chloride, in addition to ammonium sulphate and disodium hydrogen phosphate, showed that whilst satisfactory results were obtained in two clay soils, the effect of the potassium salt in a sandy granite soil was to reduce the yield to almost nothing. Addition of calcium carbonate along with the manures resulted in a very great increase over the unmanured pots. The soil, which contained only a small amount of humus, was found to give a strongly acid reaction, due to the absorption by the soil colloids of aluminium or iron compounds. In presence of potassium chloride, soluble acid aluminium or iron compounds are formed.

The examination of a considerable number of Japanese and Korean soils showed that three-fourths of them were acid, and that in the case of more than half of these the acidity was due to absorbed aluminium or iron compounds. Soils from mesozoic formations are the most frequently acid, then tertiary, palæozoic, and diluvial soils.

The examination of twenty specimens of kaolin showed that thirteen were acid, four neutral, and three alkaline. The acid kaolins behave towards neutral salt solutions in the same way as acid soils, whilst the others, after treatment with dilute acids and washing, become acid and acquire the properties of acid kaolins; similar results were obtained by subjecting granite and other alkaline rocks to the action of aqueous carbon dioxide for some weeks.

The acidity of soils is increased by treatment with dilute acids.

The filtrates from the soils treated with potassium chloride solution give with ammonia a precipitate consisting mainly of aluminium hydroxide, the amount of which corresponds with the acidity of the soil, and the amount of *N*/10-alkali used in the titration.

Soil acidity can be detected by moistening 5 grams of the soil

in a test-tube with a 10% solution of potassium nitrite, and suspending a strip of potassium iodide-starch paper in the tube by means of a cotton-wool plug. Acidity due to colloid absorption can be detected by treating the soil in a watch-glass with potassium chloride solution and testing with litmus paper.

To estimate the acidity, the air-dried soil (100 grams) is shaken for an hour with 250 c.c. of normal potassium chloride solution. One hundred and twenty-five c.c. are then boiled to remove the carbon dioxide, and titrated with *N*/10-sodium hydroxide. The treatment is repeated as long as the extract is acid, 150 c.c. of fresh potassium chloride being added each time. N. H. J. M.

**An Acid Soil in Assam.** A. A. MEGGITT (*Mem. Dept. Agric. India Chem. Ser.*, 1914, 3, 235—269).—The soil is very old alluvium and is a light loam in good physical condition, containing an adequate amount of potassium, and a moderate amount of humus, whilst it is deficient in phosphoric acid, and especially so in calcium carbonate (0.02%). The soil contains an organic acid which is toxic to some plants in solutions containing 30 per million. In the case of some plants, however, the substance is not only non-toxic, but is beneficial in concentrations which are injurious to other plants. The toxicity is more or less completely overcome by adding a complete nutritive solution, or by neutralising with lime.

In practice it has been found that whilst some plants, such as *Phaseolus mungo*, will grow on the soil and give a moderate crop, others fail to get beyond the stage of seedlings unless considerable amounts of lime are added. For neutralisation, the soil requires 880—1350 parts of lime per million.

The results of a large number of plot experiments with various manures, with and without lime, showed that in absence of lime most of the plots failed altogether, the exceptions being those which received basic manures (sodium and potassium carbonates and basic slag), and some which received superphosphate.

The fact that superphosphate, in absence of lime, enabled the plants to grow is attributed to its action in stimulating root development, resulting in extra-cellular root oxidation and the destruction of the toxic substance. The effect of superphosphate, which is very much less than that of lime, is increased by addition of sodium nitrate. N. H. J. M.

# JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

### PART II.

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#### General and Physical Chemistry.

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**The Index of Refraction at the Critical Point. Relationship between Molecular Weight, the Critical Coefficient, and the Real Critical Density.** MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1913, 11, 589—596).—A theoretical paper, in which it is shown that at the critical point the index of refraction of all substances is the same. Further, it is shown that  $M = A \cdot K_c \cdot d_c$ , where  $M$  is the molecular weight,  $K_c$  the critical coefficient, that is, the ratio of the critical temperature in absolute measure to the critical pressure, and  $d_c$  the real critical density. The value of  $A$  is calculated for a large number of substances, and shown to have a mean value of about 22. And since  $K_c \times d_c$  represents the weight of one litre of a gas at  $0^\circ$  and 760 mm.,  $A$  ought to give the gram molecular volume of the gas. These expressions are tested on numerous examples, and very good agreement is found except in the case of associated substances. J. F. S.

**Optical Properties of a Mixed Liquid Submitted Simultaneously to an Electric and a Magnetic Field.** A. COTTON, H. MOUTON, and P. DRAPIER (*Compt. rend.*, 1913, 157, 1063—1065. Compare Colton, *ibid.*, 1912, 155, 1232).—A study of the birefractation produced in a suspension of very finely divided calcium benzoate in aniline, when submitted simultaneously to a magnetic and electric field, the inclination of the electric field to the magnetic

field and the illuminating ray being varied. In no case was the effect found to be equal to the algebraic sum of the two effects produced independently.

W. G.

**The Peculiarities of the Zeeman Phenomenon in the Series Spectra of Oxygen and Hydrogen.** F. CROZE (*Compt. rend.*, 1913, 157, 1061—1063. Compare A., 1912, ii, 613; A., 1913, ii, 85).—A further reply to Paschen and Back (compare A., 1913, ii, 2), in which the author shows that the difference between his and their results for hydrogen is due to the fact that their Geissler tube was placed perpendicular to the axis of the electromagnet, whilst in his case it was parallel, the variation in the position producing a variation in the polarisation of the triplet of rays only in the case of hydrogen. His results for oxygen are in accord with theirs.

W. G.

**The Effect of the Electrical Field on Spectral Lines.** J. STARK (*Sitzungsber. R. Akad. Wiss. Berlin*, 1913, 932—946).—It has been found that certain hydrogen and helium lines belonging to the principal and subsidiary series are resolved into linearly polarised components under the influence of a very strong electrical field.

The apparatus employed in bringing about the resolution of the spectral lines consists of a discharge tube provided with a disk-shaped cathode, which is perforated with a large number of holes, 1 mm. in diameter. A non-perforated auxiliary electrode is placed behind the cathode at a distance of 1—2.5 mm., and a very intense electric field is established in the space between the cathode and the auxiliary electrode by connecting these up with the positive and negative poles of a battery of about 2000 accumulators. Under these conditions, the canal rays from the glow discharge, which pass through the perforated cathode, are subjected to the accelerating influence of the electrostatic field in the region between the cathode and the auxiliary electrode and the light emitted in these circumstances is found to be modified in the manner indicated above. Up to the present, the transverse effect only has been examined.

The  $\beta$ - and  $\gamma$ -lines of hydrogen are each resolved into five components, the vibrations of the three middle components being parallel, and that of the two exterior components perpendicular to the electric field. The two latter are much more intense than the three former, and the distance of separation of the extreme lines in a field with an intensity of 13,000 volts per cm., was found to be 5.2 Å., which is only a little less than the distance between the two  $D$ -lines.

The helium line  $\lambda$  3889 belonging to the principal series is not resolved by a field of 13,000 volts/cm. On the other hand, the lines  $\lambda$  4472 and  $\lambda$  4026, which belong to the first subordinate series, are both resolved into six components, three of which vibrate parallel, and three perpendicular to the field. The lines  $\lambda$  4713 and  $\lambda$  4121 belonging to the second subordinate series do not appear to be resolved by a field of the above intensity.

From observations on the lines of "parhelium," it has been found that  $\lambda 5016$  of the principal series, and  $\lambda 4438$  of the second subordinate series, are not measurably affected by a field of 13,000 volts per cm. The lines  $\lambda 4922$ ,  $\lambda 4388$ , and  $\lambda 4144$ , all of which belong to the first subordinate series, are, however, resolved under these conditions, and in the case of  $\lambda 4922$ , the photographic records show the existence of eight components, four of which vibrate parallel, and four perpendicular to the lines of the field.

The resolution of a particular line depends on the strength of the field, on the series to which the line belongs, and, in the case of lines belonging to the same series, on the wave-length. The magnitude of the resolution, as measured by the distance between the extreme components, is approximately proportional to the strength of the field. Lines which belong to the same series are acted on by the field in the same manner, whilst the different series of lines belonging to a given element behave in general quite differently. On comparing the displacement of the components for lines of the same series, it is found in some cases that the displacement increases as the wave-length diminishes, whilst in others the displacement is apparently independent of the wave-length.

From the few observations available, it would also appear that the action of the field is greatest in the case of those lines which belong to the so-called nebulous series. Since these are the lines which are characterised by broadening when the density of the gas increases, there would appear to be some connexion between this phenomenon and the resolution of the lines in an electric field.

H. M. D.

**The Spectra of High-frequency Discharges in Geissler Tubes.** ROBERT W. LAWSON (*Phil. Mag.*, 1913, [vi]. 26, 966—981).—An investigation has been made of the spectra emitted by nitrogen, oxygen, air, hydrogen, argon, helium, neon, and carbon dioxide when subjected to the action of the undamped, oscillatory electric discharge from a high-frequency Poulsen arc generator. Fused silica discharge tubes, provided with external mercury electrodes, were found most convenient for the observations. In general, the light emitted in this type of discharge is much greater than that obtained by other methods. The form of the discharge varies very considerably with the pressure of the gas and the current density, but is independent of the nature of the gas in the tube.

In none of the gases examined was the frequency of the discharge found to have any influence on the spectrum obtained, and in no case was it found possible to produce the condensed discharge spectrum by means of the Poulsen high-frequency generator. The view that the oscillatory character of the condensed discharge is the determining factor in the production of the elementary line spectrum is thus proved to be untenable. It seems more probable that the appearance of this spectrum in condensed discharge is dependent on the initial value of the current in the tube at each train of oscillations.



Photographs of the spectra obtained are shown in the paper, and these are discussed in detail. The air spectrum is identical with that of nitrogen under similar conditions of discharge, and in no case are oxygen lines discernable. In the case of oxygen, the compound line spectrum is obtained in all circumstances, change of voltage, current density, frequency, and gas pressure being without effect. For hydrogen, the series spectrum becomes relatively much brighter than the secondary spectrum when the discharge current is increased. This effect is similar to that observed in hydrogen with the ordinary induction-coil discharge. In the case of argon, experiments with varying currents of the same frequency show that the red spectrum is obtained with small, and the blue with large, currents, and that the current density is the main factor involved in the transition from one spectrum to the other.

In the experiments with neon, helium, and carbon dioxide, the spectrum obtained was identical with that observed when the non-condensed discharge from an induction coil is used. H. M. D.

**Series of Lines in the Spectrum of Neon.** R. ROSSI (*Phil. Mag.*, 1913, [vi], 26, 981—984).—Three series of lines have been found in the spectrum of neon. Two of these consist of doublets with constant frequency difference and common convergence frequency at  $\lambda 4119.8$  in the visible spectrum, whilst the third series consists of single lines in the ultra-violet.

The two series of doublets resemble subordinate series, but no evidence of the principal series, which might be expected to accompany them, has been obtained. The series of doublets do not correspond with any of the subordinate series of helium, for although they are nearer to the red end of the spectrum, as would be expected, the approximate relation between the separation of doublets and the square of the atomic weights does not hold.

All three series of lines are expressed by a Rydberg formula.

H. M. D.

**Measurement of Ultra-violet Spark Spectra of Metals According to the International System.** JOSEF MARIA EDER (*Sitzungsber. K. Akad. Wiss. Wien*, 1913, 122, IIa, 607—633).—A description of the methods employed to measure the ultra-violet spark spectra of the following elements: silver, aluminium, arsenic, gold, barium, bismuth, carbon, calcium, cadmium, copper, lead, antimony, tin, strontium, tellurium, and zinc; the results are exhibited in tabular form. F. M. G. M.

**Measurements in the Arc Spectrum of Nickel According to the International Normals.** SIEGMUND HAMM (*Zeitsch. wiss. Photochem.*, 1913, 13, 105—130).—The wave-lengths of lines in the arc spectrum of nickel have been measured between  $\lambda 7122$  and  $\lambda 2165$ . The recorded wave-lengths are compared with the previous data obtained by Hasselberg and by Exner and Haschek. Evidence has been obtained of the displacement of certain lines when the electrical conditions of the discharge are varied. H. M. D.

**Quantitative Study of the Absorption of Light by Bromine Vapour in the Ultra-violet.** G. RIBAUD (*Compt. rend.*, 1913, **157**, 1065—1068. Compare Henri, *J. Physique*, 1913, 305).—The author has measured the coefficients of absorption of bromine vapour in ultra-violet light, by taking two photographs side by side with the same duration of exposure, one having passed through the bromine, and the other having the intensity of light reduced in a known ratio, and seeking in the two photographs the region where the blackness is the same, thus getting the coefficient of reduction and the index of extinction for the given wave-length. Measurements were made with the bromine vapour under various pressures, the results showing that the index of extinction is proportional to the pressure. The author considers that the kinetic theory of absorption does not hold good for broad bands, but for the fine rays it accounts for the facts observed. W. G.

**Optical Studies on Carboxylic and Thiocarboxylic Acids, their Salts and Esters.** A. HANTZSCH and E. SCHARF (*Ber.*, 1913, **46**, 3570—3588).—An investigation of the aliphatic carboxylic acids and their simpler substitution products by means of their absorption spectra in the ultra-violet region. Especial care was taken to ensure the purity of the substances and of the solvents used.

The results with formic, acetic, and butyric acids (compare Bielecki and Henri, A., 1912, ii, 882; A., 1913, ii, 86, 263) indicate that association has practically no influence on the absorption; for example, acetic acid and its solutions are optically identical. From the constant behaviour of the fatty acids and their salts in aqueous solution at various concentrations, it also follows that dissociation is without appreciable effect (compare Wright, T., 1913, **103**, 528). Although the solutions of an ester in various solvents are optically identical, alcoholic solutions of an acid are slightly more absorbent than the homogeneous acid or its solutions in water or light petroleum; this is attributed to the formation of more strongly absorbent alcoholates. From the lack of influence of water (as a solvent) on the absorption of an acid, the conclusion is drawn that the hydrates which are generally believed to be formed cannot be of the structure  $RC(OH)_3$ .

In comparing the absorption of the various fatty acids, it is found that formic acid is more strongly absorbent than the other carboxylic acids, the others gradually increasing in absorption with rising molecular weight towards a limit which falls short of the effect produced by formic acid; the influence of homology on the absorption of esters derived from the same aliphatic acid is practically nil (compare Bielecki and Henri, *loc. cit.*). An aliphatic ester exerts stronger absorptive action than the isomeric acid; for example, ethyl acetate than butyric acid.

A comparison of the various derivatives of an acid shows that the absorptive power increases in the order salt—acid—ester—anhydride—chloride, probably because the less positive the group introduced, the less is the chromophoric effect of the unsaturated

carbonyl group interfered with by the action of partial valencies between it and the substituent. Similar relations are observed with oxalic acid derivatives, which, however, are much more strongly absorbent than the corresponding fatty acid derivatives.

As is already known (Purvis, Jones and Tasker, T., 1910, **97**, 2287), sulphur acts strongly as an auxochrome when introduced into the carboxyl group, the absorption increasing in the order  $R\cdot CO_2Et$ ,  $R\cdot CO\cdot SET$ ,  $RCS\cdot OEt$ ,  $RCS_2Et$ . In the third, selective absorption appears, and is strongly marked in the last class, the xanthates showing two absorption bands. Purely chemical evidence fails to suffice for a decision as to whether the acids  $RCO\cdot SH$  and  $RCS\cdot OH$  and salts, corresponding with the thiol- and thion-esters, are dynamic isomerides, but an examination of the absorption spectra of ethyl thiocarbonate,  $OEt\cdot CO\cdot SET$ , ethyl thioncarbonate,  $OEt\cdot CS\cdot OEt$ , and the potassium salt,  $OEt\cdot C(SO)K$ , demonstrates that the potassium salt is an equilibrium mixture of molecules of the thiol- and thion-structures. In a similar manner, thioacetic acid reveals itself as at least mainly of the thiol-structure,  $CMeO\cdot SH$ , whilst the potassium salt appears to be a mixture of the thiol- and thion-structures. From a comparison with methyl thiobenzoate,  $CPhO\cdot SMe$ , and thiobenzamide,  $CPhS\cdot NH_2$ , free thiobenzoic acid and also its potassium salt appear to be similar mixtures of dynamic isomerides. The relative stability of free xanthic acid in solution in light petroleum and in alcohol (compare von Halban and Kirsch, A., 1912, ii, 1046; A., 1913, ii, 312) is also readily observed from the alteration in the absorption.

D. F. T.

**Ultra-red Absorption of Gases.** EVA VON BAHR (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1150—1158. Compare A., 1913, ii, 810, 814).—The absorption bands exhibited by hydrogen chloride at  $3.5\mu$  and by carbon dioxide at  $2.7\mu$  have been further examined with the aid of a quartz prism, which affords a much greater dispersion as compared with that obtained by the use of a fluorspar prism. In these circumstances it has been possible to detect twelve maxima in the double band of hydrogen chloride. It is assumed that these maxima correspond with definite frequencies of molecular rotation. The carbon dioxide band at  $2.7\mu$  is found to consist of two separate bands, and the appearance of these suggests that these bands would be found to be double if an instrument of somewhat greater dispersive power were employed in their investigation.

H. M. D.

**Absorption of Ultra-violet Rays of Fatty Acids, their Salts, and Esters.** VICTOR HENRI (*Ber.*, 1913, **46**, 3650—3653. Compare Hantzsch and Scharf, preceding page).—The simple acids, esters, ketones, etc., show so little absorption of ultra-violet rays that even traces of impurities appreciably increase the absorption, and the compounds must be carefully purified. The agreement between the measurements of Bielecki and Henri and Hantzsch and Scharf for formic and acetic acids shows this to have been effected. The sodium salts absorb less than the acids. Acetic acid absorbs only one-third as much as the isomeric methyl formate. Propionic acid

compares with ethyl formate as 4 to 7. Accordingly, the absorption methods show differences which the refraction methods do not reveal.

E. F. A.

**Quantitative Investigation of the Absorption of Ultra-violet Rays by Aliphatic Saturated and Unsaturated Ketones and Aldehydes.** IV. JAN BIRLECKI and VICTOR HENRI (*Ber.*, 1913, **46**, 3627—3649).—The absorption curves of aliphatic ketones and aldehydes are characterised by an absorption band between 2700 and 2800. This band is characterised for the carbonyl group  $-C\leq O$ . The position of the maximum depends on the alkyl

group. It is lowest in the simplest aldehydes, and increases regularly with the number of  $CH_2$  groups. In the unsaturated ketones and aldehydes the ethylene linking causes a greater exaltation the nearer it is to the carbonyl. For shorter wave-lengths to the right of the maximum, acetone does not show a minimum until  $\lambda=2144$ , aldehydes and the more complicated ketones show a minimum, and the absorption curve rises with the complexity of the alkyl.

Comparison of the absorption curves of acids, ketones, and aldehydes indicates that the oxygen atom in carbonyl has its partial valencies free, whereas in carboxyl they are united with one another.

The absorption curve of acetone is parallel to that of acetic acid. In diacetyl the partial valencies of the oxygen atoms of the two carbonyls neutralise one another, so that the absorption curve lies but little above that of the monoketones. In acetylacetone, on the other hand, the two carbonyls augment one another.

The curves for aldehydes and ketones can be resolved into separate elemental curves. For aldehydes these are two in number, due to the carbonyl and to the alkyl respectively. For ketones the number is three, due to the carbonyl and to each of the two alkyl groups. This is in agreement with the photochemical experiments of Henri and Wurmser (*A.*, 1913, ii, 171), who have shown that the rays from  $\lambda=2800$  are absorbed by the carbonyl, and from  $\lambda=2300$  by the alkyl in the case of acetaldehyde.

Hence in the absorption of rays of different wave-length the electrons of sometimes the one and sometimes the other atomic grouping come into play. Only a part of the molecule takes part in the absorption, and this part changes when the wave-length is altered.

E. F. A.

**New Type of Absorption Spectrum.** J. KOENIGSBERGER and K. VOET (*Physikal. Zeitsch.*, 1913, **14**, 1269—1271).—It has been found that the absorption spectrum of tetrazine vapour deviates in a marked manner from the spectra which have been previously described. In a general way, it resembles the series line absorption spectra of metal vapours.

The spectrum consists of seven principal lines, the distance between successive members of this group decreasing as the wave-length diminishes. Between the principal lines are a considerable number of other lines of varying intensity. The weaker lines are very sharp, but each of the principal lines is associated with a

continuous background, the breadth of which in the case of saturated vapour at ordinary temperature amounts to about  $10 \text{ \AA}$ . When the density of the vapour is increased, a series of changes is found to occur in the neighbourhood of these lines. The first consists in the appearance of a bright line at a distance of about  $1 \text{ \AA}$  from the absorption line; the absorption of the continuous background then increases in intensity, with the result that the principal absorption line becomes less prominent, but the bright line remains when the density of the vapour is further increased, and it appears to be very nearly symmetrically situated with reference to the surrounding region of continuous absorption. Photometric observations have shown that the bright lines differ quite appreciably from the adjacent absorption region. An attempt is made to account for the appearance of the bright lines in the spectrum.

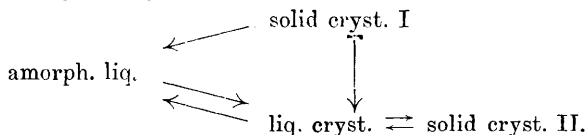
H. M. D.

**Rotation Dispersion.** V. L. TSCHUGAEV and A. OGORODNIKOV (*Zeitsch. physikal. Chem.*, 1913, **85**, 481—511. Compare A., 1911, ii, 450, 787; 1912, ii, 407).—The ultra-violet absorption spectra and the optical rotation of a large number of derivatives of *l*-menthyl-xanthic acid, *l*-bornylxanthic acid, and fenchylxanthic acid have been determined. The measurements were carried out in ethyl alcohol solution, and as light source, in the absorption spectra determinations, a spark between rhodium and nickel poles was used. In every case examined, selective absorption is observed, and in the simplest xanthates a band with its maximum at  $280\mu\mu$  is always observed. The constitution of the absorption curve is in the first place dependent on the sulphur-containing complex which plays the part of chromophore. The form of the curve remains practically constant if this group remains intact, but should this group be changed in any way, the absorption curve is changed in form. When two groups RO-CS-S- are directly united, the absorption spectrum characteristic of this group is not obtained, but one which does not contain any definite bands. If, however, the two RO-CS-S- groups are connected through one or more methylene groups, the characteristic absorption spectrum is obtained. In such compounds RO-CS-S-[CH<sub>2</sub>]<sub>n</sub>-S-CS-OR, the breadth of the band is proportional to the content of the solution in RO-CS-S- groups. A general parallelism is observed between the abnormal rotation dispersion and the characteristic selective light absorption of the active xanthates and analogous compounds. The divergences from the simplest possible relationships can be explained at least in part by the superposition of the partial rotations of the various optically active centres and by purely constitutive influences. In any given group of analogously constituted xanthates the corresponding dispersion curves can be made to coincide by a shifting in one direction, and in this connexion a relationship between the absolute rotation values and the position of the rotation maximum is established. In this respect the optically active xanthates behave like the tartaric esters, and the conclusion is drawn that the cause of the anomalous dispersion in these two cases must be similar.

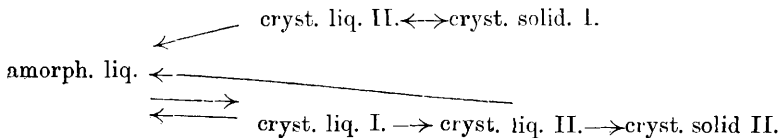
J. F. S.

**Rotation Dispersion. VI. The Influence of Temperature on Abnormal Rotation Dispersion of Coloured Compounds.** L. TSCHUGAEV and W. PASTANOGOV (*Zeitsch. physikal. Chem.*, 1913, **85**, 553—571. Compare A., 1911, ii, 450, 787; 1912, ii, 407, and preceding abstract).—The influence of temperature on the abnormal rotation dispersion has been investigated in the case of the coloured compounds methyl *l*-bornylxanthate, methyl *l*-menthylxanthate, the thioanhydride of *l*-menthylxanthic acid, the methylene ester of di-*l*-menthylxanthic acid, and the thioanhydride of *dl*-fenchylxanthic acid. The investigations were carried out at temperatures from  $-50^{\circ}$  to  $+80^{\circ}$  in toluene and acetic acid solutions. The sensitiveness to temperature change of the rotation dispersion is a constitutive property of optically active substances, and in the substances examined is not only dependent on the sulphur in the light-absorbing complex, but also on the nature of *R* in the complex  $\text{RO}\cdot\text{CS}\cdot\text{S}$ -. The temperature-coefficient of the rotation can have both positive and negative values. The temperature curves corresponding with definite wave-lengths (isochromes) can have forms which are either convex or concave to the temperature axis, and the lowest portion of these curves do not differ much from straight lines. On constantly changing the temperature the dispersion curve is shifted in a definite direction, which is usually toward the violet end of the spectrum, and this is connected with a raising of the whole curve. There is consequently no analogy to be found between the temperature influence on the dispersion curves of the xanthic acid derivatives and those of the tartaric esters. J. F. S.

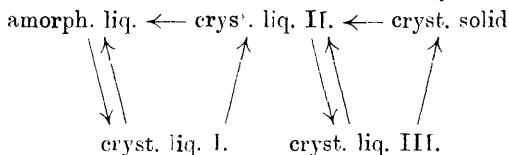
**Comparison of Liquid Crystals of Racemic and Optically Active Amyl Esters.** D. VORLÄNDER and FRANZ JANECKE (*Zeitsch. physikal. Chem.*, 1913, **85**, 691—696).—A number of amyl esters of arylideneaminocinnamic acids have been studied in connexion with their liquid crystals. *p*-Anisylideneamino- $\alpha$ -methylcinnamic acid *r*-amyl ester forms fine, light yellow needles, which show two transition points on heating, at  $66$ – $67^{\circ}$  and  $69^{\circ}$ . It forms one crystalline liquid phase and two crystalline solid phases, none of which polarise light circularly. The changes from one phase to another are given by the scheme:



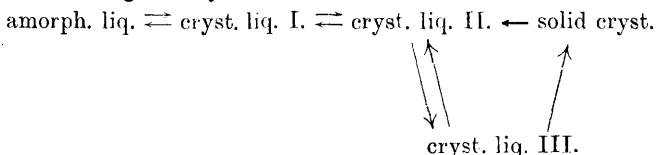
The *d*-amyl ester formed from *l*-amyl alcohol forms two solid and two liquid crystalline phases. The liquid crystals produce circular polarisation. The changes of the phases are given by the scheme:



The racemic amyl ester of *p*-ethoxybenzylideneamino- $\alpha$ -methylcinnamic acid shows two transition points at 88° and 101°, whilst the active ester has transition points at 86° and 100°. The racemic ester exists in three liquid, crystalline phases and one crystalline, solid phase, none of which are circularly polarising. The transformations of one form into another are shown by the scheme:



The active ester also has three liquid and one solid crystal phases, of which liq. cryst. I is circularly polarising. The transformations are given by the scheme:



Neither the active nor racemic ester of *p*-nitrobenzylideneamino- $\alpha$ -methylcinnamic acid produces liquid crystals. J. F. S.

**Production of Circularly Polarising Liquid Crystals from Optically Inactive Liquid Crystalline Substances.** D. VORLÄNDER and FRANZ JANECKE (*Z.-itsch. physikal. Chem.*, 1913, 85, 697—700).—It is shown that the addition of small quantities of abietic acid to optically inactive liquid crystals renders them strongly circularly polarising. Many other substances have been investigated, but none are found to be as active as abietic acid; pinene, borneol, menthol, pulegone, and camphor are active to a small extent, whilst camphoric acid, ethyl *d*-tartrate, ethyl malate, and cinchonine are entirely without action. J. F. S.

**Optical Sensitisation. II.** CHR. WINTHER and H. OXHOLT-HOWE (*Zeitsch. wiss. Photochem.*, 1913, 13, 89—104. Compare A., 1911, ii, 239).—The precipitation of mercurous chloride from Eder's solution, on exposure to light, reaches a limit when the solution still contains large quantities of mercuric chloride and ammonium oxalate. Comparative experiments, in which equal volumes of the filtrate and of a fresh solution of the same composition were exposed to the influence of light under similar conditions, indicate that the initial photochemical action leads to the formation of some substance which acts as a powerful negative catalyst.

It has been shown previously that the photo-sensitiveness of Eder's solution depends on the presence of traces of iron, which, it was thought, might be adsorbed by the precipitated mercurous chloride. This hypothesis does not, however, explain the optical insensitiveness of the filtrate, for when small quantities of ferric

chloride were added to this, it was found to be inactive on further exposure to light.

The same phenomenon is met with in the case of Eder's solution to which eosin is added. In general, the effect becomes more marked as the intensity of the light increases. If the ultra-violet rays are cut off during the preliminary exposure, the photochemical sensitiveness does not disappear. Further, it has been found that there is an appreciable loss of sensitiveness if the eosin solution is insulated before being added to the Eder's solution. The observations seem to show that the anti-catalyst which reduces the photo-sensitiveness of the solution is a product of the photochemical decomposition of eosin.

Some experiments have also been made on the photochemical oxidation of ferrous sulphate in presence of eosin. The sensitiveness increases with the quantity of eosin to a maximum value, which remains constant when the eosin concentration is further increased. The sensitising influence of a given quantity of eosin increases as the concentration of the ferrous salt diminishes. Other observations show that the bleaching of the eosin and the oxidation of the ferrous salt are to some extent independent of one another.

H. M. D.

**Wave-length and Velocity of Reaction.** L. BRUNER (*Zeitsch. Elektrochem.*, 1913, 19, 885—886).—Polemical. A reply to Plotnikov (A., 1913, ii, 898); see also Bruner (*ibid.*, ii, 745). J. F. S.

**Reversible Photochemical Reactions in Homogeneous Systems.**  $\beta$ -Methylantracene and Dimethyldianthracene. FRITZ WEIGERT and OTTO KRÜGER (*Zeitsch. physikal. Chem.*, 1913, 85, 579—622. Compare Luther and Weigert, A., 1904, ii, 463; 1905,

ii, 785).—The change  $\beta$ -methylantracene  $\xrightleftharpoons[\text{dark}]{\text{light}}$  dimethyldianthracene

has been investigated in the same way as the change anthracene  $\rightleftharpoons$  dianthracene was treated by Luther and Weigert (*loc. cit.*). It is shown that in the present case the reaction is somewhat complicated by the formation of several isomerides of dimethyldianthracene, and as it was not possible to separate the various isomerides the mixture was treated as a uniform substance, since it was shown that the various constituents behaved kinetically in an identical manner. The estimation of the amount of methylantracene which had changed was effected by removing the solvent, weighing the mixture of dimethyldianthracene and methylantracene, and then subliming the methylantracene in a specially constructed vacuum oven. The experiments were carried out in boiling solutions of phenetole, toluene, and benzene, temperature changes being brought about by reducing the pressure under which the solvents were boiling. It was found that the depolymerisation, in the dark, at temperatures 170°, 160°, and 150°, followed the course of a unimolecular reaction, and that the velocity of this reaction increased with the temperature. The temperature-coefficients  $k_{170^\circ}/k_{160^\circ} = 2.60$  and  $k_{160^\circ}/k_{150^\circ} = 2.74$  were obtained. An



equilibrium was set up in phenetole solution at  $170^{\circ}$ ,  $160^{\circ}$ , and  $150^{\circ}$  under the influence of light, which could be reached from either side; the concentration of dimethyldianthracene increased with the concentration of methylantracene at the equilibrium point, and approached a limiting value asymptotically. The limiting value became smaller with increasing temperature. On the assumption that the constants of the dark reaction were unchanged in the light, the velocities of the light reaction were calculated from the equilibrium values at  $170^{\circ}$ ,  $160^{\circ}$ , and  $150^{\circ}$ . Here, also, with increasing concentration of methylantracene, a value was obtained which approached a limiting value asymptotically. The temperature-coefficient of the light reaction, as in the case of most photochemical reactions, was approximately unity. To determine the velocity of the photochemical formation of dimethyldianthracene, experiments were carried out at temperatures from  $60^{\circ}$  to  $105^{\circ}$ . At these temperatures the reverse reaction could be neglected. The reactions were effected in benzene and toluene solutions. In these cases the velocity approached a limiting value with increasing concentration of methylantracene; the temperature-coefficient was approximately unity, but with small concentrations of methylantracene it became somewhat larger. It was also found that the amount of dimethyldianthracene formed was proportional to the surface subjected to the light, and inversely proportional to the volume of the solution. The amount of absorption of the chemically active rays effected by the solvents, methylantracene and dimethyldianthracene, were determined, and it was shown that the whole of the active light entering the vessel was absorbed by these substances. The distribution of the absorption among the various constituents of the solution was calculated, and from this the relative velocity of formation of dimethyldianthracene was calculated. The results show that over a range of  $100^{\circ}$  the reaction velocities at a stated concentration of methylantracene are practically identical, so that neither the temperature nor the solvent affects the velocity of this energy-storing photochemical reaction. On the other hand, in all solvents and at all temperatures an approximately equal increase in the reaction velocity was observed with increase in the concentration of the methylantracene. With small concentrations of methylantracene the influence is considerable, whilst with very high concentrations it is hardly noticeable. The thermodynamical significance of these facts is indicated. A specific photochemical polymerisation of anthracene and methylantracene is calculated on the basis of earlier calorimetric determinations, and the following values obtained:  $\phi_A = 6.9 \times 10^{-6}$  mols. per cal.,  $\phi_M = 5.5 \times 10^{-6}$  mols. per cal. A theoretical value for  $\phi$  is calculated for light of wavelength  $\lambda = 400 \mu\mu$  on the basis of Einstein's theory of quanta, and the value  $\phi_{th} = 2.44 \times 10^{-6}$  mols. per cal. obtained. J. F. S.

**Experimental Confirmation of Faraday's Law in Gas Reactions.** M. LE BLANC (*Zeitsch. physikal. Chem.*, 1913, 85, 511—512).—Polemical. The author claims priority over Lind (A.,

1913, ii, 898) for the proof that the chemical change brought about by  $\alpha$ -rays follows the Faraday Law (compare also Bergwitz, A., 1910, ii, 377).  
J. F. S.

**Recombination of Ions made by  $\alpha$ -Rays.** H. OGDEN (*Phil. Mag.*, 1913, [vi], 26, 991—1001).—The hypothesis of columnar ionisation is not capable of explaining the very great differences in initial recombination under  $\alpha$ -ray ionisation displayed by different gases. Some factor not yet considered enters in determining the form of the ionisation-voltage curves. It was noticed that carbon monoxide freshly prepared showed a much less tendency to recombination than after it had been stored for some weeks over water. This suggested that a very small proportion of ions of very small mobility might account for the results, and that the initial recombination in a gas should increase in the extent to which it forms such ions. The nearer the gas is to its boiling point the more does the gas exhibit initial recombination. In the following list the order, which is that of the boiling points, is also the order in which the tendency to recombination increases: hydrogen, carbon monoxide, oxygen, methane, carbon dioxide, ammonia, sulphur dioxide.  
F. S.

**Analysis of the  $\gamma$ -Rays of the Thorium and Actinium Products.** E. RUTHERFORD and H. RICHARDSON (*Phil. Mag.*, 1913, [vi], 26, 937—948. Compare *ibid.*, 25, 722, and A., 1913, ii, 324).—In addition to the known hard type [ $\mu(\text{Al})(\text{cm.})^{-1}=0\cdot096$ ], thorium-*C* and -*D*, deposited on a nickel wire, gives a soft type of  $\gamma$ -rays, comprising 20% of the total, and absorbed completely in 2 mm. of aluminium, but not exponentially. It is probable that, as in the case of radium-*C* deposited on nickel, this soft  $\gamma$ -radiation comes from the nickel under the excitation of the  $\alpha$ - or  $\beta$ -rays, and that thorium-*D* gives only one type of  $\gamma$ -rays. This was confirmed by measurement of the rays from a preparation of thorium-*D* on an aluminium plate, obtained by recoil. With the active deposit of thorium in equilibrium (thorium-*B* + -*C* + -*D*) three new types, due to thorium-*B*, for which  $\mu(\text{Al})(\text{cm.}^{-1})=160, 32, \text{ and } 0\cdot36$  respectively, were obtained. The last probably corresponds with the radiation recently observed by Marsden and Wilson (A., 1913, ii, 907) and Hahn and Meitner (*ibid.*, 906).

For mesothorium-*II* analysis showed the  $\gamma$ -rays to consist of two homogeneous types,  $\mu=26$  and  $0\cdot116$ . The  $\gamma$ -rays from a preparation of actinium-*X* in equilibrium with its products, actinium-*B* + -*C* + -*D*, consists of four types, and from analogy to the thorium series it is probable that the three for which  $\mu=120, 31, \text{ and } 0\cdot46$ , belong to actinium-*B*, and one for which  $\mu=0\cdot198$  belongs to actinium-*D*.

The  $\gamma$ -rays of radioactinium consist of two types, for which  $\mu=25$  and  $0\cdot190$ . In an ordinary electroscope the radioactinium contributes some 25% of the total  $\gamma$ -activity of actinium in equilibrium. The more penetrating type was present in very small quantity, but is the most penetrating of the actinium series.

In general, four types of  $\gamma$ -rays are distinguished: (1) those of the *B*-members,  $\mu$  varying from 120 to 250; (2) a type varying from  $\mu=26$  to 45, which are probably characteristic radiations of the *L* series; (3) a penetrating type from the *B*-members ( $\mu=0.36$  to 0.51); (4) a very penetrating type ( $\mu=0.115$  to 0.198), which are probably characteristic radiations of the *K* series.

Types (1) and (2) are less penetrating than average *X*-rays, although (2) is present in *X*-rays from a platinum anticathode. Type (3) is similar to *X*-rays from a very hard bulb. Type (4) are altogether more penetrating than any *X*-rays. F. S.

**The High-frequency Spectra of the Elements.** H. G. J. MOSELEY (*Phil. Mag.*, 1913, [vi], 26, 1024—1034).—A method for obtaining photographs of *X*-ray spectra is described, which makes the analysis of these rays as simple as that of the rays in the visible spectrum. The element under investigation is excited by a stream of sufficiently fast cathode rays, whereby it emits its characteristic *X*-radiation. A narrow beam of these rays is allowed to fall on the cleavage face of a crystal of potassium ferrocyanide suitably mounted on the prism-table of a spectrometer. The characteristic rays of definite frequency will be reflected only when they strike the surface at certain definite angles, which are afforded by the relation  $n\lambda=2d\sin\theta$ , in which  $\theta$  is the glancing angle of incidence,  $\lambda$  the wave-length of the rays,  $d$  the "grating constant" of the crystal, and  $n$  an integer which determines the "order" of the spectrum. The angle  $\theta$ , at which the characteristic rays are reflected, has been measured in the second and third order spectra given by calcium (scandium), titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc. These elements form an unbroken series, in which the atomic weight increases, except that the positions of cobalt and nickel are reversed.

The spectrum of each element consists of two lines of different intensity, the stronger line being designated by  $\alpha$  and the weaker by  $\beta$ . When other lines were found on the photographs it was possible to refer them to impurities in the metal under examination. The prevalence of these lines due to impurities suggests that the examination of the *X*-ray spectra may prove to be a valuable method of chemical analysis. Its advantage over ordinary spectroscopic methods lies in the simplicity of the spectra and the impossibility of one substance masking the radiation from another.

The spectra of the different elements are very similar. This is shown not only in the relation between the intensities of the two lines, but also by the fact that the ratio of the wave-lengths  $\lambda_\alpha/\lambda_\beta$  remains practically constant throughout the series.

The significance of the *X*-ray spectra is discussed from the point of view of the constitution of the atoms. A table is given in which the values of  $Q=\sqrt{\nu/0.75\nu_0}$  are recorded,  $\nu$  being the frequency of the  $\alpha$  line and  $\nu_0$  the fundamental frequency of ordinary line spectra. The quantity  $Q$  is represented almost exactly by a series of successive integers, beginning with

calcium=19. This is regarded as evidence of the existence in the atom of a fundamental quantity, which increases by perfectly regular steps on passing from one element to the next. This quantity can only be the charge on the positive nucleus, and this has been shown previously by Rutherford to be approximately equal to that of  $A/2$  electrons, where  $A$  is the atomic weight. It thus appears that the quantity referred to above, increases from atom to atom by a single electronic unit, and that its magnitude is represented by the number of the place which the element occupies when the elements are arranged in the usual order indicated by the periodic system. Its value for hydrogen is therefore 1, helium 2, lithium 3, . . . calcium 20, . . . and zinc 30.

From the close similarity between the X-ray spectra of the different elements, it may be inferred that these radiations originate inside the atom, and on that account have no connexion with the complicated light spectra and chemical properties which are determined by the structure of its surface. H. M. D.

[Doppler Spectrum of Hydrogen Canal Rays.] J. STARK (*Ber. Deut. physikal. Ges.*, 1913, 15, 1235—1236).—The interpretation of the Doppler spectrum due to hydrogen canal rays, which was given by the author in a previous paper (*A.*, 1913, ii, 901), has been misunderstood by Gehrcke and Reichenheim (*ibid.*, ii, 1004). Apart from this, the author considers that the three maxima on the intensity distribution curve are due to the singly charged ions represented by  $\text{H}^+$ ,  $\text{H}_2^+$ , and  $\text{H}_3^+$ , and not, as supposed by Gehrcke and Reichenheim, to atom ions carrying respectively three, two, and one unit of charge. H. M. D.

Ionisation of Gases by Collision with Low Electric Forces. F. W. WHEATLEY (*Phil. Mag.*, 1913, [vi], 26, 1034—1043).—Experiments have been made on the ionisation which results from the collision between molecule and ions, the radiation from polonium being used as a source of  $\alpha$ -rays. The results obtained with air indicate that the ionisation produced by the  $\alpha$ -rays is identical with that produced by Röntgen or Becquerel rays or by ultra-violet light.

According to Townsend's theory of ionisation by collision, the current potential curves for different distances between the electrodes do not intersect. On the other hand, the results obtained by Barss (*A.*, 1912, ii, 884) seem to show that these curves cross in the case of vapours at higher pressures. In view of this discrepancy, the author has repeated Barss's experiments with sulphur dioxide, the pressure of the gas, the distances between the electrodes, and the applied potential being the same as those used by Barss. The current potential curves for different distances between the electrodes do not intersect one another, and there is therefore no evidence that the behaviour of sulphur dioxide is at all inconsistent with the theory of ionisation by collision.

H. M. D

**Ionisation by Heated Metals.** HENRI JACQUES PROUMEN (*Bull. Soc. chim. Belg.*, 1913, **27**, 295—300).—In the first series of experiments an internally oxidised brass spiral was heated at 125—130° in an atmosphere of dry, filtered air, and the ionisation determined by means of an electrometer. After seven days, renewed heating produced a second definite ionisation (positive and negative ions). On prolonged heating, the effect disappears, and the tube shows a fatigue which may persist for a long period.

In a second series of experiments, rusty iron nails were used, the flask containing them being heated for three minutes at 135—145°, and the gas then conveyed to the condenser. The ionic content of the gas was found to be very variable, and the effects less marked than when clean iron nails were employed. Similar results were obtained with other metals which had been oxidised or superficially attacked, and the phenomena of ionisation were then observed in cases where the metals themselves only show slight effects. Prolonged or repeated heating causes the metals to become fatigued, and the original properties are only regained after a rest more or less prolonged, according to the metal, the superficial layer, and the heating.

The author is led to attribute these phenomena to the disruption of the surface layers by the escape of the gas occluded in these layers, and especially between them and the metal. Fatigue occurs when the gas has been completely evolved or the surface so broken up that a fresh fracture of it cannot take place. Renewed activity is observed when, for example, the broken surface becomes cemented together by a new layer of oxide, etc. It is not improbable that the effect is also due to the formation of ions during slow oxidation which are occluded between the metal and the layer of oxide and disengaged by heat.

H. W.

**Diffusion and Valency of the Radio-elements.** G. von HEVESY (*Physikal. Zeitsch.*, 1913, **14**, 1202—1209).—The earlier determination of the valency of thorium-*B* and radium-*E* (*A.*, 1913, ii, 174) having given a value one unit too low, the diffusion experiments were repeated. For nearly saturated lead chloride solution in water, the diffusion coefficient corresponded with  $D_{18^\circ} = 1.06(\text{cm.}^2 \text{ day}^{-1})$ , which gives for the valency of the lead ions 1.64, in agreement with the work of Ende that 6.2% of the substance is undissociated, 43.7% of the lead is present as  $\text{PbCl}^+$ , and 50.1% as  $\text{Pb}^{++}$ . For thorium-*B* in presence of lead chloride,  $D_{18^\circ} = 1.07$ ; in absence of lead,  $D_{18^\circ} = 0.67$ . The latter corresponds with a bivalent ion, in agreement with Fleck's conclusion that it is non-separable from lead. The earlier value found was that of the (thorium-*B*) $\text{Cl}^+$  ion. For radium-*E*, convection was prevented by adding 5% of alcohol to the upper layer, and the diffusion constant compared with that for radium-*D* under similar conditions. For radium-*E*,  $D_{18^\circ} = 0.38$ , and for radium-*D*, 0.56, the effect of the alcohol being a reduction of the value in the latter case by 16%. The corrected value 0.45 for radium-*E* corresponds with a trivalent ion, in agreement with its chemical non-separability from bismuth.

The results for actinium, the measurements being taken immediately after the completion of the experiments, gave  $D_{18} = 0.69$ ; corresponding with the bivalent actinium- $X$ , and after six months  $D_{18} = 0.47$ , corresponding with tervalent actinium. In this case the method of determining the valency, by finding the common element with which the radio-element is identical in chemical properties, fails, but the result confirms the opinion that actinium is the missing homologue of lanthanum.

[With F. PANETH.]—The diffusion coefficients of polonium and thorium- $B$  in ammonia solution gave values for the diffusion coefficients in agreement with the view that the substances are present as colloids. Polonium in  $N/2$ -ammonia gave  $D_{18} = 0.19$ , corresponding with eight atoms, and thorium- $B$  in  $N/12$ -ammonia,  $D_{18} = 0.37$ , corresponding with two atoms to the molecule. In neutral aqueous solution, thorium- $B$  behaves as if largely present in the colloidal state, whereas polonium, which in alkaline solution is largely colloidal, and in acid solution is electrolytic, is in neutral and feebly acid solution still largely present in the electrolytic condition. Radium- $E$  is intermediate between polonium and radium- $D$  (or thorium- $B$ ) and in neutral solution is largely colloidal.

The question of the possibility of separating, by diffusion, the members of a chemically non-separable group of elements is discussed theoretically, and it is shown that in liquids any separation would be improbable, whereas in gases, in accord with Graham's law, a 1% difference of atomic mass will give rise to a 0.5% difference of diffusion coefficient.

F. S.

**The Disintegration Constant of Actinium- $X$ .** HERBERT N. MCCOY and EDWIN D. LEMAN (*Physikal. Zeitsch.*, 1913, **14**, 1280—1282).—Radioactinium was freed from actinium by adding a trace of thorium and precipitating the latter repeatedly with hydrogen peroxide. After some days' accumulation of actinium- $X$ , the peroxide precipitation was repeated, leaving the actinium- $X$  in the filtrate. This was purified from radioactinium by further additions of thorium and precipitations with peroxide, and was finally prepared by precipitating with barium sulphate. The decay of the activity was measured by the  $\alpha$ -rays, and the mean value found was  $\lambda(\text{day})^{-1} = 0.0611$ , which corresponds with the half-period of 11.35 days. This is near the value, 11.6 days, recently found by Hahn and Rothenbach (*A.*, 1913, ii, 463), and differs considerably from the earlier value, 10.2 days.

F. S.

**The Existence of Uranium- $Y$ .** G. N. ANTONOV (*Phil. Mag.*, 1913, [vi], **26**, 1058).—Uranium- $Y$  has been separated from some of the pure uranyl nitrate, lent by Soddy, with which Fleck was unable to obtain the results (*A.*, 1913, ii, 464). The activity of uranium- $Y$  must be more than 2% of that of uranium- $X$ , when the most penetrating rays of the former are compared with those of the latter, and this ratio is of the expected order of magnitude if the actinium series branches off at uranium- $Y$ .

F. S.

**Fractional Adsorption and Fractional De-adsorption of Radium-Barium Salts by Colloidal Manganese Perhydroxide.** E. EBELER and W. BENDER (*Zeitsch. anorg. Chem.*, 1913, 84, 77—91).—The use of colloidal silica for the adsorption of radium salts (Ebeler and Fellner, A., 1911, ii, 957) presents experimental difficulties. Better results are obtained with hydrated manganese dioxide, and special care in the preparation of the gel is not necessary. The precipitate is best obtained from potassium permanganate and manganous sulphate, and washed until free from acid. Shaking for an hour with the barium-radium solution at the ordinary temperature is sufficient for equilibrium. The precipitate may also be produced in presence of the active solution. The manganese precipitate always contains relatively more radium than the original solution of radium and barium salts. The extent of the concentration varies with the quantity of precipitate used. With 20 mols.  $\text{MnO}_2$  to 1 mol. of the mixed salts, the adsorption of radium is complete. The presence of a large excess of a neutral salt is favourable. De-adsorption is brought about by dissolving in hydrochloric acid and passing hydrogen chloride, when radium is selectively precipitated, or an electro-cataphoretic method may be used (compare A., 1913, ii, 659). An apparatus for this purpose is described. C. H. D.

**The Decomposition of Hydrogen Sulphide by the Radiation of Emanation.** EUG. WOURTZEL (*Compt. rend.*, 1913, 157, 929—931).—A quantitative study of the decomposition of hydrogen sulphide by radium emanation. The author has determined the amount of gas decomposed by a unit of radiant energy, absorbed under definite conditions, and has studied the variation of this constant with temperature and pressure. The ratio of the amount of hydrogen formed to the amount of radiation destroyed diminishes as the experiment proceeds owing to diminution in pressure caused by decomposition of the hydrogen sulphide. In the several experiments performed under like conditions, the calculated amount of hydrogen formed, corresponding with the total destruction of the emanation and complete use of its radiation, was constant. The velocity of decomposition diminishes with the temperature. The author calculates that the number of molecules of hydrogen sulphide decomposed by the radiation from the emanation exceeds 3·3 times the number of ions produced in air under the same conditions. The relative amounts of water and hydrogen sulphide decomposed by a given amount of radiation are as 1:4·7, expressed as gram-molecules. W. G.

**A Method for the Determination of the Molecular Weights of the Radioactive Emanations with Application to Actinium Emanation.** E. MARSDEN and A. B. WOOD (*Phil. Mag.*, 1913, [vi], 26, 948—952).—The method, due to Bohr, consists in allowing actinium emanation supplied at a constant rate from an actinium preparation in one vessel to diffuse through a hole in the wall into a second similar vessel in a free-path vacuum, equilibrium being

arrived at when as many molecules of emanation pass through the hole as decay in the second vessel. This condition leads to the relation:  $M = [3636 \cdot 5(N_1/N_2 - 1)(A/V_2\lambda)]^2\theta$ , where  $M$  is the molecular weight of the emanation,  $N_1/N_2$  the ratio of the number of emanation molecules in the two chambers, found by comparing the ratio of the active deposits in the two chambers after equilibrium is attained,  $A$  is the area of the hole,  $V_2$  the volume of the second chamber,  $\lambda$  the disintegration constant of the emanation, and  $\theta$  the absolute temperature. With a hole  $1 \cdot 022 \text{ mm.}^2$  area,  $M$  was found to be 236, and with one  $0 \cdot 4075 \text{ mm.}^2$  area,  $M$  was 228. The difference is well within the error of measurement. The chief uncertainty is in  $\lambda$ , which enters into the expression as the second power. The mean value 232 would make the atomic weight of actinium itself 240, or slightly greater than that of uranium.

F. S.

**Colloidal Solutions of Radioactive Substances. II.** FRITZ PANETH (*Kolloid Zeitsch.*, 1913, 13, 297—305).—Previous observations (A., 1913, ii, 747) on the dialysis of solutions of certain radioactive substances have shown that the degree of dispersity of the radioactive substance depends on whether the solution is acid, neutral, or alkaline. These observations have now been extended to other substances and combined with measurements of the rate of diffusion and observations relating to the direction in which the colloidal particles move in an electric field.

All the radioactive substances behave normally on dialysis in acid solution, but the velocity of dialysis is found to be greatly reduced in the case of neutral solutions of polonium and radium-*E* and of ammoniacal solutions of thorium-*B*. In agreement with this, it was found that the coefficient of diffusion of polonium, radium-*E* and thorium-*B* is much smaller in ammoniacal as compared with the value for acid solution.

Under the influence of an electric field, polonium and thorium-*B* move towards the cathode in an acid solution, whilst the direction of migration is reversed in an ammoniacal solution. Radium and thorium-*X* move towards the cathode in both acid and ammoniacal solutions. The retardation of the particles, which is observed when a parchment membrane is interposed between the electrodes, is found to be much more pronounced in the case of the particles which migrate towards the anode.

The observations seem to show that some of the radioactive elements assume the colloidal form under certain conditions. Polonium and radium-*E* give rise to these particles in neutral solution, thorium-*B* and radium-*D* in ammoniacal solution, whilst radium and thorium-*X* do not assume this form either in neutral or in alkaline solution.

In an appendix, attention is drawn to the fact that the solutions are of such extreme dilution that there can be no question of saturation with respect to a solid. It has been suggested that the observed phenomena are not due to colloidal particles of the radioactive substances, but that the particles consist of inactive sub-



stances, such as silicic acid or aluminium hydroxide, by which the radioactive substances have been adsorbed. H. M. D.

**Conductivity and Viscosity of Solutions of Rubidium Salts in Mixtures of Acetone and Water.** P. B. DAVIS, H. HUGHES, and HARRY C. JONES (*Zeitsch. physikal. Chem.*, 1913, **85**, 513—552. Compare A., 1911, ii, 863; 1912, ii, 1124).—The electrical conductivity and viscosity of solutions of various strengths of the chloride, bromide, iodide, and nitrate of rubidium have been determined in solutions of acetone and water. The solutions varied from those containing 75% to those containing 12.5% of acetone, and the measurements were carried out at 15°, 25°, 35°, and 45°. Measurements were also carried out with the mixed solvents, and in all cases the temperature-coefficients were calculated. It is shown that rubidium salts increase the viscosity of all solutions which contain a large percentage of acetone. The fluidity curve of all solutions cuts the fluidity curve of the mixed solvents in the region of the 50% mixture. Negative viscosity-coefficients, where they were found, were always much smaller than in the corresponding glycerol-water solutions. The temperature-coefficients of the fluidity of acetone-water mixtures were very small, and decrease with increasing temperature. The greatest temperature-coefficient lies in the region of 50% acetone-water mixture. The minima of the conductivity curves for rubidium salts correspond with a higher percentage of acetone in the acetone-water mixture than those in the fluidity curves, whereas the curves for other salts run parallel. A comparison of the temperature-coefficients of the conductivity and the fluidity shows these are as would be expected from a non-solvate forming salt in a mixture of associated solvents.

J. F. S.

**Electrical Conductivity of Solutions of Certain Acetates in Acetic Acid.** K. HOPFGARTNER (*Monatsh.*, 1913, **34**, 1313—1326. Compare A., 1912, ii, 320).—Measurements have been made of the electrical conductivity of solutions of rubidium, silver, glucinum, calcium, and barium acetates in acetic acid at 18°, 25°, 30°, and 40°. Owing to the smaller solubility of the silver, glucinum, and calcium salts, the conductivity could only be examined over a relatively small range of concentration, but measurements were made for the rubidium salts from  $v=60$  to  $v=0.55$ , and for the barium salt from  $v=587$  to  $v=0.46$ . For both these salts, the equivalent conductivity concentration curve exhibits a maximum and a minimum within the range of concentrations examined. These salts behave therefore quite similarly to the potassium, sodium, and lithium salts investigated in the previous paper (*loc. cit.*).

In both the alkali metal and alkaline earth metal groups, the conductivity of equivalent solutions of the acetates increases with the atomic weight of the metal. The difference between the maximum and minimum conductivities also increases with the atomic weight in the case of the alkali metals. For both rubidium and barium acetate solutions the temperature-coefficient of the

conductivity exhibits a minimum at the concentration which corresponds with maximum conductivity. A similar result was previously found in the case of the potassium, sodium, and lithium salts.

H. M. D.

**Electrical Conductivity in Hydrocarbons and their Halogenated Derivatives, and in Esters and Bases as Solvents.** I. P. WALDEN (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 907—936).—The author gives a summary of the investigations published on the conductivity of solutions in the so-called non-ionising solvents, the contradictory results obtained by different authors being explained as due to the use of different solutes, dilutions, and temperatures. The results of his own measurements on solutions of various tetralkylammonium salts in a number of different solvents are briefly as follows.

In chloroform all the salts exhibit similar behaviour, the conductivity showing a maximum for high concentrations ( $V=1-1.5$ ), and a minimum for high dilutions ( $V=300-450$ ); in the latter case,  $\lambda_v$  increases with the magnitude of the cation, and, with the same cation, it increases in the series, chloride, bromide, nitrate, iodide.

In dichloromethane, seven tetra-alkylammonium salts were examined, and in all cases the molar conductivity attained a minimum at  $V=50-60$ . With tetrapropylammonium iodide, a maximum value was observed for  $V=\text{about } 3$ . Distinct differences are found in the values of  $\lambda_v$  for the different salts. For similar dilutions ( $V=20, 100, \text{ or } 500$ ), the conductivity increases in the series, chloride, bromide, nitrate, iodide, the cation being  $\text{NEt}_4$  in all cases. Further, with salts containing the same anion, the conductivity and hence the apparent velocity of migration of the cation increase with the complexity of the latter; this result is the opposite of those obtained with solvents having high ionising capacities. Apparently the tendency of the salts to ionise diminishes from iodide to chloride, whilst, in general, the capacity for forming complexes and solvates increases in passing from the chlorides to the bromides to the iodides.

Solutions of tetra*iso*amylammonium iodide and of tri*iso*amylamine thiocyanate in carbon tetrachloride exhibit measurable conductivity, but the values of  $\lambda_v$  are abnormally small, and diminish with increase of the dilution, slowly with the former, and very rapidly with the latter salt.

Comparison of the results obtained with solutions of tetra*iso*amylammonium iodide in di-, tri-, and tetra-chloromethane shows (1) that the value of  $\lambda_v$  increases as the dielectric constant of the solvent increases, and as its viscosity decreases, and (2) that the diminution of the value of  $\lambda_v$  with increased dilution is small with solvents having high dielectric powers, and large when the latter are smaller.

The molar conductivity of tetra*iso*amylammonium iodide in methyl iodide is small, and passes through a distinct minimum for  $V=150-200$ .

The value of  $\lambda_v$  for a solution of tri*iso*amylammonium thiocyanate

in carbon disulphide falls in the ratio of 100:1 on increasing  $V$  from 1 to 18.

Solutions in ethyl bromide show a minimum conductivity at certain dilutions, and the same is the case with some salts in *s*-dichloroethane.

Solutions in *s*-tetrachloroethane, *s*-tetrabromoethane, *n*-propyl chloride, allyl chloride, benzene, toluene, and benzyl chloride have also been investigated, with results similar to those described above.

T. H. P.

### Potential Drop on the Surface between Liquid and Gas.

LADISLAUS VON PUTNOKY (*Zeitsch. Elektrochem.*, 1913, **19**, 920—923).—It is shown theoretically that the potential drop at the surface of contact of a gas and a liquid can be calculated from the velocity at which a gas rises in a liquid, if the velocity is measured in the absence and in the presence of an electrical field. The author makes use of the expression  $\epsilon = \Delta n/n \cdot n' \times 4\pi\eta_r c/HD$ , which he deduces, for calculation of the potential drop;  $\epsilon$  is the contact potential,  $n$  the time required for a bubble of radius  $r$  to rise through a length  $c$  when no electrical field is operative,  $n'$  the time when an electrical field is operative,  $\eta_r$  the viscosity of the liquid,  $D$  the dielectric constant of the liquid, and  $H$  the strength of the electrical field. Experiments are described on the velocity of air through conductivity water, and through water saturated with camphor. The values obtained for  $\epsilon$  are  $0.06 \pm 0.019$  volt and  $0.07 \pm 0.023$  volt. These results are not regarded as accurate, but serve to show the existence of a contact potential between gas and liquid. The author considers that there is an error of about 33% attached to the figures.

J. F. S.

**Couples Formed by Flames.** G. MOREAU (*Compt. rend.*, 1913, **157**, 922—924).—A simple electric couple is obtained by inserting in a Bunsen flame a clean platinum wire and one coated with an alkali salt or an oxide of one of the alkaline earths. On joining these a current of the order of 1/10th microampere is set up, passing through the flame from the coated to the clean platinum electrode. With the electrodes at 1400° absolute, the following values were obtained for the *E.M.F.* of the couple:

Electrode coated with	CaO.	BaO.	SrO.	K <sub>2</sub> CO <sub>3</sub> .	Na <sub>2</sub> CO <sub>3</sub> .	RbCl.
<i>E.M.F.</i> in volts ... ..	0.55	0.70	0.54	0.68	0.69	0.56

The *E.M.F.* is increased by cooling the clean electrode, rising in the case of CaO to 1.16 volts. The introduction of different alkali salts as vapour into the flame causes a diminution in the *E.M.F.*, varying with the nature of the salt used.

W. G.

**Couples with Two Flames.** G. MOREAU (*Compt. rend.*, 1913, **157**, 1070—1072. Compare preceding abstract).—An electric couple is produced by means of two Bunsen flames burning vertically in contact, one being charged with saline vapour, and there being inserted in each a platinum electrode either pure or coated with

the oxide of an alkaline-earth metal. In the case where both electrodes are coated and one flame is charged with vapour, on joining the electrodes a current is set up which transports the negative ions from the concentrated to the dilute flames. It increases with the concentration, and the values obtained for the *E.M.F.* agree closely with those calculated by Nernst's formula:  $E = 0.173 \log n_1/n_2$  volts.

A mixed series is similarly obtainable, one electrode being coated, the other clean, and one flame charged with vapour, the other not. The resulting *E.M.F.* is greater when the clean electrode is in the flame charged with vapour, and the coated electrode in the pure flame, than when the positions are reversed. W. G.

**The Relationship of the Electromotive Force of the Lead Accumulator to Temperature and Acid Density.** R. THIBAUT (*Zeitsch. Elektrochem.*, 1913, 19, 881—885).—The electromotive force of small lead accumulators has been determined at temperatures from 13° to 49°, and with acid concentrations varying from 0.2 to 5.03 mols. per litre. It is shown that if the curve representing the dependence of the temperature-coefficient of the *E.M.F.* on the acid density is compared with the curve previously given by Dolezalek, and also with the curve obtained from the heat of reaction by calculation, it is seen that the latter curve runs parallel with the curve experimentally determined, whilst the steep portion of Dolezalek's curve is not found in the experimental curve. J. F. S.

**Valve Action of Zirconium Anodes.** L. H. WALTER (*The Electrician*, 1913, Oct. 3).—Zirconium anodes have been prepared from small zirconium crystals by binding thin copper wire round one end of the crystal, and then embedding the whole in Chatterton cement so that a surface of 3 mm. by 2 mm. of zirconium was left exposed. Using these electrodes as anodes, it is shown that the ratio of the resistance in the effective direction to that in the non-effective direction is of the order  $10^6$ . A series of measurements of the leakage current at various potentials is given for solutions of 3% sulphuric acid, sodium tungstate, lithium citrate, ammonium borate, potassium dichromate, and sodium carbonate. In the case of sulphuric acid, the valve action breaks down at about 105 volts, whilst in other solutions a higher potential can be applied without destroying the valve action. Zirconium is the only metal of the fourth group of the periodic system which has been shown to exert a valve action. J. F. S.

**Connexion between Electrolytic and Chemical Processes.** II. D. REICHSTEIN (*Zeitsch. Elektrochem.*, 1913, 19, 914—920).—Compare A., 1913, ii, 843).—The processes occurring at the surface of contact of an electrode and an electrolyte are considered theoretically. The older theory postulates the existence on this surface of a metal-gas alloy, the chief characteristic of which is that a condition of equilibrium always exists, even whilst current is passing, between the electrode and the alloy. The author as a

result of the present consideration draws the conclusion that this theory must be changed in the sense that the equilibrium is disturbed during the passage of current. The important process, which is connected with the chemical inertia and is determinative of the polarisation relationships, on the present theory occurs between the constituents of the hypothetical alloy. The theory also demands a constant sum of the constituents of the alloy, and allows of the mechanism of a number of processes being described, chief among which is the passive condition of metals. J. F. S.

**The Magnetisation of Nitric Oxide and Magneton.** PIERRE WEISS and AUGUSTE PICCARD (*Compt. rend.*, 1913, **157**, 916—918).—The authors have determined the coefficient of magnetisation of nitric oxide by the method employed for oxygen (compare A., 1913, ii, 17), finding the value  $\chi_m = 1400.3 \times 10^{-6}$ . The correction for dimagnetism as deduced from the values obtained by Pascal for the other oxides of nitrogen is  $10.1 \times 10^{-6}$ . These results give 9039 magnetons per molecule. W. G.

**Magnetic Susceptibility of Paramagnetic Salts in Solution.** ADOLF HEYDWEILLER (*Ber. Deut. physik. Ges.*, 1913, **15**, 1120—1122).—From observations on the influence of concentration on the magnetic susceptibility of ferric chloride, manganous sulphate and nitrate, chromic sulphate and nitrate, and cobalt nitrate in aqueous solution, it is found that the molecular magnetic susceptibility shows a maximum value at a particular concentration which depends on the nature of the dissolved salt. In the case of ferric chloride and the two manganous salts, a minimum is also exhibited at smaller concentrations.

It is suggested that the magnetic susceptibility decreases with a diminution in the degree of ionisation, and that the increase which is observed as the concentration of the solution increases is due to the formation of magnetic chains of molecules. The subsequent decrease in the magnetic susceptibility when the concentration is further increased is attributed to the formation of astatic ring groupings of the molecules. H. M. D.

**The Magneto-chemistry of Iron Compounds. II.** B. CABRERA and E. MOLES (*Arch. Sci. phys. nat.*, 1913, [iv], **36**, 502—518; *Anal. Fis. Quim.*, 1913, **11**, 398—419).—The authors have improved the apparatus previously used by them for determining the magnetic susceptibility of solutions (compare A., 1913, ii, 553).

In the case of aqueous solutions of ferric sulphate, the number of magnetons tends to approach the value 27 for the most concentrated solutions. In the presence of increasing quantities of sulphuric acid, whereby the hydrolysis is diminished, the number of magnetons approaches the value 29, in agreement with the result previously found (*loc. cit.*), namely, that hydron tends to restore the molecule to its original condition, the number of magnetons approaching 29.

The magnetic susceptibility of solutions of potassium ferricyanide is practically independent of the dilution.

Experiments with  $M/10$ -,  $M/20$ -, and  $M/40$ -solutions of ferric chloride showed that the susceptibility diminished after heating for fifteen minutes at  $80^\circ$ . The diminution was the greater the diluter the solution, in agreement with the fact that the hydrolysis increases with the dilution.

T. S. P.

**The Magnetisability of Titanium Compounds.** E. WEDEKIND and P. HAUSKNECHT (*Ber.*, 1913, **46**, 3763—3768).—Measurements with the following compounds of titanium: titanium dioxide and disulphide, the sulphide,  $Ti_2S_3$ , titanous sulphide,  $TiS$ , the oxide,  $Ti_3O_5$ , showed that the magnetic susceptibility increases as the valency of the titanium diminishes (compare Wedekind and Horst, A., 1912, ii, 228). Titanium peroxide,  $TiO_3 \cdot 3H_2O$ , is feebly diamagnetic.

Comparison with the compounds of manganese, chromium, and vanadium shows that the susceptibility decreases with decreasing atomic weight, reaching its lowest value in the compounds of titanium.

The oxide,  $Ti_3O_5$ , was obtained by heating the dioxide at  $1250^\circ$  for eighteen hours in a current of oxygen and nitrogen-free hydrogen. It has, with the exception of the density, the same properties as the oxide,  $Ti_7O_{12}$ , obtained by Ruff, Seiferheld, and Suda (A., 1913, ii, 960).

T. S. P.

**Mendeléev's Equation on the Thermal Expansion of Liquids.** W. HERZ (*Zeitsch. physikal. Chem.*, 1913, **85**, 632—638).—A theoretical paper. The Mendeléev equation has been examined for thirty-two organic liquids, including aliphatic acids, paraffins, alcohols, nitriles, and paraffin haloids. It is shown that the equation  $V_t = V_0 / (1 - Kt)$ , in which  $V_t$  and  $V_0$  are the volumes at  $t^\circ$  and  $0^\circ$ , and  $K$  is a constant, holds to within 4.5% at temperatures up to the boiling point. A number of regularities in the value of  $K$  are observed: (1) In homologous series the value of  $K$  decreases with increasing carbon content. (2) In analogous chlorine derivatives the value of  $K$  decreases with increasing chlorine content. (3) *iso*-Compounds have a larger  $K$  value than the corresponding normal compounds. (4) Geometric isomerides have different  $K$  values. (5) The halogen derivatives of benzene have smaller values for  $K$  than benzene itself, the value being smaller the higher the atomic weight of the substituting halogen atom. It is shown also that the  $K$  value for the halogens themselves decreases with increasing atomic weight.

J. F. S.

**An Improved Thermoregulator.** WM. MANSFIELD CLARK (*J. Amer. Chem. Soc.*, 1913, **35**, 1889—1891).—The sensitiveness of a mercury thermoregulator, operated electrically, is seriously affected by the adherence of mercury to clean platinum. When this occurs, the breaking of the circuit takes place at an appreciably lower temperature than the "make." By substituting a nickel or

nichrome wire for platinum, the making and breaking of the circuit may be made to occur at temperatures much closer to one another.

The preservation of a clean mercury surface at the contact is aided by first removing oxidisable metals from the mercury by distilling it according to Hulett's method; also by protecting the surface of the mercury with hydrogen, and a method by which this may be done is given.

T. S. P.

**Dependence of the Specific Heat and of the Melting Point of Certain Alloys on the Previous Thermal Treatment and its Connexion with the Magnetic Properties in the Case of Heusler's Alloys.** ERNST DIPPEL (*Ann. Physik*, 1913, [iv], 42, 889—902).—According to Richter's measurements (*A.*, 1913, ii, 184) of the specific heats of bismuth-lead alloys, a minimum is exhibited by the alloy which contains 93% of lead. It was also found that the specific heat of this alloy varies to some extent with the previous thermal treatment. The further investigation of this has shown that when the alloy is heated just above its melting point and rapidly cooled, its specific heat is greater than when the alloy is heated to a much higher temperature and allowed to cool slowly. If the rapidly cooled alloy of high specific heat is heated for about twenty-four hours, at the temperature of boiling xylene, the specific heat diminishes to a measurable extent. From cooling-curve observations it has been found that this change in the specific heat is accompanied by a lowering of the melting point.

Similar changes in the specific heat with the rate of cooling have been found in the case of a Heusler's alloy containing 14.25% of manganese and 10.15% of aluminium, the remainder consisting of copper except for traces of iron. These changes in the specific heat appear to run parallel with previously observed variations in the magnetic properties of the alloy.

It is supposed that the observed changes in the specific heat, melting point, and magnetic properties are dependent on the formation of larger molecular aggregates during the slow cooling of the alloys. In the case of the rapidly cooled alloys, little opportunity is afforded for the process to take place. With regard to the magnetic properties, it would appear that the formation of elementary magnets is also of influence.

H. M. D.

**Aluminium Bromide as a Solvent in Cryoscopy.** W. A. ISBEKOV (*Zeitsch. anorg. Chem.*, 1913, 84, 24—30. Compare *A.*, 1911, ii, 493).—The value 268 is found for the cryoscopic constant of aluminium bromide (compare Kablukov, *A.*, 1908, ii, 499). Non-electrolytes have a normal molecular weight in this solvent. Antimony and bismuth bromides form solid solutions with aluminium bromide. Electrolytes are associated in solution, and only the complex molecules are ionised. Zinc bromide gives a high conductivity with normal molecular weight, which may be accounted for by complete dissociation of the double molecules into ions.

C. H. D.

**Vapour Pressures of Hydrogen from the Boiling Point down to near the Triple Point.** H. KAMERLINGH ONNES and W. H. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 440—445).—The vapour pressure of liquid hydrogen has been measured at a series of temperatures between  $-252.63^{\circ}$  and  $-258.31^{\circ}$ . The pressures corresponding with these extreme temperatures are 789.1 and 86.0 mm. respectively. The experimental data are satisfactorily represented by the formula:

$$\log p = 4.6063 - 58.40/T + 61/T^2.$$

According to this formula, the boiling point of hydrogen is  $-252.76^{\circ}$ . The triple-point temperature was found to be  $-259.14^{\circ}$ , and by extrapolation the above formula gives 54.1 mm. for the pressure at the triple point. If the temperature-coefficient of the vapour pressure is employed in calculating the latent heat of vaporisation, the value obtained for a pressure of 751.5 mm. is  $\lambda = 105.5$  cal. This is somewhat smaller than the value (110.9 cal.) found by experiment. H. M. D.

**The Vapour Tension of Hydrogen Chloride.** E. CARDOSO and A. F. O. GERMANN (*J. Chim. Phys.*, 1913, 11, 632—637).—The vapour tension of hydrogen chloride has been determined from the critical temperature  $51.4^{\circ}$  down to  $-24.4^{\circ}$ . The method employed was similar to that used for the determination of the critical constants of this substance (A., 1913, ii, 111). As heating liquids, acetone was used for temperatures between  $51.4^{\circ}$  and  $35^{\circ}$ , between  $35^{\circ}$  and  $0^{\circ}$  a glycerol-water mixture, and between  $0^{\circ}$  and  $-24.4^{\circ}$ , alcohol to which solid carbon dioxide was added. The vapour pressures can be expressed by means of the formula  $p = ae^{bt+ct^2}$ , which, with the constants evaluated, has the form:

$\log p = 1.152048 + 0.010312(t - 10.2) - 0.000019989(t - 10.2)^2$ , and holds between  $10^{\circ}$  and  $51.4^{\circ}$ ; with other constants the formula holds between  $-24.2^{\circ}$  and  $10^{\circ}$ , and then has the form:

$$\log p = 1.10106 + 0.013277(t + 24.2) - 0.000039978(t + 24.2)^2.$$

The difference between the values calculated on the basis of these formulæ and the experimental values is very slight, never amounting to as much as the error of observation. J. F. S.

**Vapour Pressures at Very Low Reduced Temperatures. II. The Vapour Pressure of Carbon Dioxide in the Range from  $-140^{\circ}$  to about  $-160^{\circ}$ .** SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 445—454. Compare A., 1913, ii, 1023).—The hot wire manometer, described in a previous paper, has been used in the measurement of the vapour pressure of carbon dioxide at temperatures ranging from  $-134.67^{\circ}$  to  $-168.83^{\circ}$ . Over this interval, the pressure, corrected for the thermal molecular effect, falls from 1430.5 to 0.802 baryes. The observations are in agreement with the values given by the Nernst formula:  $\log p$  (in atmospheres)  $= -6000/4.571T + 1.75 \log T - 0.00913T/4.571 + 3.1700$ . It is improbable that this formula will represent the experimental data at temperatures higher than that for which pressures are recorded in the present paper. H. M. D.



**Isothermals of Monatomic Substances and their Binary Mixtures. XV. The Vapour Pressure of Solid and Liquid Argon from the Critical Point down to  $-206^{\circ}$ .** C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 477—485. Compare A., 1913, ii, 474).—A table is given in which the vapour pressures of liquid argon are recorded from the triple point ( $-189.30^{\circ}$ ) to the critical point ( $-122.44^{\circ}$ ) and of solid argon from  $-206^{\circ}$  to the triple point. In the case of liquid argon the observations can be more accurately represented by Rankine and Bose's formula than by that of Nernst. The formula  $\log p = a + bT^{-1} + cT^{-2} + dT^{-3}$ , in which  $a = +4.85033$ ,  $b = -634.391$ ,  $c = +30769.09$ , and  $d = -1076464$ , yields pressure values which are in good agreement with the experimental numbers.

For solid argon, Nernst's formula gives a better result, and the observations can be expressed by the formula  $\log p = A/T + BT + D \log T + C$ , in which  $A = +9034.32$ ,  $B = -1.42112$ ,  $C = -1014.0278$ , and  $D = +533.0275$ .

From Clausius's equation the author has calculated the molecular heat of vaporisation of liquid argon at a series of temperatures. The molecular latent heat increases from 12.92 at  $-125.49^{\circ}$  to 24.01 and  $-140.80^{\circ}$  and 35.00 cal. at  $-183.06^{\circ}$ . H. M. D.

**Experimental Determination and Theoretical Calculation of Small Vapour Pressures at Low Temperatures.** CURT FERDINAND MÜNDEL (*Zeitsch. physikal. Chem.*, 1913, 85, 435—467).—The vapour pressures of chlorobenzene, bromobenzene, iodobenzene, benzene, *n*-hexane, *n*-heptane, *n*-octane, stannic chloride, carbon tetrachloride, acetic acid, ethyl ether, methyl alcohol, ethyl alcohol, and propyl alcohol have been determined at low temperatures; measurements were also made with solid ammonia and nitric oxide. The present measurements were made by means of a differential mercury manometer, which is described in the paper; the temperature measurements were made by means of a platinum resistance thermometer. The temperatures between  $-10^{\circ}$  and  $-80^{\circ}$  were obtained by means of ether and solid carbon dioxide,  $-60^{\circ}$  and  $-130^{\circ}$  by light petroleum cooled by liquid air,  $-187^{\circ}$  and  $-199^{\circ}$  by liquid air, and  $-252^{\circ}$  by liquid hydrogen. The results generally are in accord with the demands of the Nernst vapour pressure formula. The constants of the Nernst formula as determined in the present work were used to calculate the vapour pressures at higher temperatures, and the values obtained are shown to agree very satisfactorily with the experimental values of Sidney Young. J. F. S.

**A Simple Still-head.** W. PLÜCKER (*Chem. Zeit.*, 1913, 37, 1441).—The still-head is similar in arrangement to a reflux double-surface condenser, the prolongation of the inner tube at the top, however, being fitted with a side-tube. The vapour space in the still-head is filled with glass-heads; the double-jacket round this vapour space is filled with a liquid which has the same boiling

point as the distillate to be collected, the jacket being connected with a reflux condenser.

With this apparatus a 14.48% (vol.) alcohol gave 93.23% alcohol in one distillation. T. S. P.

**Calculation of the Molecular Heats of Metallic Sulphides and of the Electrochemical Potential of Sulphur.** L. ROLLA (*Gazzetta*, 1913, 43, ii, 545—555).—In view of the complexity of the sulphur molecule, the Nernst-Lindemann formula is insufficient for the exact calculation of the specific heat of this element at constant volume. But the formula,  $v = 2.8 \cdot 10^{12} \sqrt{T_f/mV^{2/3}}$ , in which  $v$  is the atomic vibration frequency at the melting point,  $T_f$  the absolute melting point,  $m$  the atomic weight, and  $V$  the atomic volume, gives  $\beta v = 430$ , and introduction of this value into the Nernst-Lindemann expression gives approximately the atomic heats of rhombic sulphur at constant volume over a moderately wide interval of temperature.

In the case of the oxides studied by Russell (A., 1912, ii, 232), the formula  $v^1/v = \sqrt{T_f/T'}$ , in which  $v^1$  represents the atomic vibration frequency of the element in combination, and  $T'$  the absolute melting point of the compound, answers sufficiently well. But to three of the sulphides it cannot be extended, since cupric sulphide yields sulphur and cuprous sulphide when heated at the ordinary pressure, whilst cadmium and mercuric sulphides sublime without melting. The author has determined the specific heats of silver and lead sulphides at various temperatures with a view to ascertaining with what degree of approximation it is possible to measure the affinity between sulphur and lead or silver as a function of the atomic weights, densities, and melting points, and of the thermal changes of the reactions  $\text{Pb(or } 2\text{Ag)} + \text{S} = \text{PbS(or } \text{Ag}_2\text{S)}$ . The experimental numbers are found to be in good agreement with the molecular heats calculated by means of the expression  $\sum_{v=n}^{\nu=1} f(\beta v)$ , where  $n$  is the number of atoms in the molecule (see also Debye, A., 1912, ii, 1134). For  $U - A$ , where  $U$  is the thermal change and  $A$  the affinity, the value 1610.66 cal. per gram-equivalent at 18° is found for  $\text{Pb} + \text{S} = \text{PbS}$  and 521.26 cal. for  $\text{Ag}_2 + \text{S} = \text{Ag}_2\text{S}$ .

The values of the affinity thus obtained indicate that the value found by Lucas (A., 1904, ii, 715) and by Bruner and Zawadski (A., 1910, ii, 945) for the potential of sulphur against the hydrogen electrode should be modified to +0.575. Assuming the accuracy of this number, the solubility product for fused lead sulphide is calculated to be  $6.7 \cdot 10^{-30}$ . Calculation by means of this value, on the basis of Nernst's osmotic theory, indicates that the electromotive force of the cell, lead|saturated solution of lead sulphide in decinormal sodium hydrogen sulphide|normal electrode, should be 1.089 volt. Experimental determination of this magnitude by a method substantially that used by Immerwahr (A., 1901, ii, 301) gives at 18° the value 0.816 volt, which is in marked agreement with the value obtained by Immerwahr for amorphous lead sulphide under slightly different conditions, its divergence from the theoretic-

cal value being explainable by the uncertainty regarding the hydrolysis of sodium hydrogen sulphide, and by the paucity of our knowledge of the dissociation of lead salts. T. H. P.

**Thermochemistry of Acetylenic Compounds.** CHARLES MOUREU and ÉMILE ANDRÉ (*Compt. rend.*, 1913, **157**, 895—898).—The authors have determined the heats of combustion of some thirty-three acetylenic compounds and some compounds containing an ethylene linking or a simple linking in place of the triple linking, the chemical natures of these compounds being very varied. From their results, which are set out in detail, they calculate the heats of formation, and draw the following conclusions. The heat of hydrogenation of acetylenic to saturated compounds is considerable, being of the order of 80 cal. in the aliphatic series, but less in the aromatic. The fixation of the first two hydrogen atoms generally liberates more than half the total heat liberated in complete saturation. The excess of energy of the triple over the simple linking in the hydrocarbon series is about 70 cal. The fixation of the elements of water on to an acetylenic hydrocarbon with formation of a ketone liberates about 40 cal., and thus the reaction is, in all probability, irreversible. W. G.

**Heat of Formation of Additive Organic Compounds. III. Racemates (Camphor and Camphoroxime).** B. L. VANZETTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 379—385. Compare A., 1913, ii, 1026).—In the case of camphor, the heats of solution of the antipodes, of the inactive mixture obtained by crystallisation from solutions of the two antipodes, and of the inactive mixture obtained by fusing equal quantities of the antipodes are equal within the limits of experimental error. Hence the inactive mixtures are not true racemates. This is confirmed by adding one of the antipodes in small quantities to a solution of the other; as soon as equilibrium is reached in the solution after each addition, the optical rotation is measured. In the case of camphor, a gradual increase in the rotatory power of the solution is observed, whilst in the case of camphoroxime (where a true racemate is formed) a maximum is quickly reached. The difference between the heats of solution in alcohol of the antipodes and of the racemate in the case of camphoroxime is 823 cal., and this accordingly is the heat of combination of the two active molecules to form the racemic compound. R. V. S.

**The Heats of Dilution to Infinity of Molecular Aqueous Solutions of Hydrochloric and Sulphuric Acids.** J. A. MULLER (*Bull. Soc. chim.*, 1913, [iv], **13**, 1053—1056).—A determination of the heats of dilution to varying concentrations at different temperatures of solutions of hydrochloric and sulphuric acids containing in each case a gram-molecule per litre. By extrapolation, the author has determined the heat of dilution to infinite volume, and finds for hydrogen chloride at 15° the value 17·5 cal., and for sulphuric acid at 14° the value 19·60 cal. W. G.

**The Heats of Ionisation of Hydrochloric and Sulphuric Acids.** J. A. MULLER (*Bull. Soc. chim.*, 1913, [iv], 13, 1057—1060. Compare preceding abstract).—By a method already described for hydrochloric acid (compare A., 1913, ii, 11), the author has determined the coefficients of ionisation of different solutions of sulphuric acid at 14°, 26°, and 38°. From these and the heat of dilution he has calculated the heat of ionisation of a gram-molecule of the acid infinitely diluted, the values obtained being 1.44 cal. at 14°; 4.21 cal. at 26°; and 3.09 cal. at 36°. From this value and the heat of ionisation of the pure acid at 14°, he calculates the heat of dilution to infinity, supposing that no ionisation takes place. This value will differ from the heat of dilution with total ionisation in the case of sulphuric acid, whereas in the case of hydrochloric acid they will be practically equal.

W. G.

**The Bertrand Formula and its Relationship to the Heat of Vaporisation and the Boiling Point of Liquids.** A. SPERANSKI (*Zeitsch. physikal. Chem.*, 1913, 85, 623—631).—A mathematical paper, in which the Bertrand formula is discussed. It is shown that for different liquids which have the same value of  $n$  in the formula  $p = \kappa(T - l)^n / T^n$  the following regularities are observed: (1) The ratio of the molecular heat of vaporisation of two liquids  $a$  and  $b$ , at temperatures at which both liquids have the same vapour pressure, is constant if  $pv = RT$  for the liquid,  $Q_a/Q_b = Q'_a/Q'_b = \text{const.}$  (2) In the case of liquids where the relationship  $T_a/T_b = T'_a/T'_b$  holds, the constant  $\kappa$  of the Bertrand formula is the same, and the constants  $l$  are in the proportion of the boiling points.  $T_a$  and  $T_b$  are the temperatures at which the vapour pressures of  $a$  and  $b$  are  $p_1$  and  $T'_a$ , and  $T'_b$  the temperatures at which the vapour pressure is  $p_2$ . (3) In these liquids the Trouton rule is applicable, not only at 760 mm. pressure, but also at other vapour pressures. (4) In the case of those liquids where the above expression does not hold, an equation is deduced which has the form:

$$(T_a - T'_a)/(T_b - T'_b) \cdot T_b \cdot T'_b / T_a T'_a = l_b / l_a = \text{constant.}$$

J. F. S.

**Viscosity of the Vapour of  $n$ -Butane.** J. P. KUENEN and S. W. VISSER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 5, 355—362).—The viscosity of  $n$ -butane has been determined by Rankine's transpiration method (A., 1910, ii, 188). Assuming the viscosity of air at 15.5° to be 0.0001803, that for  $n$ -butane is found to be 0.00008404 at 14.7°, 0.00008413 at 16.0°, and 0.0001092 at 100°.

In consequence of the difference in curvature of the two surfaces of the falling mercury drop, a correction has to be made for capillary action, and a method is described for obtaining this correction without introducing different quantities of mercury into the apparatus.

H. M. D.

**The Virial-coefficient  $B$  for  $n$ -Butane.** J. P. KUENEN and S. W. VISSER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 350—355).—The vapour density of  $n$ -butane has been measured

with great care at temperatures between  $0^{\circ}$  and  $21^{\circ}$  and pressures ranging from 186 to 760 mm. The data are employed to calculate the second virial coefficient  $B$  in the equation:

$$pv = RT(1 + Bp/RT + (C - B^2)p^2/R^2T^2),$$

from which  $B = -0.0431$  at  $0^{\circ}$ . The value of  $C$  need not be known very accurately, and its approximate value was deduced from observations made on other substances. The theoretical normal volume of 1 gram of butane is 386.0 c.c., whilst that derived from the above equation is 388.1 c.c. The discrepancy is shown to be due to the presence of a small quantity of a more volatile substance (probably ethane) in the *n*-butane. H. M. D.

**The Weight of a Falling Drop and the Laws of Tate. XV. The Drop Weights of Certain Organic Liquids and the Surface Tensions and Capillary Constants Calculated from them.** J. LIVINGSTON R. MORGAN and PHILIP M. CHAZAL (*J. Amer. Chem. Soc.*, 1913, **35**, 1821—1834).—The following organic liquids have been studied by the aid of the Morgan drop-weight apparatus: benzonitrile, *o*-, *m*-, and *p*-toluonitriles, hexane, ethyl mercaptan, phenyl mercaptan, phenylthiocarbimide, ethyl acetoacetate, acetonitrile, butyronitrile, valeronitrile, ethylthiocarbimide, allylthiocarbimide, methyl and ethyl malonates, ethyl dimethylacetoacetate, ethyl diethylacetoacetate, ethyl oxalate, methyl and ethyl cinnamates, amyl succinate, acetylacetone, phenylhydrazine, and monoacetin. Of these, the first nine are normal and non-associated according to the definition requiring constancy in the value of the critical temperature,  $t_c$ , calculated at all temperatures of observation; the remaining liquids are associated.

In some cases the agreement of the authors' results with those of other observers is very good, whilst in other cases, especially with those liquids which are difficult to obtain and retain in the pure state, the results differ widely.

In the case of the toluonitriles the order of magnitude of the surface tensions is ortho, para, meta (compare Turner and Merry, T., 1911, **99**, 2075), in place of the usual order: ortho, meta, para (Feustel, T., 1911, **99**, 2074).

From the fluctuations observed in the Ramsay and Shields temperature-coefficient for acetylacetone and ethyl acetoacetate, Schenck and Ellenberger (A., 1904, ii, 721) have drawn the conclusion that these liquids are composed of tautomeric components. This conclusion may be correct, but the authors point out that the observed fluctuations may be caused by experimental errors, and hence are meaningless. T. S. P.

**The Weight of a Falling Drop and the Laws of Tate. XVI. The Drop Weights of Certain Organic Liquids and the Surface Tensions and Capillary Constants Calculated from them.** J. LIVINGSTON R. MORGAN and BENJAMIN J. KRAMER (*J. Amer. Chem. Soc.*, 1913, **35**, 1834—1845).—The surface tensions and capillary constants of the following twenty-four organic liquids have been determined by the Morgan drop-weight method at various temperatures,

and the equations deduced showing the relation between the temperature and the capillary constants: Dipropyl ketone; ethyl and amyl formates; ethyl and amyl malates; amyl stearate, succinate, malonate and phthalate; *iso*amyl butyrate and trichloroacetate; *isobutyl* valerate; ethyl lactate, phthalate, and sulphite; ethyl benzoyl-lactate; the diethyl esters of butyroxyl-, heptoyloxyl-, octoyloxyl-, nonoyloxyl-, and decoyloxyl-succinic acids; methyl, ethyl, and amyl chlorofumarates.

Of these liquids only dipropyl ketone and amyl malate are non-associated according to the Morgan definition (compare preceding abstract).

The results obtained by the authors agree with those obtained by Homfray and Guye (A., 1904, ii, 388), and in some cases with those of Walden and Swinne (A., 1912, ii, 628). In certain cases they are 2—4% lower than those obtained by the last-named investigators.

T. S. P.

**The Weight of a Falling Drop and the Laws of Tate. XVII. The Drop Weights and Surface Tensions of Molten Hydrated Salts and their Solutions.** J. LIVINGSTON R. MORGAN and EDWARD SCHRAMM (*J. Amer. Chem. Soc.*, 1913, 35, 1845—1856).—The drop weights have been determined, and the surface tensions calculated, for thirty-two concentrations of calcium chloride in aqueous solution (at 30°), for sixteen of zinc nitrate (at 45°), for fourteen of sodium chromate (at 30°), and for fifteen of sodium thiosulphate (at 40°).

The relationship between surface tension and concentration was found to be curvilinear in all cases, the curves being convex to the axis of concentration. No discontinuity in the surface tension was observed in passing from stable to metastable, that is, supersaturated solutions; nor was there any discontinuity indicating the presence of hydrates in solution.

Valson's relationship, namely, that salt solutions of equivalent concentration possess the same surface tension, was found to be true within 4—5% for solutions of the above four salts.

Heydweiller's relationship (*Ann. Physik*, 1911, [iv], 33, 145), connecting the surface tension of solutions with the number of equivalents present and the ionisation of the substance, was found not to hold for solutions of calcium chloride, but to give good results for solutions of zinc nitrate and sodium chromate.

T. S. P.

**The Weight of a Falling Drop and the Laws of Tate. XVIII. The Drop Weights, Surface Tensions, and Capillary Constants of Aqueous Solutions of Ethyl, Methyl, and Amyl Alcohols, and of Acetic and Formic Acids.** J. LIVINGSTON R. MORGAN and MARKS NEIDLE (*J. Amer. Chem. Soc.*, 1913, 35, 1856—1865).—The drop weights at 30° of various concentrations of aqueous solutions of ethyl, methyl, and amyl alcohols, and of acetic and formic acids have been determined, and hence the surface tensions and capillary constants calculated. For certain concen-

trations the variation of the surface tensions and capillary constants with the temperature has also been ascertained.

Amyl alcohol, even in minute amounts, has a very marked lowering effect on the surface tension of water, and it is suggested that this might be used as the basis of a delicate method for the quantitative estimation of solutions of this substance in water.

The relationship of Duclaux: that, for aqueous solutions of homologous alcohols and acids the ratio of the concentrations of any two homologues in solutions exhibiting the same surface tensions is constant, is confirmed.

Calculation of the Ramsay and Shields' constant for solutions of these associated liquids does not show it to approach the normal value, 2.12, more closely than the constituents themselves, as it should do if each of the associated liquids dis-associated the other in accordance with the theory advanced by Jones and Lindsay.

The surface tension of a mixture of associated liquids is not equal to the mean of the surface tensions of the two constituents, as is the case with a mixture of two non-associated liquids. T. S. P.

[Tension of Metal Ammonias.] WILHELM BILTZ (*Zeitsch. physikal. Chem.*, 1913, 85, 639—640).—Polemical. A reply to Ephraim (A., 1913, ii, 677. Compare also Biltz, *ibid.*, ii, 404, and Ephraim, *ibid.*, ii, 129, 130). J. F. S.

**Solubility in Chlorinated Aliphatic Hydrocarbons.** WALTER HERZ and W. RATHMANN (*Zeitsch. Elektrochem.*, 1913, 19, 887—888).—The solubilities of iodine, benzoic acid, phenylacetic acid, phenylpropionic acid, cinnamic acid, phenylpropionic acid, and salicylic acid have been determined in chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, tetrachloroethane, and penta-chloroethane. The following values are obtained in millimols. per 10 c.c. of solvent: Iodine, in  $\text{CHCl}_3$  3.52,  $\text{CCl}_4$  2.37,  $\text{C}_2\text{HCl}_3$  3.12,  $\text{C}_2\text{Cl}_4$  2.41,  $\text{C}_2\text{H}_2\text{Cl}_4$  2.44,  $\text{C}_2\text{HCl}_5$  2.72; benzoic acid in  $\text{CHCl}_3$  14.77,  $\text{CCl}_4$  5.49,  $\text{C}_2\text{HCl}_3$  11.16,  $\text{C}_2\text{Cl}_4$  6.60,  $\text{C}_2\text{H}_2\text{Cl}_4$  12.43,  $\text{C}_2\text{HCl}_5$  8.93; phenylacetic acid in  $\text{CHCl}_3$  44.22,  $\text{CCl}_4$  18.42,  $\text{C}_2\text{HCl}_3$  32.99,  $\text{C}_2\text{Cl}_4$  15.58,  $\text{C}_2\text{H}_2\text{Cl}_4$  45.13,  $\text{C}_2\text{HCl}_5$  32.53; phenylpropionic acid in  $\text{CHCl}_3$  54.44,  $\text{CCl}_4$  46.04,  $\text{C}_2\text{HCl}_3$  51.40,  $\text{C}_2\text{Cl}_4$  47.25,  $\text{C}_2\text{H}_2\text{Cl}_4$  54.30,  $\text{C}_2\text{HCl}_5$  50.19; cinnamic acid in  $\text{CHCl}_3$  8.16,  $\text{CCl}_4$  1.18,  $\text{C}_2\text{HCl}_3$  4.08,  $\text{C}_2\text{Cl}_4$  1.72,  $\text{C}_2\text{H}_2\text{Cl}_4$  7.46,  $\text{C}_2\text{HCl}_5$  3.74; phenylpropionic acid in  $\text{CHCl}_3$  7.89,  $\text{CCl}_4$  2.27,  $\text{C}_2\text{HCl}_3$  3.82,  $\text{C}_2\text{Cl}_4$  3.24,  $\text{C}_2\text{H}_2\text{Cl}_4$  7.18,  $\text{C}_2\text{HCl}_5$  4.10; salicylic acid in  $\text{CHCl}_3$  1.57,  $\text{CCl}_4$  0.30,  $\text{C}_2\text{HCl}_3$  1.10,  $\text{C}_2\text{Cl}_4$  0.80,  $\text{C}_2\text{H}_2\text{Cl}_4$  1.51,  $\text{C}_2\text{HCl}_5$  0.77. A number of solubility determinations of cinnamic acid in the binary mixtures  $\text{CHCl}_3$ — $\text{CCl}_4$  and  $\text{C}_2\text{HCl}_3$ — $\text{C}_2\text{HCl}_5$  are given. It is shown that the factor  $(\eta_0 - \eta)/n\eta_0$  is constant, where  $\eta_0$  is the solubility in chloroform,  $\eta$  the solubility in the mixture, and  $n$  the concentration of carbon tetrachloride in the mixture. J. F. S.

**The Formation of [Vitreous Material] from Vapour.** J. D. STARINKEVITSCH and G. TAMMANN (*Zeitsch. physikal. Chem.*, 1913, 85, 573—578).—The condensation of vapours of papaverine, betol, and piperine has been studied by the authors. It is shown that liquids

with small spontaneous crystallisation tendency condense on mica plates as isotropic drops, whereas substances which can only be slightly supercooled condense as crystals. When the spontaneous crystallisation tendency of a liquid substance is small, the vapour will also have but a slight tendency to form crystals. From this is drawn the conclusion that the cause of the tendency of a substance to great supercooling is not to be attributed to large viscosity, but to a peculiarity of the molecule itself, which can be expressed as follows: The molecule of a substance with small spontaneous crystallisation tendency can only with difficulty assume the anisotropic form, and the molecule of a substance with a large spontaneous crystallisation tendency can assume the anisotropic form easily.

J. F. S.

**Mutual Relations between Colloids and Crystalline Substances and between Crystalloids and Amorphous Substances together with Lecture Experiments for the Demonstration of these Relations.** R. MARC (*Kolloid-Zeitsch.*, 1913, 13, 281—289).—Experiments are described, which show that finely powdered, crystalline substances, such as barium carbonate, barium sulphate, and calcium carbonate, readily adsorb colloidal substances from solution, and that amorphous substances, such as kaolin, powdered glass, and charcoal, adsorb crystalloids more readily. A number of simple experiments suitable for the lecture-table are described, which show the difference in the adsorption capacity of the two groups of solid substances towards colloids and crystalloids respectively.

Crystalline substances which have adsorbed colloids assume a more or less pronounced colloidal character, which is exhibited in the fact that such substances can adsorb both colloids and crystalloids from solution, and further by the fact that the rate at which the finely divided substance settles after being shaken with water is greatly increased by the addition of electrolytes.

In connexion with the above experiments, the author discusses the relationship between the crystalline and amorphous conditions, and considers that the difference in the behaviour of crystalline and amorphous solids towards solutions of colloids and crystalloids is distinctly opposed to von Weimarn's view that there is no fundamental difference between the two solid states of aggregation beyond that which is determined by the difference in the degree of dispersity.

In an appendix, some experiments are described, in which the author has investigated the possibility of utilising gum arabic as a means of facilitating the precipitation of barium sulphate in the estimation of sulphates. Although the results do not suggest that the method can be applied generally to quantitative work, it may be found convenient as a means of removing sulphates from neutral solutions in the cold.

H. M. D.

**Physical Chemistry of Colloidal Sulphur.** M. RAFFO and G. ROSSI (*Kolloid-Zeitsch.*, 1913, 13, 289—297. Compare A., 1912, ii, 1037).—Measurements have been made of the quantity of sulphur



which is precipitated from colloidal solutions of sulphur on the addition of equivalent quantities of different electrolytes. The colloidal solutions had been subjected to dialysis, but still contained considerable quantities of sodium sulphate and sulphuric acid. For a series of salts of the same metal, the quantity of sulphur precipitated increases in general with the formula weight of the anion, but the nitrates form an exception to this rule. From experiments with colloidal solutions containing different quantities of sodium sulphate and sulphuric acid it appears that the amount of sulphur precipitated by a fixed quantity of the same electrolyte diminishes as the concentration of the sodium sulphate and sulphuric acid increases. These observations support the view, expressed in the previous paper, that the sulphates originally present in the colloidal solution are intimately associated with the disperse phase.

Conductivity measurements have also been made in which the influence of added electrolytes has been examined. The observed conductivity is compared with that calculated on the assumption that the conductivities of the colloidal solution and of the solution of the added electrolyte remain unchanged when mixing occurs. In some cases the observed conductivity is slightly greater, in others much smaller than the calculated value. H. M. D.

**Ultramicroscopic Investigation of the Cataphoresis of Colloidal Solutions and a Theory of the Coagulation.** MASAMICHI KIMURA (*Mem. Coll. Sci. Eng. Kyōtō*, 1913, 5, 175—199).—The changes which occur in the nature and distribution of the particles in a colloidal solution, subjected to the action of an electric field, have been investigated by means of the ultra-microscope. As a result of the application of a difference of potential to the electrodes, the colloidal particles arrange themselves in distinct zones, and the behaviour of the particles in each of these regions has been examined in detail.

In general, the Brownian movement of the particles is not appreciably affected by an electrostatic field of considerable intensity. When a current is first sent through the colloidal solution, the translational motion is not very evident, but becomes much more marked after the current has passed for some time. When this condition has been attained, the colloidal particles begin to move at once if the electric circuit is broken and re-established. The motion of the particles is quite irregular—some become suddenly accelerated and others retarded; some come apparently to rest, but these may start to move again either in the original or in the opposite direction. These observations seem to show that the electrical double layer remains intact even when a field of considerable intensity is applied to the solution, but that dissociation occurs when the ions begin to move. It would also appear that some of the colloidal particles collide with ions, and undergo changes in respect of the charge which they carry. Coagulation occurs when oppositely charged particles come into close proximity. The coagulation produced by an electrolyte is determined by the formation

of positive and negative colloidal particles, which subsequently combine together.

It has been observed that a negative platinum hydrosol is rapidly coagulated when a current of oxygen is passed through the solution, but that hydrogen is inactive. This is attributed to the fact that the water becomes positively charged in the former case and negatively in the latter.

H. M. D.

**The Nature of the Double Layer in Colloidal Particles.** MASAMICHI KIMURA (*Mem. Coll. Sci. Eng. Kyōtō*, 1913, 5, 201—209. Compare preceding abstract).—An attempt is made to explain the formation of the electrical double layer on the surface of colloidal particles, in which the effect is attributed to the ionising action of the dispersive medium.

In the case of a colloidal solution of a metallic hydroxide in water, the hydroxide is ionised to a small extent, and a double layer is formed in consequence of the greater mobility of the hydroxyl ion as compared with that of the metal ion. In this case the positive coating will be on the colloidal particle, and the negative coating on the water side of the surface of separation.

A similar explanation is applied to the case of the negative particles of a colloidal metal. By the action of the water on the surface molecules, both positive and negative metal ions are supposed to be formed. Since the latter cannot exist in the free condition, the negative ions remain associated with the colloidal particle, forming the inner coating of the double layer. The positive metal ions form the outer coating on the water side of the surface of separation.

It is shown that this view of the nature of the electrical double layer in colloidal particles affords a satisfactory explanation of the influence of electrolytes and non-electrolytes on the stability of colloidal solutions.

H. M. D.

**A Method of Disintegrating Metals and their Oxides into a Colloidal State.** MASAMICHI KIMURA (*Mem. Coll. Sci. Eng. Kyōtō*, 1913, 5, 211—213).—If a metal is heated in the Bunsen flame and quickly plunged into distilled water, a solution is obtained which contains large numbers of colloidal particles in a state of Brownian motion. Such solutions were obtained with platinum, silver, copper, aluminium, zinc, tin, bismuth, and lead. In an electric field some of the particles move towards the anode and others towards the cathode. It would thus appear that the colloidal solutions contain both particles of metal and particles of the corresponding hydroxide. This view is supported by the observation that a zinc rod when heated in the reducing part of the flame gives a solution in which all the particles move towards the anode, whereas, when the rod is heated in the ordinary flame, the majority of the particles were found to migrate towards the cathode. Similar results were obtained with nickel, copper, aluminium, tin, bismuth, and lead. H. M. D.

**The Corrosion of Metals Covered with a Thin Layer of Water or Alcohols and Subjected to the Action of Ultra-violet Rays.** MASAMICHI KIMURA (*Mem. Coll. Sci. Eng. Kyōtō*, 1913, 5, 253—260).—When silver, zinc, gold, platinum, or copper is covered with a thin layer of water and exposed to the action of ultraviolet rays, a colloidal solution is obtained which contains both the metal and its hydroxide. At the same time the surface of the metal is corroded, and a deposit is formed on the walls of the vessel.

In order to ascertain the influence of the surrounding medium on the corrosion, experiments were made with an alloy containing 90% of cadmium and 10% of antimony. After exposure to the ultraviolet rays for two hours, it was found that there was no corrosion in a vacuum, but that the alloy was slightly corroded in air, somewhat more in oxygen, and strongly corroded in water. These results indicate that the corrosion of the metals cannot be regarded as a direct effect of the action of the ultraviolet rays, and that the corrosion is mainly determined by the nature of the medium surrounding the metal. It is probable that the corrosion in air and oxygen is due to the formation of ozone, and in water to the formation of hydrogen peroxide. Experiments on the corroding action of a very dilute solution of hydrogen peroxide show, in fact, that the structural changes in the surface layer are very similar to those brought about by the action of pure water and ultraviolet rays.

The formation of the colloidal particles cannot, however, be attributed to the action of hydrogen peroxide, and it is supposed that this effect is directly due to the action of the ultraviolet rays on the metal. By this action, electrons are liberated from the surface of the metal, and some of these combine with the metal ions in the adjacent liquid layer, whereby neutral atoms are formed. In some cases these coalesce to form colloidal metal particles, whilst others act on the water and form the hydroxide, which gives rise to the colloidal particles of opposite sign. H. M. D.

**Colloidal Solutions of Dyes and Colophony in Liquid Crystals.** D. VORLÄNDER (*Zeitsch. physikal. Chem.*, 1913, 85, 701—705).—Colloidal solutions of crystal-violet and colophony in the ethyl ester of *p*-ethoxybenzylideneamino- $\alpha$ -methylcinnamic acid have been examined by means of a paraboloid ultramicroscope. In the liquid crystal I distinct particles are not visible, but in the liquid crystal II a large number of submicrons are visible, which exhibit the Brownian movement. It is shown that the nature of the double refraction of both liquid crystal forms is not affected by the solution of dyes in them. J. F. S.

**The Precipitation of Colloids.** H. PECHSTEIN (*Biochem. Zeitsch.*, 1913, 58, 171—174).—A criticism of the results obtained by Spiro (A., 1913, ii, 934). The author calls attention to the sources of error in the determination of the hydrogen ion concentration, especially that due to the carbon dioxide of the atmosphere. He shows, furthermore, that effect of protein on some salt solutions is

the same as that which can be produced by the addition of any "buffers." Other salts employed by Spiro can by themselves act as "buffers."

S. B. S.

**Importance of Adsorption in the Precipitation of Colloidal Suspensions.** II. H. FREUNDLICH and H. SCHUCHT (*Zeitsch. physikal. Chem.*, 1913, 85, 641—660. Compare A, 1907, ii, 939; 1910, ii, 692).—The Freundlich theory of coagulation of colloidal suspensions has been tested by means of a large number of experiments on the coagulation of mercury sulphide sols by electrolytes and the absorption of the same electrolytes by mercury sulphide. It is shown that the cation of the electrolyte is the important factor in coagulating the sols, and that the influence is greater the larger the valency. The absorption was determined in the case of the cations  $\text{NH}_4^+$ ,  $\text{Ag}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Ce}^{+++}$ , and several dyes; in no case was a saturation observed, but the absorption isothermal  $a = ac^{1/n}$  held in all cases. The quantity of the cation absorbed by the coagulated sol, that is, the precipitation value of the electrolyte, lies on the absorption isothermal. The amounts of cation absorbed at the precipitation value were approximately in equivalent proportion. The absorption isothermals have, however, different forms for the various electrolytes: Strong absorption is shown for the dyes and  $\text{Cu}^{++}$  ions, and weaker absorption for  $\text{Ba}^{++}$  and  $\text{Ce}^{+++}$ . It follows of necessity from this that the precipitation value of the electrolytes is so strongly dependent on the valency and absorption value of the different cations, because very different concentrations of the various cations are required in solution in order that equivalent quantities may be absorbed by the colloidal particles. This constitutes a complete confirmation of the Freundlich theory. It is also shown that a mercury sulphide sol, containing hydrogen sulphide, has a much larger kataphoric migration velocity than one from which the hydrogen sulphide has been removed.

J. F. S.

**The Velocity of the Absorption Reversal owing to the Transformation of Mercury Sulphide from the Amorphous Form to the Crystalline.** H. FREUNDLICH and H. SCHUCHT (*Zeitsch. physikal. Chem.*, 1913, 85, 660—680. Compare preceding abstract).—The coagulated mercury sulphide which has been precipitated from the sol by the addition of auramine or new-magenta is shown to change to the crystallised form on keeping, and in the process to give up to the solution the coloured substance which it had previously absorbed. This constitutes an absorption reversal in consequence of the change from the amorphous to the crystalline state. It also shows that an amorphous substance is a stronger absorbent than a crystalline substance. The velocity of the reversal was studied with new-magenta as absorbed substance at  $0.2^\circ$ ,  $25^\circ$ , and  $35^\circ$ . The reaction is autocatalytic, and can be represented by the expression  $dx/dt = 2kt(1+bx)(1-x)^2$ , in which  $k$  and  $b$  are constants,  $x$  the increase in concentration of the solution, and  $t$  the time. The influence of temperature on the velocity of the reversal is expressed by the Arrhenius formula  $\log_e k = -A/T + B$ . The

value of the constant  $A$  is very large, about 14,000, and an increase of  $10^\circ$  in the temperature quadruples the value of  $k$ . The autocatalytic course of this reaction is shown to be analogous to the course of the coagulation of aluminium hydroxide sols by electrolytes, and to many other colloid reactions. The conclusion is drawn that the velocity of coagulation and the spontaneous precipitation velocity of colloids have an autocatalytic character. The Liesegang layers are explained on the same basis. J. F. S.

**The Laws of Displacement of Chemical Equilibrium at Constant Temperature or Pressure.** E. ARIÈS (*Compt. rend.*, 1913, **157**, 1074—1077).—A theoretical discussion of the laws governing chemical reactions at constant pressure or constant temperature. W. G.

**Critical Phenomena in Binary Systems.** FRITZ FRIEDRICHS (*J. Amer. Chem. Soc.*, 1913, **35**, 1866—1883; *Zeitsch. anorg. Chem.*, 1913, **84**, 373—400).—Using temperature-concentration diagrams, the author puts forward a classification of binary systems which is based on solubility, miscibility, and critical relations of the components. In each of the diagrams two types of curve are distinguished: the solubility curve, which is regarded as the boundary line between solid and liquid; and the critical curve, which serves as the boundary between liquid and gas. In systems, the components of which in liquid form show a limited miscibility, a third type of curve appears, namely, the curve of heterogeneous liquids or the miscibility curve.

A qualitative examination of a large number of solutions of inorganic salts and of iodine, sulphur, and phosphorus in liquid ammonia and in liquid sulphur dioxide has been made at temperatures varying between  $-80^\circ$  and  $+160^\circ$ , and the results obtained have been tentatively arranged in the proposed classification.

The behaviour of various ammoniates, which are insoluble in liquid ammonia, has been studied at the critical temperature of ammonia, but no indication of decomposition was observed.

T. S. P.

**The System Hexane-Water.** F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 404—418).—The equilibrium relations exhibited by the system hexane-water have been investigated in the neighbourhood of the critical solution temperature. The critical temperature of synthetic hexane (b. p.  $69.0^\circ$ ) was found to be  $234.6^\circ$ , and the critical pressure  $30.15$  atmospheres. The critical solution temperature is  $222.05^\circ$ , and the corresponding pressure  $52.05$  atmospheres.

When the pressures in the three phase (liquid, liquid, vapour) equilibria are compared with the vapour pressures of the pure components, it is found that the three-phase pressure is considerably greater than the sum of the pressures of the components at the same temperature. The difference increases from  $1.1$  atmospheres at  $195^\circ$  to  $3.25$  atmospheres at  $222.05^\circ$ . It is supposed that this rather

remarkable result is brought about by deviations from the simple gas laws.  
H. M. D.

**The Ionisation Products from the Salts of Phenolphthalein.** LUDWIG ROSENSTEIN and E. Q. ADAMS (*J. Amer. Chem. Soc.*, 1913, 35, 1883—1888).—The distribution ratio of phenolphthalein between benzene and water was found, by a colorimetric method, to be 13·1, the concentration in the benzene phase being the greater. (The temperature is not stated.) The fraction of non-ionised phenolphthalein in solutions of different hydrion concentration was then determined by shaking out with benzene, and also the fraction of bivalent (coloured) ion in the same solutions by colorimetric measurements. The sum of these two fractions was always less than unity, the maximum observed difference being 0·509 at a hydrion concentration of  $7\cdot63 \times 10^{-10}$  mols. per litre; this difference represents the fraction of phenolphthalein present as the univalent intermediate ion.

Using the two ionisation constants for phenolphthalein previously determined (Rosenstein, A., 1912, ii, 893), and assuming that the bivalent ion from phenolphthalein alone is coloured, it was shown by means of the various equilibrium equations that in a solution in which the hydrion concentration is  $5\cdot71 \times 10^{-10}$  mols. per litre the concentration of the intermediate ion should be a maximum and equal to 50·2% of the phenolphthalein present, 24·9% of the phenolphthalein should be present as bivalent ion, and 24·9% as non-ionised phenolphthalein. From the graphic representation of the experimental results, it was actually found that at a hydrion concentration of  $5\cdot8 \times 10^{-10}$  mols. per litre the concentration of the intermediate ions is a maximum, and equal to 50·5% of the phenolphthalein present.  
T. S. P.

**Equilibria in Ternary Systems. IX.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 385—395).—A theoretical paper, in which the four-phase equilibrium relationships characteristic of a ternary system are discussed in detail.

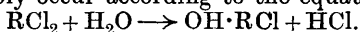
H. M. D.

**Esterification of Dibasic Acids by means of Alcoholic Hydrogen Chloride.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1913, 85, 706—762).—The rate of esterification of oxalic acid, malonic acid, succinic acid, glutaric acid, malic acid, and tartaric acid by absolute and aqueous alcohol in the presence of hydrogen chloride has been determined at 25°. It is shown that the influence of water is approximately the same in all cases, although somewhat less than that previously observed in the case of monobasic aromatic acids (A., 1906, ii, 659; 1907, ii, 158). The decrease of the constant of the unimolecular reaction in the case of all these acids, except oxalic acid, can be explained by the influence of the water. It is also shown that the velocity of the esterification to the ester acid is the same as the formation of the normal ester from the ester acid, except in the case of oxalic acid, where the lengthening

of the carbon chain exercises a retarding influence. Reasons for the step-wise course of the esterification are advanced. In aqueous alcohol it is shown that except in the case of succinic acid and glutaric acid, a saponification occurs in quantities which cannot be neglected. In the case of oxalic acid, malic acid, and tartaric acid it is shown that the same equilibrium can be reached and the same constant obtained from both sides. Formulæ are deduced which express the unimolecular reaction for succinic acid and tartaric acid as a function of the water content of the alcohol and the hydrochloric acid. The velocity constants are compared with constants obtained previously. J. F. S.

**Determination of the Velocity of Formation of Diazo-compounds.** E. TASSILLY (*Compt. rend.*, 1913, 157, 1148—1150).—The author has studied the rate of diazotisation of aniline by removing from time to time 10 c.c. of the liquid wherein the reaction was proceeding, coupling the diazo-compound with sodium  $\beta$ -naphtholsulphonate, and measuring the absorption of this liquid by a spectrophotometer. The results show that, for aniline, the maximum is reached at the end of five hours, and that the reaction is bimolecular. W. G.

**Hydrolysis of Some Inorganic Salts.** CARL KULLGREN (*Zeitsch. physikal. Chem.*, 1913, 85, 466—480).—The hydrolysis of the chlorides, nitrates, and sulphates of aluminium, mercury, copper, lead, ammonium, zinc, cobalt, nickel, cadmium, manganese, and magnesium has been determined in dilute solutions at 100° and 85.5° by means of the inversion of sucrose. The hydrolysis constants obtained experimentally are corrected for the influence of the neutral salt. It is shown that the hydrolysis of salts of the type  $RCl_2$  must probably occur according to the equation:



The nitrates and chlorides are hydrolysed to about the same extent in water. The dissociation constant of the metal hydroxide is calculated for the cases investigated at 100°. J. F. S.

**The Kinetics of Glycolysis.** ARISTIDES KANITZ (*Biochem. Zeitsch.*, 1913, 57, 437—440).—The author quotes a series of results obtained by Vandeput, which indicate that the destruction of dextrose by blood is a reaction of the first order. S. B. S.

**Catalysis.** E. ABEL (*Zeitsch. Elektrochem.*, 1913, 19, 933—951).—A lecture delivered to the 85th Versammlung Deutscher Naturforscher und Aerzte at Vienna, 1913, in which the author reviews the present opinions held with respect to catalysis, and work which is in progress on catalytic reactions. J. F. S.

**Degree of Dispersity and Catalytic Action.** STEPHAN RUSZNYÁK (*Zeitsch. physikal. Chem.*, 1913, 85, 681—690).—The decomposition of hydrogen peroxide solution by gold sols of varying dispersity has been studied in weakly alkaline solution. The

reactions were carried out at  $25^{\circ}$ , and the same quantity of gold used in each experiment. It is shown that the sol with the smallest dispersity has the strongest catalytic action, although no proportionality has been established between the degree of dispersity and the catalytic action. This result is remarkable, since an increased catalytic action is to be expected, both on account of the increased surface and the increased Brownian movement of the smaller particles.

J. F. S.

**Catalytic Studies. V. and VI. Inactivation of a Non-colloidal Inorganic Catalyst by Rise of Temperature. I. and II.** E. ABEL (*Monatsh.*, 1913, **34**, 1349—1360, 1361—1391.)—I. The velocity of the reaction between hydrogen peroxide and sodium thiosulphate in dilute aqueous solution is considerably increased when a small quantity of a copper salt is added to the solution. The observed acceleration is apparently due to the catalytic action of the cupric ions.

If the catalyst and the thiosulphate are heated together for a short time at  $100^{\circ}$  in presence of a small quantity of acetic acid, and the hydrogen peroxide is added to the solution after this has been cooled to  $25^{\circ}$ , it is found that the activity of the catalyst has been destroyed by the preliminary thermal treatment. Although the presence of hydrogen ions may not be necessary for the inactivation of the catalyst, the process is greatly facilitated if a small quantity of acid is present. If the solution containing thiosulphate, acid, and catalyst is heated at a somewhat lower temperature ( $90^{\circ}$ ) it is possible to trace the gradual decay of the activity of the catalyst as a result of the exposure to the high temperature.

The author calls attention to the similarity between the behaviour of this inorganic catalyst and that of enzymes.

II. The nature of the reaction between hydrogen peroxide and sodium thiosulphate in presence of a small quantity of copper salt as catalyst has been examined in detail by measurements of the reaction velocity at  $25^{\circ}$  under different conditions. At this temperature inactivation of the catalyst is not observed, and the activity remains practically constant. For a given concentration of sodium thiosulphate and of the catalyst, the reaction velocity is proportional to the concentration of the hydrogen peroxide. If the peroxide concentration is fixed, it is found that the velocity increases less rapidly than the concentration of the thiosulphate. In other words, the order of the reaction with respect to thiosulphate is less than unity, but greater than zero. The value obtained depends on the ratio of the concentration of the catalyst to that of the thiosulphate, and as this ratio increases the order of the reaction decreases. For a given solution of peroxide and thiosulphate, the increase in the reaction velocity is proportional to the concentration of the copper salt.

It is supposed that the catalytic effect of the copper salt is due to the oxidation of the cuprous salt, which results from the interaction of the thiosulphate with the cupric salt, by the hydrogen peroxide. If the concentrations of the several substances involved



are expressed in gram-equivalents per litre and the time in minutes, the velocity of the reaction can be expressed by the equation:

$$-d[\text{H}_2\text{O}_2]/dt = [\text{H}_2\text{O}_2](1.53[\text{Na}_2\text{S}_2\text{O}_3] + 10^3[\text{Cu}^{++}]).$$

The reaction in question is also accelerated by iodides, and from experiments in which both  $\text{Cu}^{++}$  and  $\text{I}^-$  ions were employed as catalysts, it appears that the composite catalysing effect is the sum of the separate effects due to the two catalysts. H. M. D.

**Structure of the Atom.** Sir J. J. THOMSON (*Phil. Mag.*, 1913, [vi], 26, 1044. Compare A., 1913, ii, 942).—The assumption that the regions, to which the electrical forces inside the atom are confined, are bounded by conical surfaces, is found to require modification, and it is now suggested that the boundaries of these regions are cylindrical. H. M. D.

**Properties of the Elements and the Periodic System.** NILRATAN DHAR (*Zeitsch. Elektrochem.*, 1913, 19, 911—913).—The author has calculated the heat of ionisation and the temperature-coefficient of the ionic velocities for several ions, and shown that these properties are periodic functions of the atomic weights of the elements concerned. J. F. S.

**Curious Atomic Weight Relations.** F. H. LORING (*Chem. News*, 1913, 108, 247).—It is suggested that hydrogen, glucinum, chlorine, gallium, and nitrogen, chromium, ruthenium, gadolinium represent quaternian series of elements of the type described in previous papers (compare A., 1913, ii, 944). H. M. D.

**The Electron Conception of Valence. IV. The Classification of Chemical Reactions.** J. M. NELSON, H. T. BEANS, and K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, 35, 1810—1821).—The authors define the valence of an element as the number of corpuscles (negative electrons) an atom of that element loses or gains to form chemical bonds. Chemical bonds are thus formed by the transfer of electrons, and on this basis and on that of the electrical state of the atoms involved the authors classify various chemical reactions, using the general views of structure outlined in previous papers (compare A., 1913, ii, 768).

The term "adduction" is used instead of oxidation, and as opposed to "reduction," for reactions in which the increase in the number of positive charges, or the decrease in the number of negative charges, of an atom or group of atoms is the main feature. T. S. P.

**A Generalised Maxwell Formula.** A. BERTHOUD (*J. Chim. Phys.*, 1913, 11, 577—583).—A mathematical paper, in which the Maxwell formula for the division of the velocities of the molecules of a gas is considered. The equation:

$$\Delta n = Cne^{-C_v u^2/Rg^2}(u^2/g^2)^{C_w/R} \Delta u/u$$

is given, which applies to all gases (compare A., 1911, ii, 578). J. F. S.

**Origination of Experimental Method and Practice.** Work of Vannoccio Biringuccio. ALDO MIELI (*Gazzetta*, 1913, 43, ii, 555—562).—Historical. T. H. P.

**A Simple Form of Absorption Bulb.** ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1913, 35, 1888—1889).—Three bulbs of the required size are blown at intervals of about three inches in a rather thick-walled glass tube. The intervening portion between two bulbs is then heated, drawn out to a length of some six inches, and then bent into a S-shape. The portion of tubing leading to the first bulb is bent into a U-shape, and has a small bulb blown in it to prevent possible loss from back pressure when the current of gas is stopped. T. S. P.

**A Simple Suspension Condenser.** M. RÜDIGER (*Chem. Z.-t.*, 1913, 37, 1465).—The condenser consists of a glass tube bent into the form of a spiral, with a straight return piece passing through the centre of the spiral. If hung in the neck of a flask, and of such dimensions that the spiral almost touches the sides of the neck, it forms a very efficient condenser, the cold water being sent in through the spiral, and passing out through the straight tube. T. S. P.

**An Apparatus for Circulating Gases in a Closed Circuit.** M. SKOSSAREWSKI and F. GERMANN (*J. Chim. Phys.*, 1913, 11, 584—588).—Two pieces of apparatus are described, constructed entirely of glass, by means of which gases may be continuously circulated in a closed circuit. The apparatus consists essentially of two glass reservoirs, filled with mercury, which are attached each to mercury levelling bulbs. These bulbs are attached one to each end of a wooden rod, which is pivotted in the centre, and can be worked up and down by means of a motor. The effect is that whilst one reservoir is extracting the gas from the circuit, the other is forcing fresh gas into the circuit. The second apparatus is based on the same principle, but is more simply constructed. J. F. S.

**A Modified Hittorf's Apparatus for Demonstrating the Migration of Ions.** FRITZ WEIGERT (*Zeitsch. Elektrochem.*, 1913, 19, 886—887).—An apparatus for lecture demonstration of the migration of ions is described. The object is by means of glass and metal plates to show the concentration changes when soluble and insoluble electrodes are used in electrolysis. J. F. S.

**Demonstration of Cohesion of Liquids.** A. URSPRUNG (*Ber. Deut. Botan. Ges.*, 1913, 31, 388—400).—The apparatus employed consists of an inverted filter candle (Kitasato) attached to a capillary tube (about  $\frac{1}{2}$  mm.)  $1\frac{1}{2}$  metre long, by means of indiarubber tubing and a mercury joint. To remove all the air, the candle is first immersed in alcohol, which has been boiled for a long time, and connected with a pump. It is then quickly transferred to boiling distilled water, which has been boiled for some hours, and again

attached to a pump until all the alcohol is replaced by water. The candle is then cooled with cold water, and the open end of the tube placed in mercury.

When evaporation is increased by means of a small electric ventilator the mercury will rise over 1 metre in ten minutes.

Results obtained with water and with sap from *Carpinus betulus* are given.  
N. H. J. M.

**Lecture Experiment to Show the Formation of Aluminium Nitride.** F. Russ (*Zeitsch. Elektrochem.*, 1913, 19, 923—925).—A quantity of very finely divided aluminium is packed in a carbon or alundum cylinder, and a thin rod of carbon pushed through the powder. This carbon rod is placed in contact with two graphite poles, which are connected to a current source of 35 amperes. The whole is placed inside an air-tight glass vessel, into which nitrogen can be led. The current is passed, and in about two minutes the mass is ignited by the glowing carbon rod, and the reaction between aluminium and nitrogen being strongly exothermic, the whole of the nitrogen is converted into nitride without any further heating. A second piece of apparatus is described, which allows of a somewhat purer nitride being formed. This differs from the apparatus described inasmuch as it can be exhausted, and all oxygen can therefore be removed from the aluminium powder before the nitrogen is allowed to enter. Quantities up to 30 grams of aluminium nitride can be prepared in one operation by means of this apparatus.  
J. F. S.

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## Inorganic Chemistry.

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**Surface Tension and Molecular Complexity of Chlorine.** E. MARCHAND (*J. Chim. Phys.*, 1913, 11, 573—576).—The surface tension of chlorine has been measured by the method of capillary rise in narrow tubes at temperatures from 0° to 50°, and from the results the values of the constant  $K$  of the Eötvös formula have been calculated. It is shown that the value of  $K$  lies between 2.07 at 0° and 2.14 at 50°, and consequently liquid chlorine is to be regarded as a non-associated liquid. J. F. S.

**The Neutralisation of Periodic Acid.** RENÉ DUBRISAY (*Compt. rend.*, 1913, 157, 1150—1153).—A study of the neutralisation of periodic acid by a method already described and applied to chromic acid (compare A., 1913, ii, 388, 712). The results, which are set out in tables and curves, show that periodic acid, in solution, behaves as a tribasic acid. W. G.

**Melting Point of Oxygen.** TAD. ESTREICHER (*Zeitsch. physikal. Chem.*, 1913, 85, 432—434).—The author shows from some results

previously published (A., 1904, ii, 477) that in accord with Wahl's suggestion (A., 1913, ii, 208) the melting point  $-227^{\circ}$  is most probably the transition temperature of the one modification of solid oxygen into the other. The melting points at different pressures are extrapolated, and found to be 0.46 mm.  $-221.8^{\circ}$ , 0.87 mm.  $-219.9^{\circ}$ , and 1.12 mm.  $-219.1^{\circ}$ . It is shown also that the heat of change of one form of solid oxygen into the other is probably less than that of sulphur, which has a value of  $2.5K$  per gram.

J. F. S.

**Revision of the Density of Oxygen: Density of the Air at Geneva** F. O. GERMANN (*Compt. rend.*, 1913, 157, 926—929).—The author has determined the density of oxygen as prepared by heating recrystallised potassium permanganate, and subjecting the gas to liquefaction and subsequent fractional distillation. As a mean of fifteen determinations he finds the weight of a normal litre of oxygen to be 1.42905. In four of the determinations the oxygen was passed over platinised asbestos at  $400^{\circ}$ , prior to measuring the density. Two diagrams are given showing the arrangement of the apparatus used. This apparatus has also been used to determine the density of the air at Geneva in March on two different dates. The mean value found was 1.2930 for a normal litre of air (compare Guye, Kovacs, and Wourtsel, A., 1912, ii, 636).

W. G.

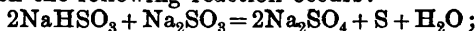
**The Solubility of Atmospheric Oxygen in Water.** TOR CARLSON (*Zeitsch. angew. Chem.*, 1913, 26, 713—714).—The author has collected the most trustworthy data obtained by previous investigators, and also made fresh experiments himself, using a modification of Winkler's method, with respect to the solubility of atmospheric oxygen in water at temperatures varying from  $0^{\circ}$  to  $25^{\circ}$ . From the results obtained a table is given showing the solubility for every degree between  $0^{\circ}$  and  $25^{\circ}$ , (a) at 760 mm., (b) at  $(760-f)$  mm., where  $f$  is the vapour pressure of water at the particular temperature.

T. S. P.

**Formation of Ozone at Various Pressures.** H. VON WARTENBERG and L. MAIR (*Zeitsch. Elektrochem.*, 1913, 19, 879—881).—The formation of ozone by a silent discharge has been studied at a series of pressures. It is shown that there is a point between 0.5 and 1.0 atmospheres where the formation is at a maximum. The experiments were continued up to 5 atmospheres pressure, and so arranged that the molecules of the gas were always under the influence of the discharge for the same time.

J. F. S.

**Preparation of Sulphur and Sulphates by Heating Sulphites under Pressure.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 265167).—Sulphur and sulphates can be obtained by heating a mixture of a sulphite and a hydrogen sulphite under pressure, when the following reaction occurs:



for example, 150 parts of ammonium hydrogen sulphite, 90 parts

of ammonium sulphite, and 200 parts of water are heated in an autoclave at 150° for a few hours. J. C. C.

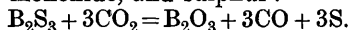
**The Alloy of Selenium and Iodine.** ERNST BECKMANN and ERICH GRÜNTAL (*Zeitsch. anorg. Chem.*, 1913, **84**, 97—102. Compare Beckmann and Hanslian, A., 1913, ii, 402; Pellini and Pedrina, A., 1908, ii, 833).—The tendency to undercooling, and the difficulty of making cryoscopic observations, increase with the concentration of the selenium. A eutectic point is found at 50 atomic % and 58°. The eutectic mixture retains iodine even after extraction with solvents until colourless, but at 100—110° all the iodine can be removed by heat. C. H. D.

**The Existence of Compounds of Selenium and Iodine.** ERNST BECKMANN and OTTO FAUST (*Zeitsch. anorg. Chem.*, 1913, **84**, 103—112. Compare preceding abstract).—The question whether the dissociation of selenium when dissolved in iodine is to be explained by the formation of loose compounds is not readily answered by thermal analysis, on account of the liability to undercooling. Dilatometric experiments, with sulphuric acid as filling liquid, show that the volume change of the eutectic on melting may be calculated from that of the components by the mixture rule. This is also true of the specific volumes, whilst the expansion in the formation of the tellurium compound,  $\text{TeI}_2$ , is ten times the experimental error. The electrical conductivity shows the eutectic to be a mixture of crystalline iodine and amorphous selenium. Tellurium iodide shows an entirely different behaviour.

The molecular weight of selenium,  $\text{Se}_{10}$ , in methylene iodide is not changed by the presence of iodine,  $\text{I}_2$ . The cause of the dissociation of selenium in iodine solution must therefore be physical, not chemical. C. H. D.

**Nitrogen Hexoxide and Nitrogen *iso*Tetroxide.** F. RASCHIG (*Zeitsch. anorg. Chem.*, 1913, **84**, 115—120. Compare A., 1912, ii, 346; Müller, *ibid.*, 753).—A reply to Müller's criticisms as to the point at which the analysis of the residual solid, after the oxygen has evaporated, should be made. On washing with liquid nitrogen a dull blue residue is obtained, having the composition  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$ . This is nitrogen *isotetroxide*. The hexoxide is perhaps only stable in presence of an excess of liquid oxygen. C. H. D.

**The Action of Carbon Dioxide on Boron Sulphide.** N. D. COSTEANU (*Compt. rend.*, 1913, 157, 934—935. Compare A., 1913, ii, 694).—Carbon dioxide reacts with boron sulphide in the same way as with silicon sulphide (compare *loc. cit.*), giving rise to boric anhydride, carbon monoxide, and sulphur:



The reaction commences at 300°, and is increased by prolonging the heating and by rise in temperature, but is never very rapid, being hindered by the formation of a layer of boric anhydride.

W. G.

**The Action of Carbonyl Chloride on the Natural Phosphates and Silicates.** J. BARLOT and ED. CHAUVENET (*Compt. rend.*, 1913, 157, 1153—1155. Compare A., 1911, ii, 602).—Carbonyl chloride will attack numerous natural phosphates, such as vivianite, pyromorphite, uranite, and monazite, and natural silicates, such as thorite, gadolinite, cerite, and zircon, yielding in each case the anhydrous metallic chloride. The phosphates are attacked at temperatures between 300° and 500°, whilst the silicates require temperatures above 1000°, emerald not being decomposed at 1400°. This reaction forms a ready method of analysis of such minerals, and also of preparing anhydrous metallic chlorides from these minerals. W. G.

**Corrosion of Metals by Water.** A. T. STUART (*J. Ind. Eng. Chem.*, 1913, 5, 905—906).—Experiments carried out with raw and filtered peaty waters showed that, although the waters attacked iron to the same extent, in the case of the raw waters a large proportion of the metal removed by corrosion remained in solution, possibly in a colloidal state, whilst the filtered waters deposited a ferruginous sediment. W. P. S.

**Solubility of Metals in Water.** VICENTE M. ISNARDI (*Anal. Soc. Quim. Argentina*, 1913, 1, 214—221).—The course of solution was traced by electrical-conductivity determinations, plates of metal 4 cm. long by 2 cm. wide being placed in contact with 70 c.c. of twice distilled water for ten, twenty, and thirty days at 18—22°, and for one, two, and three hours at 100°.

Tin and silver are the least soluble. Copper is more soluble than lead, although the latter is more corroded. The solution of lead is proportional to the time. In the case of zinc the solubility rises very rapidly after twenty days. G. D. L.

**Tendency of Haloids and Other Salts of the Same Metals to Combine.** Fluorides, Chlorides, and Carbonates. M. AMADORI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 366—372. Compare A., 1913, ii, 216).—The paper deals with the thermal analysis of the systems  $\text{NaF-Na}_2\text{CO}_3$ ,  $\text{KF-K}_2\text{CO}_3$ ,  $\text{NaCl-Na}_2\text{CO}_3$ , and  $\text{KCl-K}_2\text{CO}_3$ .

Sodium fluoride and sodium carbonate do not form any compound, and are not miscible in the solid state. There is an eutectic corresponding with 39 mol. % of sodium fluoride and 690°.

In the system  $\text{KF-K}_2\text{CO}_3$ , the curve of crystallisation of the carbonate descends to an eutectic at 688° (about 46 mol. % KF), and that of the fluoride to an eutectic at 682° (about 60 mol. % KF). Mixtures containing 46—60 mol. % KF solidify between these temperatures, a compound,  $\text{KF.K}_2\text{CO}_3$ , being formed which gives with the components two eutectics which melt almost at the same temperature as itself.

Sodium chloride and sodium carbonate do not form compounds, and are practically immiscible in the solid state. There is an eutectic at 636° and 59 mol. % NaCl.

The system  $\text{KCl-K}_2\text{CO}_3$  is analogous to the preceding; the eutectic temperature is  $636^\circ$ , corresponding with 65 mol. %  $\text{KCl}$ .

R. V. S.

**Crystalline Form of Cæsium and Rubidium Nitrates.** A. DUFFOUR (*Bull. Soc. franç. Min.*, 1913, 36, 136—143).—Crystals of cæsium nitrate crystallised from a solution containing also cæsium dichromate are of two habits: one as a hexagonal prism terminated by a hexagonal pyramid and much resembling crystals of quartz; the other as pseudo-cubic forms. The system is rhombohedral with the rhombohedral angle  $89^\circ 54'$ , and this pseudo-cubic form is further emphasised by twinning. Rubidium nitrate is orthorhombic with  $a:b:c=0.5789:1.07108$ , the angles here also being very near to those of cubic crystals. The two salts are isomorphous, and form mixed crystals. In both salts the double refraction is feeble, and at a lower temperature it disappears altogether, the crystals then being truly cubic. There is thus a passage from the orthorhombic through the rhombohedral to the cubic form. L. J. S.

**Ammonium Peroxide.** P. MELIKOV (*Ber.*, 1913, 46, 3899).—A correction to the communication of D'Ans and Wedig (*A.*, 1913, ii, 1051). The compound  $\text{NH}_4\text{O}_2\text{H}$  of these two authors is identical with the compound  $(\text{NH}_4)_2\text{O}_2\cdot\text{H}_2\text{O}_2$ , prepared by Melikov and Pissarievski.

T. S. P.

**The Hydrates of Silver Fluoride.** A. GUNTZ and A. A. GUNTZ, jun. (*Compt. rend.*, 1913, 157, 977—981).—A reply to Vanino and Sachs (compare *A.*, 1911, ii, 884), and a study of the conditions governing the formation of the various hydrates of silver fluoride. Their formation is dependent on the temperature, the content of the solution with respect to hydrofluoric acid, and is also a function of the nature of the saturated solution for a metastable or stable phase at the given temperature. The starting material was prepared by saturating concentrated hydrofluoric acid with freshly precipitated silver hydroxide, concentrating on a water-bath, filtering hot, and cooling. The crystals obtained were collected and dissolved in distilled water. On evaporating in a vacuum at  $10^\circ$  a neutral solution containing 120 grams of silver fluoride in 100 grams of water and suitably seeding the liquid, colourless, transparent, voluminous crystals of the hydrate,  $\text{AgF}\cdot 4\text{H}_2\text{O}$ , m. p.  $18.5^\circ$ , were obtained, having at  $13^\circ$  a heat of solution  $-4.93$  cal. Below  $18.5^\circ$  this is the only hydrate stable in neutral solution. A solution containing 170 grams of silver fluoride allowed to crystallise between  $18^\circ$  and  $38^\circ$  gives deliquescent prisms of a hydrate,  $\text{AgF}\cdot 2\text{H}_2\text{O}$ , m. p.  $42^\circ$ , decomposing to the anhydrous fluoride. Its heat of solution is  $-1.5$  cal. at  $10^\circ$ . The presence of hydrofluoric acid lowers the transition temperature of  $\text{AgF}\cdot 4\text{H}_2\text{O}$  to  $\text{AgF}\cdot 2\text{H}_2\text{O}$ , 5.5% of acid lowering it to  $0^\circ$ . On evaporating a neutral, saturated solution of silver fluoride at  $26-36^\circ$ , hard, highly refractive, slightly yellow, deliquescent crystals are obtained of a hydrate,  $\text{AgF}\cdot \text{H}_2\text{O}$ . The heat of solution of this hydrate is  $+0.85$  cal. at



10°. By repeating this crystallisation at the ordinary temperature there is formed round each nucleus of the monohydrate, voluminous, colourless rosettes of a hydrate,  $3\text{AgF}\cdot 5\text{H}_2\text{O}$ . Both the latter forms are unstable in the presence of crystals of  $\text{AgF}\cdot 2\text{H}_2\text{O}$ , giving this hydrate and anhydrous silver fluoride.

Each of these hydrates dried in a vacuum over sulphuric acid yields the anhydrous fluoride in an amorphous form. This can be obtained crystalline, in the form of ruby-red cubes, by evaporation, in a vacuum, of a solution of silver fluoride containing 5% of hydrofluoric acid. It has heat of solution 4.3 cal. at 16°.

Supersaturated solutions of the above hydrates attack silver more or less rapidly according to the temperature, giving crystalline silver subfluoride,  $\text{Ag}_2\text{F}$ .

W. G.

**Preparation of Metallic Chlorides and Sulphates in a Solid, Soluble Colloidal Condition.** LADISLAUS KARCZAG (D.R.-P. 263286).—Metallic chlorides or sulphates in a dry colloidal condition can be prepared by the action of thionyl chloride, sulphuryl chloride, or chlorosulphonic acid on the metallic salts of organic carboxylic acids; when calcium salicylate is warmed with thionyl chloride, the mixture divides into two separable layers, the under one consisting of colloidal calcium chloride, which can be finally isolated by the addition of ether and dried in a vacuum.

F. M. G. M.

**A Formation of Calcium Carbono-phosphate of the Paleolithic Age.** P. TEILHARD DE CHARDIN (*Compt. rend.*, 1913, 157, 1077—1079).—An account of a deposit of calcium phosphate in the grotto of Castillo (near Santander) exposed by excavations. The phosphate is found covering corroded calcite, and appears to be localised in a region of persistent dampness. Analyses are quoted showing its composition, and examination of the deposit shows the similarity both in site and mineralogical character between these phosphates and those of Quercy (compare Lacroix, A., 1910, ii, 622), and also the possibility of fixing a date for the commencement of the formation of these phosphates.

W. G.

**Crystallographic and Thermal Investigation of the Ternary System: Barium Chloride, Potassium Chloride, and Sodium Chloride.** HANS GEMSKY (*Jahrb. Min. Beil.-Bd.*, 1913, 36, 513—558).—The author has made a detailed examination of the equilibrium relationships characteristic of the above ternary system by means of cooling curves for liquid mixtures containing the three chlorides in different proportions and by the investigation of the crystallographic structures presented by the solid products.

The data obtained for the three pairs of binary systems indicate that barium chloride and potassium chloride form a compound of the formula  $\text{BaCl}_2\cdot 2\text{KCl}$ . The melting points recorded are: potassium chloride, 775°; barium chloride, 955°;  $\text{BaCl}_2\cdot 2\text{KCl}$ , 663°. The eutectic temperatures are 660° for  $\text{BaCl}_2\cdot 2\text{KCl} + \text{KCl}$  and 652° for  $\text{BaCl}_2\cdot 2\text{KCl} + \text{BaCl}_2$ . At 930° the singly refracting modification

of barium chloride which crystallises out at  $955^{\circ}$  is transformed into a doubly refracting form. This is the usual monoclinic modification, stable at ordinary temperatures.

Barium chloride and sodium chloride yield freezing-point curves which intersect at a point corresponding with 39 mols. % of barium chloride and a temperature of  $654^{\circ}$ .

Potassium chloride and sodium chloride form mixed crystals, and the freezing-point curve exhibits a minimum at about 50 mols. % of each constituent, the temperature of the minimum being  $660^{\circ}$ . On cooling the mixed crystals, they give rise to mixtures of potassium and sodium chloride at temperatures between  $300^{\circ}$  and  $400^{\circ}$ .

The data obtained in the investigation of mixtures containing all three chlorides indicate the existence of a ternary eutectic at about  $540^{\circ}$ . At this temperature the co-existing solid phases are barium chloride, the compound  $\text{BaCl}_2 \cdot 2\text{KCl}$ , and mixed crystals containing potassium and sodium chloride, which represent the limiting mixture for the sodium chloride end of the series. The limiting mixed crystals rich in potassium chloride are resorbed at a temperature higher than the eutectic.

H. M. D.

**Allotropy of Cadmium.** ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 485—489).—When cadmium is heated for a considerable time at  $70$ — $100^{\circ}$  in contact with a solution of cadmium sulphate, its density diminishes to a small but measurable extent. Observations with a dilatometer containing 360 grams of cadmium, which had been previously heated for twenty-four hours in contact with a solution of cadmium sulphate, have shown that this change in the density is due to an enantiotropic transformation which occurs at  $64.9^{\circ}$ . The observation affords an explanation of the disintegration which was found by Matthiessen and Bose to occur in cadmium wires heated at  $80^{\circ}$ .

H. M. D.

**Anhydrous Sulphates. VII. Cadmium Sulphate with Lithium, Sodium, and Potassium Sulphates.** G. CALCAGNI and D. MAROTTA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 373—379).—The m. p. of cadmium sulphate is  $1000^{\circ}$ , but there is a marked thermal effect at  $820^{\circ}$ , indicating a transformation at this temperature.

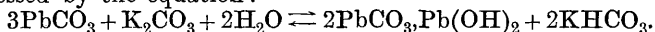
Cadmium sulphate and lithium sulphate behave like the other sulphates of bivalent metals hitherto described; there is an eutectic at  $551^{\circ}$  (45%  $\text{CdSO}_4$ ).

The reactions which occur between the solid components of the system  $\text{CdSO}_4$ — $\text{Na}_2\text{SO}_4$  are very complicated and numerous, and the diagram of the system differs entirely from that given for it by Le Chatelier (*Ann. des Mines*, 1897, [ix], **11**, 209). Three compounds are formed, namely,  $\text{CdSO}_4 \cdot 3\text{Na}_2\text{SO}_4$  (at  $351^{\circ}$ ),  $\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$  at ( $551^{\circ}$ ), and  $3\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$  (at  $746^{\circ}$ ). The compound  $\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$  shows a transformation at about  $496^{\circ}$ , and the compound  $3\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$  has a transformation point at about  $456^{\circ}$ .

R. V. S.

**The Behaviour of Lead Carbonate, Basic Lead Carbonate, and Lead Sulphate in Aqueous Solutions of Alkali Carbonates.** FRIEDRICH AUERBACH and HANS PICK (*Arb. Kais. Gesundh. Amt.*, 1913, 45, 113—165. Compare Pleissner, A., 1908, ii, 40; Herz, A., 1911, ii, 972).—In connexion with the fate of lead paints in the human body, the behaviour of lead carbonate, basic lead carbonate (white lead) and lead sulphate towards solutions of the alkali carbonates has been investigated.

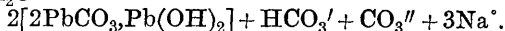
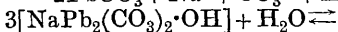
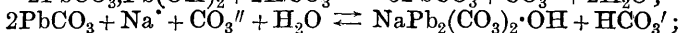
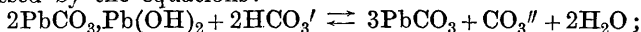
Lead carbonate is transformed into basic lead carbonate by solutions of potassium carbonate, whilst the basic carbonate is changed to the normal carbonate by the action of potassium hydrogen carbonate. These two reactions lead to the equilibrium expressed by the equation:



The ratio of the potassium carbonate to the potassium hydrogen carbonate concentration is displaced in the direction of higher carbonate concentration as the total alkali concentration increases, and in the direction of higher hydrogen carbonate concentration with increasing temperature.

The two lead carbonates behave similarly towards solutions of sodium carbonate and sodium hydrogen carbonate as long as the total sodium concentration does not exceed 0.077*N*. Above this concentration, a double salt, *basic sodium lead carbonate*,  $\text{NaPb}_2(\text{CO}_3)_2 \cdot \text{OH}$ , is formed, the stability of which increases with increasing sodium concentration. This salt is quite different in appearance from the normal and basic lead carbonates, being greyish-yellow in colour. The conditions necessary for its formation and decomposition were thoroughly investigated.

By experiments carried out at 18° and 37°, using solutions in which the total sodium concentration varied up to 0.25*N*, the existence domains of the two lead carbonates and of the double salt were ascertained, and the constants calculated for the equilibria expressed by the equations:



The constants had respectively the approximate values 32.5, 12, and 0.05 at 18°, the concentrations of the substances on the right-hand side of the above equation being in the numerator. From these results the dissociation pressure of carbon dioxide in the change from normal to basic lead carbonate was calculated to be about 0.1 mm. Hg at 18°. Also, from these results, the authors were able to devise methods for the preparation of pure basic lead carbonate and pure basic sodium lead carbonate.

Solutions of sodium carbonate and hydrogen carbonate, which also contain varying quantities of sodium sulphate, behave qualitatively towards normal and basic lead carbonate in the same way as sulphate-free solutions; quantitatively, the equilibrium concentrations are altered in a regular manner.

The formation of lead carbonate and a solution of sodium

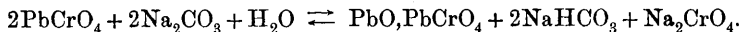
sulphate, by the action of a solution of sodium carbonate on lead sulphate, is not a direct reaction. Basic lead carbonate is first formed, and then basic sodium lead carbonate, which, in the presence of sufficient lead sulphate, is transformed into normal lead carbonate.

Lead sulphate and sodium hydrogen carbonate interact according to the equation:  $\text{PbSO}_4 + 2\text{NaHCO}_3 \rightleftharpoons \text{PbCO}_3 + \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$ , from which it follows that lead carbonate suspended in a solution of sodium sulphate can be transformed into lead sulphate by the action of carbon dioxide under pressure.

From the various equilibrium constants ascertained in the above experiments, the following solubility products (at  $18^\circ$ ) were calculated:  $[\text{Pb}^{++}][\text{CO}_3^{''}] = 10^{-13}$ ;  $[\text{Pb}^{++}]^3[\text{CO}_3^{''}]^2[\text{OH}']^2 = 3.5 \times 10^{-46}$ ;  $[\text{Pb}^{++}]^2[\text{Na}^{+}][\text{CO}_3^{''}]^2[\text{OH}'] = 10^{-81}$ . T. S. P.

**The Behaviour of Lead Chromate and Basic Lead Chromate in Aqueous Solutions of Alkali Carbonates.** FRIEDRICH AUERBACH and HANS PICK (*Arb. Kais. Gesundh.-Amt.*, 1913, **45**, 166—190. Compare Lehmann, *Arch. Hyg.*, 1893, **16**, 315; Golblum and Stoffella, A., 1910, ii, 698).—The authors have investigated the behaviour of lead chromate, basic lead chromate, and lead carbonate towards dilute solutions of sodium carbonate, sodium hydrogen carbonate, sodium chromate, and mixtures of the same.

In dilute solutions of sodium carbonate, the following equilibrium is formed:



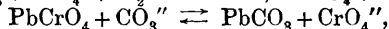
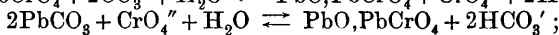
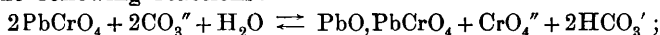
With increasing dilution and rise in temperature the equilibrium is displaced towards the right-hand side of the above equation. When the equilibrium is approached from the side of the basic lead chromate, exactly the same results are not obtained as from the side of the normal lead chromate, but this point was not further investigated.

The reversible reaction expressed by the equation:



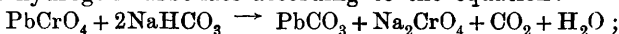
only takes place in the presence of considerable quantities of hydrogen carbonate in solution, otherwise basic lead chromate is formed.

The existence domains of the two lead chromates and of lead carbonate in solutions in which the total sodium concentration was  $0.05N$  and  $0.1N$  were ascertained at  $18^\circ$ ; the equilibrium constants for the following reactions:



were found to be respectively 0.057, 1.95, and 0.23, the concentrations of the substances on the right-hand side of the equations being in the numerator.

Lead chromate enters into reversible reaction with a solution of sodium hydrogen carbonate according to the equation:



equilibrium is attained at a much lower pressure of carbon dioxide than is the case with lead sulphate (compare preceding abstract).

The following solubility products at 18° were calculated from the various equilibrium constants:  $[\text{Pb}^{++}][\text{CrO}_4^{--}] = 2 \times 10^{-14}$ ;  $[\text{Pb}^{++}]^2[\text{CrO}_4^{--}][\text{OH}]^2 = 6 \times 10^{-35}$  (compare Beck and Stegmüller, A., 1910, ii, 1067). T. S. P.

**The Amount of Lead given up by Sparingly Soluble Lead Salts to Solutions containing Sodium Hydrogen Carbonate.** FRIEDRICH AUERBACH and HANS PICK (*Arb. Kais. Gesundh.-Amt.*, 1913, 45, 191—196).—Dilute solutions, 0.02*N* and 0.1*N*, of sodium hydrogen carbonate, which may also contain sodium chloride and free carbon dioxide, dissolve only 0.3—0.4 mg. of lead per litre when shaken up at 37° with lead carbonate, lead chromate, or basic lead chromate. It follows that injurious quantities of lead cannot be dissolved from the above compounds by the action of the pancreatic and intestinal juices in the human body. T. S. P.

**Alkaline Cuprothiosulphates.** PIERRE DUTOIT (*J. Chim. Phys.*, 1913, 11, 650—673).—The author has studied the titration of copper salts (nitrate and sulphate) by thiosulphates (sodium, potassium and calcium), making use of electrical conductivity, electric potential, and lowering of the freezing point of the solutions to determine the end points. The titrations are carried out in both ways, that is, adding the copper salt to the thiosulphate solution, and by adding the thiosulphate to the copper salt. It is shown that by all methods the titration is complete when 0.9 mol. of a copper salt has been added to 2 mols. of the thiosulphate, or when 2.2 mols. of thiosulphate has been added to 1 mol. of the copper salt. The author isolates from these reactions the salt,  $4\text{CuS}_2\text{O}_3 \cdot 3\text{Na}_2\text{S}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , which is the least soluble product formed. In the titrations two inflexion points are noted in the precipitation curves; the first is held to correspond with the formation of the complex  $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 9\text{M}_2\text{S}_2\text{O}_3$ , and the second to the complex  $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 5\text{M}_2\text{S}_2\text{O}_3$ . If the titration is carried out very slowly, it is possible to get products of the formula  $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{M}_2\text{S}_2\text{O}_3$ . In these salts the copper is shown to exist in the anion complex. J. F. S.

**The Chemical and Physical Nature of Colloidal Hydrrous Aluminate Silicates.** R. GANS (*Centr. Min.*, 1913, 699—712, 728—741).—Aluminate silicates, with the composition 3—4 mol.  $\text{SiO}_2$ , 1 mol.  $\text{Al}_2\text{O}_3$ , 1 mol. base ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ), are prepared by the action of a solution of alkali aluminate on silicic acid, but not by the interaction of alkali silicate and aluminium hydroxide. They are colloidal, and very readily dissociated, and resemble the zeolitic silicate of soils and the artificial product called permutite. Detailed arguments are given in favour of regarding them as definite chemical compounds rather than as adsorption compounds. L. J. S.

**Hypereutectic Alloys of Iron and Carbon.** H. HANEMANN (*Zeitsch. anorg. Chem.*, 1913, **84**, 1—23).—The investigation of Wittorf (A., 1912, ii, 259) leads to the assumption of several iron carbides,  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_4\text{C}$ ,  $\text{FeC}$ , and possibly  $\text{FeC}_2$ . The experiments are open to the objection that the optical examination of the surface in contact with carbon vapour did not give the correct temperature of the molten mass. In the present experiments, electrolytic iron and sugar charcoal are fused together, stirred with a carbon rod, and cast in iron chills, after observing the temperature by an optical pyrometer. The cementite contents, obtained by analysing the chilled specimens, give points which lie between the curves found by Wittorf and by Ruff (A., 1911, ii, 897). The higher the temperature the less accurate is the determination of these points, but the assumption of distinct breaks in the curve does not seem to be justified. On quenching from temperatures of  $1400^\circ$  and upwards, graphite is always present as a primary product, and not as a product of the decomposition of cementite. Microscopical examination shows that the cementite in quenched specimens crystallises radially from the centre, indicating that it is formed during cooling.

The mechanical separation of crystals from the mother liquor at a very high temperature, as in Wittorf's experiments, cannot be used to determine the composition of the solid phase, as the separation is always imperfect. Mixtures of molten iron and carbon become very viscous above  $1700^\circ$ , and heating to  $2500^\circ$  does not reduce the viscosity. At  $2500^\circ$  a quenched specimen contains nearly 14% of carbon, mostly as graphite entangled in the highly viscous liquid. During cooling the liquid becomes less viscous at  $1700^\circ$ . Ruff's conclusion, that the solubility of carbon again diminishes at very high temperatures, is not confirmed.

The dendrites, described by Wittorf as a carbide,  $\text{Fe}_4\text{C}$ , are shown to be austenite, as they are converted into martensite by cooling in liquid air and into pearlite by annealing. The supposed carbides,  $\text{FeC}$  and  $\text{FeC}_2$ , are both regarded as graphite. After treatment with nitric acid, the residual carbon is convertible into graphitic oxide, and does not contain amorphous carbon, as it would do if derived from a carbide.

C. H. D.

**Influence of Silicon on the Solubility of Carbon in Iron.** GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1913, **157**, 901—903. Compare A., 1913, ii, 602).—The authors have determined the solubility of carbon in samples of ferro-silicon, containing varying amounts of silicon, at temperatures varying from  $600^\circ$  to  $1000^\circ$ . The results show that silicon causes a gradual diminution in the solubility of carbon in iron, the solubility becoming practically nil at  $900^\circ$  if the silicon content is above 4%, and at  $1000^\circ$  if the silicon content exceeds 7%. At lower temperatures 2% of silicon suffices.

W. G.

**Some Hydrothermal Syntheses.** PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1913, **84**, 31—55. Compare Morey and Niggli, A., 1913, ii, 861).—A principal difficulty in hydrothermal syntheses is the

low velocity of reaction when amorphous (labile) substances are present. Such syntheses aim at the formation of those minerals which can exist at high temperatures in contact with aqueous solutions. Pressure is only used to maintain the system in the required condition. The products generally result from partial reactions in the amorphous mass, and so may contain metastable crystals.

The present preliminary syntheses do not therefore necessarily indicate the true stable phases. The apparatus used is that of Baur (A., 1911, ii, 991). The materials used are amorphous silica, potassium aluminate and silicate, and aluminium and ferric hydroxides. The minerals identified are: hæmatite, potassium ægirite, orthoclase, and potassium nepheline hydrate.

Hæmatite occurs in good, six-sided leaflets. Potassium-ægirite,  $K_2O, Fe_2O_3, 4SiO_2$  or  $KFeSi_2O_6$ , is not found in nature, whilst its sodium analogue has not yet been obtained synthetically. Another product, not definitely identified, may be an anhydrous potassium nepheline. Amorphous material is always present. At  $450^\circ$  hæmatite is obtained, together with aluminium feldspar free from iron. The presence of hæmatite in natural feldspars is not to be attributed to alteration, but to separation during cooling from an originally isomorphous mixture in which ferric iron replaces alumina. The conversion of minerals in eruptive rocks into analcite, zeolites, and muscovite corresponds with the hydrothermal changes during cooling.

C. H. D.

**Alterability and Instability of Cobaltamines.** NILRATAN DHAR (*Zeitsch. anorg. Chem.*, 1913, 84, 224—226).—Great care must be exercised in the preparation of the cobaltamines. The use of rather more dilute ammonia in the preparation of dinitrotetramminecobalt chloride than is prescribed in text-books leads to the formation of trinitrotetramminecobalt chloride, whilst an increase in the proportions of ammonia and ammonium chloride leads to the formation of nitropenta-amminecobalt chloride.

Carbonatotetra-amminecobalt nitrate,  $[Co(NH_3)_4CO_3]NO_3, \frac{1}{2}H_2O$ , is slowly decomposed by boiling with water.

C. H. D.

**Ternary Alloys of Nickel-Gold-Silver.** P. DE CESARIS (*Gazzetta*, 1913, 43, ii, 609—620).—These alloys have been investigated by methods similar to those used for nickel-copper-silver alloys (A., 1913, ii, 1061), similar results being obtained.

The mutual solubilities of nickel and gold at the eutectic temperature are somewhat higher than the values given by Levin (A., 1905, ii, 532), gold dissolving about 8% of nickel, and the latter about 20% of gold.

The space-diagram is described, and reproductions of microphotographs given.

T. H. P.

**The Neutralisation of Chromic Acid.** L. MARGAILLAN (*Compt. rend.*, 1913, 157, 994—995).—A study of the neutralisation of chromic acid by sodium hydroxide, the acidity of the solution

being measured by determining the *E.M.F.* of a pile in which intervenes the half element hydrogenised platinum|solution, the other half being mercury|calomel|*N*/10-HCl. The curves given show, by sudden alteration in direction, the two acid functions of chromic acid; these two points on the curves correspond with the end points obtained with helianthine and phenolphthalein as indicators respectively.

W. G.

**Iso- and Hetero-poly-salts. IX. Molybdo-phosphites, -hypophosphites, and -hypophosphates.** ARTHUR ROSENHEIM, WALTER WEINBERG, and JAKOB PINSKER (*Zeitsch. anorg. Chem.*, 1913, **84**, 217—223. Compare A., 1913, i, 413).—The oxygen atoms of the alkylarsinic acids are replaceable by  $\text{MoO}_4$  or  $\text{Mo}_2\text{O}_7$  residues, and the more alkylated the acid the smaller the number of molybdic residues taken into the compound. Alkylphosphinic acids are difficult to prepare, but phosphorous and hypophosphorous acids may be regarded as derived from them by the replacement of alkyl by hydrogen.

An acid solution of ammonium molybdate is precipitated by phosphorous acid, and the yellow, crystalline precipitate, which has the composition  $(\text{NH}_4)_2[\text{HP}(\text{Mo}_2\text{O}_7)_3] \cdot 2\text{H}_2\text{O}$ , may be used as a delicate test for phosphorous acid. The *sodium* salt,  $\text{Na}_2[\text{HP}(\text{Mo}_2\text{O}_7)_3] \cdot 11\text{H}_2\text{O}$ , is slightly more soluble. It loses all its water at  $110^\circ$ . Conductivity measurements show the absence of an acid salt, and the salts must be regarded as containing the anion  $\left[ \text{P}(\text{Mo}_2\text{O}_7)_3 \right]^-$ . The acid, like phosphorous acid, is dibasic. The *potassium* salt is  $\text{K}_2[\text{HP}(\text{Mo}_2\text{O}_7)_3] \cdot 11\text{H}_2\text{O}$ , and the *guanidinium* salt,  $(\text{CN}_3\text{H}_6)_2[\text{HP}(\text{Mo}_2\text{O}_7)_3]$ .

Corresponding tungsten compounds have not been obtained, the tungsten salts being tribasic, as  $\text{Na}_3[\text{P}(\text{W}_2\text{O}_7)_3] \cdot 16\text{H}_2\text{O}$ .

*Guanidinium molybdoarsenite*,  $(\text{CN}_3\text{H}_6)_3[\text{As}(\text{Mo}_2\text{O}_7)_3] \cdot \text{H}_2\text{O}$ , has a similar constitution.

A mixture of sodium hypophosphite (1 mol.) and sodium molybdate (4 mols.) gives precipitates with ammonium, potassium, or guanidinium chloride. The ammonium salt has the composition  $\text{NH}_4[\text{H}_2\text{P}(\text{Mo}_2\text{O}_7)_2] \cdot 6\text{H}_2\text{O}$ , and these salts may be regarded as derived from the hypophosphite anion  $\left[ \text{P}(\text{O})_3\text{H}_2 \right]^-$  by replacement of oxygen atoms by molybdic acid residues.

Sodium hypophosphate,  $\text{NaHPO}_3 \cdot 2\text{H}_2\text{O}$  (1 mol.), sodium hydroxide (1 mol.), and molybdic acid (6 mols.) yield a yellow, crystalline *sodium* salt,  $\text{Na}_2[\text{P}(\text{Mo}_2\text{O}_7)_3] \cdot 8\text{H}_2\text{O}$ . C. H. D.

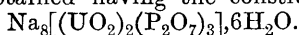
**Complex Salts of Uranium.** PAUL PASCAL (*Compt. rend.*, 1913, **157**, 932—934).—A large number of uranyl salts can be converted into complex salts by the addition of the corresponding alkali salts, and, according to the acid radicle, they possess one of two constitutions:  $\text{M}_4[\text{UO}_2\text{X}_6]$  and  $\text{M}_2[\text{UO}_2\text{X}_4]$ .

The first type, where the bivalent radicle  $\text{UO}_2$  possesses the maximum index of co-ordination, is always very stable, resisting hydrolysis and having the reactions of uranium completely masked.



The second type behaves in dilute solution as a double salt, and to check dissociation a large excess of the corresponding alkali salt is often necessary. The author has studied the pyrophosphates and the cyanates.

On dissolving uranyl pyrophosphate in sodium pyrophosphate solution, the freezing point rises to a maximum corresponding with  $3\text{Na}_4\text{P}_2\text{O}_7, (\text{UO}_2)_2\text{P}_2\text{O}_7$ , and then descends to a minimum at  $2\text{Na}_4\text{P}_2\text{O}_7, (\text{UO}_2)_2\text{P}_2\text{O}_7$ , up to which stage the characteristic reactions of uranyl salts are not obtainable. If this solution is evaporated and the gummy residue treated with alcohol, a very soluble, hygroscopic powder is obtained having the constitution:



From a solution of sodium pyrophosphate saturated with uranyl pyrophosphate there is precipitated by alcohol a yellow powder,  $\text{Na}_6\text{UO}_2[(\text{UO}_2)_2(\text{P}_2\text{O}_7)_3] \cdot n\text{H}_2\text{O}$ , which rapidly passes into  $\text{Na}_2(\text{UO}_2)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , insoluble in water.

A mixture of alcoholic solutions of potassium and uranyl cyanates gives a microcrystalline precipitate, having the constitution  $\text{K}_2[\text{UO}_2(\text{CNO})_4]$ , very soluble in water, gradually dissolving in this solvent to yield an anhydrous, orange-yellow double salt,  $\text{KCNO} \cdot 2\text{UO}_2(\text{CNO})_2$ . An excess of alkali cyanate added to the preceding solution gives a golden-yellow precipitate of a double salt,  $\text{KCNO} \cdot \text{UO}_2(\text{CNO})_2$ , whilst an excess of uranyl cyanate in slightly alcoholic solution precipitates anhydrous uranyl cyanate as a golden-yellow powder,  $\text{UO}_2(\text{CNO})_2$ . W. G.

**The Isomerism of the Stannic Acids. III.** WERNER MECKLENBURG (*Zeitsch. anorg. Chem.*, 1913, **84**, 121—143. Compare A., 1912, ii, 355).—The peptonisation of a stannic acid preparation does not depend directly on the size of its primary particles.

Readily peptonised preparations are obtained by using nitric acid containing hydrochloric acid. The greater the concentration of the nitric, and the less that of the hydrochloric acid, the more completely gelatinised is the precipitate. Hydrochloric acid also lessens the oxidation, causing the product to contain stannous as well as stannic compounds, but in more concentrated solutions the quantity of stannous compound formed is less. If a solution containing stannous salts is heated on the water-bath, complete oxidation to the stannic condition takes place violently. The precipitate has sometimes a crystalline appearance, but cannot be recognised as crystalline under the microscope.

The peptonising action of the reagents examined on the same stannic acid precipitate decreases in the order  $2\text{NHCl} \rightarrow 22\%\text{HCl} \rightarrow 2\text{NHNO}_3 \rightarrow \text{alcohol} \rightarrow \text{NH}_2\text{SO}_4 \rightarrow \text{water} \rightarrow \text{ether}$ . The preparations have not shown any considerable change in four years.

The colloidal solutions obtained by peptonisation have been examined by Tyndall's method. Hydrochloric acid favours the formation of fine particles. The precipitate contains adsorbed hydrochloric acid. The protective action of this electrolyte closely resembles that of a protective colloid. Alkali hydroxide is also a protective electrolyte. C. H. D.

**Zirconium Hypophosphite, a Zirconium Salt Sensitive to Light.** O. HAUSER and H. HERZFELD (*Zeitsch. anorg. Chem.*, 1913, **84**, 92—94).—*Zirconium phosphite*,  $\text{Zr}(\text{PO}_3)_2 \cdot \text{H}_2\text{O}$ , is readily obtained by precipitation.

*Zirconium hypophosphite*,  $\text{Zr}(\text{OPH}_2\text{O})_4 \cdot \text{H}_2\text{O}$ , is obtained by adding hypophosphorous acid to a solution of zirconium nitrate until the precipitate has completely redissolved, and then adding alcohol. It forms colourless, highly refracting crystals, which become deep violet very rapidly in direct sunlight, or in the course of several weeks in diffused daylight, without any other perceptible change.

C. H. D.

**Organosols of Metals of the Platinum Group.** CONRAD AMBERGER (*Kolloid-Zeitsch.*, 1913, **13**, 310—313. Compare A., 1912, ii, 1053, 1059).—The preparation of organosols of metallic palladium and platinum is described, in which lanolin plays the part of a protective colloid. The lanolin is impregnated with aqueous solutions of salts of bivalent platinum or palladium, and the resulting paste triturated with the calculated quantity of alkali metal hydroxide or carbonate. The hydroxides of the platinum metals are then reduced by addition of hydrazine hydrate. On treatment with light petroleum or chloroform, the palladium or platinum dissolves, together with the lanolin, and the colloidal metals can be precipitated from these solutions by the addition of alcohol. Since only a portion of the lanolin separates out on the addition of alcohol, this process serves for the concentration of the metal in the preparation. The pasty, black substances which are obtained in this way dissolve very readily in chloroform and carbon tetrachloride, and are also readily soluble in ethyl ether, light petroleum, liquid paraffin, and fatty oils. The liquid organosols appear to be quite transparent when examined in a very thin layer

H. M. D.

**Organosols of the Hydroxides of Bivalent Platinum and Palladium.** CONRAD AMBERGER (*Kolloid-Zeitsch.*, 1913, **13**, 313—317. Compare preceding abstract).—Colloidal hydroxides of platinum and palladium in admixture with lanolin as protective colloid have been prepared by the method described in the previous paper. In this case the addition of hydrazine hydrate is omitted. The pasty substances obtained are readily soluble in light petroleum and other organic liquids which dissolve lanolin. The solution of palladium hydroxide in liquid paraffin has found therapeutic application in the treatment of obesity.

The preparation of a palladium oleate organosol is also described. The only modification of the process consists in the substitution of potassium oleate for the hydroxide or carbonate. H. M. D.

## Mineralogical Chemistry.

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**Water and the Volcanic Gases.** ARTHUR L. DAY and E. S. SHEPHERD (*Compt. rend.*, 1913, 157, 958—961).—A study of the volcanic gases collected from the crater of Kilauea during the summer of 1912. Contrary to the results recorded by Brun (compare *Recherches exhalaison volcanique*, 1911), the authors obtained abundant evidence of the presence of water in these gases, by inserting a collecting tube into crevices in the lava, behind the flames, and withdrawing a sample by means of a pump. The gases collected consisted mainly of carbon dioxide and sulphur dioxide, with small quantities of carbon monoxide, hydrogen, and nitrogen. The water condensed in the sample tube was found to contain fluorine, chlorine, sodium, potassium, calcium, iron, and aluminium in the form of dissolved salts, and free sulphur, but no titanium.

W. G.

**Conclusions to be Drawn from the Analysis of the Gases from the Crater of Kilauea.** ARTHUR L. DAY and E. S. SHEPHERD (*Compt. rend.*, 1913, 157, 1027—1030. Compare preceding abstract).—In the gases as collected, analysis reveals the presence of gases which are unable to co-exist at a temperature equal to or above 1000°. Consequently reactions will take place, particularly at the surface, with the development of heat, and the authors have found temperature variations of as much as 115°. The gases exhaled undoubtedly contain water, 300 c.c. having been condensed in the experimental tubes. The visible volcanic cloud is constituted essentially by free sulphur, and not by chlorides, and contains both sulphur dioxide and sulphur trioxide. The analyses of the gases show that the chlorine content is less than 0.02%. The nitrogen collected contains no argon, this being further proof of the absence of atmospheric contamination.

W. G.

**Bournonite from St. Kreuz, Alsace.** HUGO BÜCKING (*Mitt. Geol. Landesanst. Elsass-Lothringen*, 1913, 8, 201—213).—Crystallographic descriptions are given of bournonite and xanthoconite from St. Kreuz near Markirch. Analysis by L. Dürr of the bournonite gave:

Pb.	Cu.	Sb.	S.	Total.	Sp. gr.
43.35	12.86	24.53	19.17	99.91	5.81

L. J. S.

**Dolomite (variety Miemite) from Croatia.** FR. TUČAN (*Jahrb. Min.*, 1913, ii, *Ref.* 377—378; from *Soc. Sci. Nat. Croat.*, 1913, 25, 194).—The miemite variety of dolomite (anal. I), long known from Croatia, occurs as small veins in serpentine and trachyte at Mount Fruska. It is pale green with a pisolitic structure. The pisolites measure up to 5 cm. across, and have polyhedral outlines; in cross-

section they show a concentric structure, and usually a nucleus of decomposed dacite, but in one instance of magnesite (anal. II). Occasionally the mineral occurs as masses with a banded structure III.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	NiO	MnO	CaO	MgO	CO <sub>2</sub>	H <sub>2</sub> O	Total
I.	0.28	0.18	—	3.17	0.23	0.12	30.01	17.63	47.58	—	99.20
II.	0.79	0.01	3.62	1.03	—	trace	6.04	39.80	48.71	0.63	100.63
III.	2.53	0.38	—	1.21	trace	trace	29.58	20.28	45.56	—	99.54

L. J. S.

**Cerussite from Otavi, German South-West Africa.** HEDWIG DÜBIGK (*Diss. Münster, i. W.*, 1913; *Jahrb. Min., Beil.-Bd.*, 1913, **36**, 214—246).—A brief account is given of the deposits of copper and lead ores in the Otavi Mountains. Beautifully crystallised specimens of cerussite from Tsumeb show associated malachite and chessylite on a matrix of aplite and cellular dolomite. The axial ratios of the crystals are:  $a:b:c=0.610160:1:0.723182$ . Refractive indices (Na-light),  $\alpha=1.80258$ ,  $\beta=2.07420$ ,  $\gamma=2.07618$ . The optic axial angle increases with the temperature,  $2E(\text{Na})$  at  $25^\circ$  being  $17^\circ 50'$ , and at  $180^\circ$  the value is  $22^\circ 45'$ . Analysis of pure crystals gave:

PbO.	CO <sub>2</sub> .	Insol.	Total.
83.27	16.64	0.24	100.15

L. J. S.

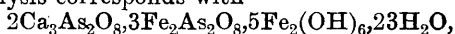
**Natural Chilean Aluminium Sulphate.** ATELIO A. BADO (*Anal. Soc. Quim. Argentina*, 1913, **1**, 129—130).—Keramohalite or alunogen, occurring as a white, fibrous mass soluble in water, gave on analysis:

Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	SO <sub>3</sub> .	H <sub>2</sub> O.	Total.
17.76	0.05	0.04	37.38	44.77	100.00

agreeing with the formula  $\text{Al}_2\text{O}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

G. D. L.

**Yukonite, a New Hydrous Arsenate of Iron and Calcium from Yukon, Canada.** JOSEPH B. TYRRELL and RICHARD P. D. GRAHAM (*Trans. Roy. Soc. Canada*, 1913, [3], **7**, sect. 4).—The mineral described occurs as small, irregular masses with oxidised galena in a quartz-vein near Tagish Lake in the southern portion of Yukon territory. It is brownish-black, resinous, and amorphous, breaking with a smooth, conchoidal fracture, thus resembling pitticite in appearance. It is very brittle, and under water it breaks up with a crackling noise, giving off a considerable quantity of gas, which consists mainly of carbon dioxide. Whilst immersed in water D increases from 2.65 to 2.86. The mineral is completely soluble in hydrochloric acid, and it fuses readily to a black, magnetic globule, giving off fumes of arsenic oxide. About half of the total water is lost in a vacuum or at  $100^\circ$ , whilst the remainder is expelled only at a high temperature, together with some arsenic oxide. The following analysis corresponds with



or nearly  $(\text{Ca}_3, \text{Fe}_2)\text{As}_2\text{O}_8, \text{Fe}_2(\text{OH})_6, 5\text{H}_2\text{O}$ . This composition is similar to that of arseniosiderite with the addition of water.

CaO.	Fe <sub>2</sub> O <sub>3</sub> .	As <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.
10.07	36.26	33.94	20.28	100.55

Coating the yukonite is a yellow, ochreous material of apparently the same composition, and embedded in this are small, green fibres of symplectite.

L. J. S.

**Anthophyllite from Elba.** GIOVANNI D'ACHIARDI (*Jahrb. Min.*, 1913, ii, *Ref.* 381; from *Proc. Verb. Soc. Toscana Sci. Nat.*, 1912, Reprint 5 pp.).—Radially-fibrous anthophyllite with a silky lustre and salmon colour is found in quantity in the magnesite mine at San Piero in Campo. It exhibits all the characters of an orthorhombic amphibole. Analysis agrees with  $(\text{Mg}, \text{Fe})\text{SiO}_3$ .

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	Na <sub>2</sub> O.	(at 160°).	H <sub>2</sub> O (ign.).	Total.	Sp. gr.
58.75	1.27	5.60	31.53	0.51	0.25	1.70	99.61	2.95

L. J. S.

**Tremolite from Elba.** PIERO ALOISI (*Jahrb. Min.*, 1913, ii, *Ref.* 382; from *Proc. Verb. Soc. Toscana Sci. Nat.*, 1912, Reprint 4 pp.).—Fibrous to columnar tremolite fills crevices in peridotite on Monte Perone. Analysis gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
54.21	0.74	2.22	13.56	24.86	1.10	0.35	2.54	99.58

L. J. S.

**Magnesia-Tourmalines.** KARL BECHT (*Diss. Heidelberg*, 1913, 1—75); ERNST A. WÜLFING and KARL BECHT (*Sitz.-Ber. Heidelberger Akad. Wiss.*, 1913, A, Abh. 20, 1—10).—Determinations were made of the crystallographic and optical constants of a number of brown magnesia-tourmalines. Analyses, by M. Dittrich, are given of the following: I, yellowish-brown from Macomb, New York; II, dark brown from Post Sonjo, East Africa; III, pale brown from Ceylon; IV, medium brown from Ceylon; V, dark brown from Ceylon:

	B <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	Ti <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	Na <sub>2</sub> O.	Li <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	F.	Total.	Sp. gr.
I.	10.25	37.05	0.56	28.61	0.44	1.31	13.66	2.97	1.45	—	0.31	3.05	1.23	100.89	3.066
II.	11.11	36.98	0.02	32.77	—	3.85	9.59	0.26	1.42	—	0.19	2.98	0.14	99.31	3.055
III. [11.36]	35.46	—	—	29.58	—	0.45	14.04	5.13	0.23	n.d.	0.20	3.55	n.d.	100.00	3.059
IV. [10.57]	36.51	n.d.	—	30.00	—	0.74	12.84	3.91	0.72	n.d.	0.54	4.17	n.d.	100.00	3.059
V.	11.47	35.15	3.43	25.30	1.07	5.21	10.16	3.07	0.83	0.15	0.28	2.88	0.12	100.22	3.142

The composition is expressed as the isomorphous mixing of the three molecules:  $\text{Si}_{12}\text{B}_6\text{Al}_{16}\text{Na}_4\text{H}_8\text{O}_{63}$ ,  $\text{Si}_{12}\text{B}_6\text{Al}_{12}\text{Fe}_8\text{H}_8\text{O}_{63}$ , and  $\text{Si}_{12}\text{B}_6\text{Al}_{10}\text{Mg}_{12}\text{H}_6\text{O}_{63}$  (A., 1913, ii, 718). Tables are given showing the variation of the crystallographic and optical constants with the density of the chemical composition.

L. J. S.

**Calcium-iron Garnet from China.** JOHN B. SCRIVENOR (*Min. Mag.*, 1913, 17, 51—52).—The samples examined have the form of a pale green sand obtained as a concentrate from the Yong Choon district in province Kwang Tung. Mixed with it are small quantities of malachite, calcite, quartz, etc. The grains are optically

isotropic, and occasionally show cubic forms. The mineral is attacked by cold hydrochloric acid, and when powdered it is readily and completely decomposed by hot acid. Analysis of a cleaned sample gave:

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on ignition.	Total.	Sp. gr.
40.26	28.62	2.61	28.29	trace	0.94	100.72	3.69

proving the mineral to be andradite, but the fact that it is so readily decomposed by acid before ignition is remarkable for a garnet.

L. J. S.

**Hodgkinsonite, a New Mineral from Franklin Furnace, New Jersey.** C. PALACHE and W. T. SCHALLER (*J. Washington Acad. Sci.*, 1913, 3, 474—478).—This occurs, together with barytes and native copper, in films and thin seams in the granular willemite-franklinite ore. It is bright pink to pale reddish-brown, with a vitreous lustre and white streak. D 3.91, H nearly 5. The crystals are monoclinic ( $a:b:c=1.539:1:1.1165$ ;  $\beta=84^{\circ}33\frac{1}{2}'$ ) with an acute pyramidal habit and a perfect basal cleavage. The optic axial plane is parallel to the plane of symmetry, and the mean refractive index is 1.73. The mineral decrepitates when heated, and fuses to a brown enamel; no water is lost at 110°. It is readily soluble in acid, yielding gelatinous silica. Analysis gives the formula  $3\text{RO}, \text{SiO}_2, \text{H}_2\text{O}$ , or nearly  $\text{MnO}, 2\text{ZnO}, \text{SiO}_2, \text{H}_2\text{O}$ , or  $\text{Mn}(\text{ZnOH})_2\text{SiO}_4$ .

SiO <sub>2</sub> .	MnO.	ZnO.	CaO.	MgO.	H <sub>2</sub> O.	Total.
19.86	20.68	52.93	0.93	0.04	5.77	100.21

L. J. S.

**Presence of Manganese, Cobalt, and Nickel in Coloured Clays.** L. AZEMA (*Bull. Soc. franç. Min.*, 1913, 36, 133—135).—The minerals examined include montmorillonite from Bordes (A., 1913, ii, 784) and other French localities and from Branchville, Connecticut; also delanouite, dubuissonite, and landevanite. All these contain traces of manganese, and with the exception of montmorillonite from Branchville and landevanite, also traces of cobalt and nickel. These coloured clays usually occur in proximity to deposits of manganese ores. Psilomelane from various French localities was found to contain, besides cobalt, also appreciable traces of nickel.

L. J. S.

**Meteoric Stones of Baroti, India, and Wittekrantz, South Africa.** GEORGE T. PRIOR (*Min. Mag.*, 1913, 17, 22—32).—A meteorite fell at Baroti, Bilaspur district, Punjab, on September 15th, 1910, and several fragments of the stone, the largest weighing  $4\frac{1}{4}$  lbs., were collected. D 3.54. A few chondrules are visible. From analyses of the portions of the powdered stone attracted and unattracted by a magnetic comb, the bulk-analysis I is deduced. A partial analysis of the soluble silicate in the unattracted portion

gave  $3\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4$  as the composition of the olivine. The mineral composition is under Ia:

Metallic.			FeS.		SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .
Fe.	Ni.	Co.	Fe.	S.					
I. 8.13	0.75	0.03	4.32	2.47	39.68	0.16	2.40	0.44	0.18
II. 7.65	0.75	0.02	2.20	1.26	41.12	0.17	2.54	0.48	0.36
FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.	
I. 13.99	trace	1.79	24.71	0.91	0.04	0.25	0.17	100.42	
II. 14.51	0.15	2.12	25.40	1.16	0.14	0.16	0.16	100.35	
Felspar.	Magnet-ite.	Chrom-ite.	Apat-ite?	Bronzite.	Oli-vine.	Troil-ite.	Nickel-iron.	Water.	
Ia. 10.25	0.63	0.31	0.27	0.56	30.38	42.12	6.79	8.91	0.17
Ila. 11.95	0.70	0.32	0.52	0.37	26.89	47.42	3.46	8.42	0.16

The meteoric stone of Wittekrantz, Beaufort West, Cape Colony, fell on December 9th, 1880, and fragments weighing  $4\frac{1}{2}$  lbs. and 113 grams were preserved. D 349. Chondrules are few. Bulk-analysis (combined result of the analyses of the attracted and unattracted portions) under II, and the mineral composition under IIa. The olivine has the composition  $3\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4$ . L. J. S.

**The Remarkable Similarity in Chemical and Mineral Composition of Chondritic Meteoric Stones.** GEORGE T. PRIOR (*Min. Mag.*, 1913, 17, 33—38).—The close similarity between the Baroti and Wittekrantz meteorites (preceding abstract) suggested a comparison with other chondritic meteoric stones, and the results of previously-published analyses of forty-one such stones are tabulated. The mineral composition approximates in all cases to the following mean value:

Nickel-iron (with Fe:Ni=10:1).	Troilite.	Olivine (with Mg:Fe=3:1).	Bronzite (with Mg:Fe=4:1).	Felspar (oligoclase).	Chromite. etc.
9	6	44	30	10	1%

Although so similar in chemical and mineral composition these stones have been assigned to a number of different groups in the Brezina and quantitative rock classifications (A., 1912, ii, 361), the differences in the latter case being due to errors in analysis, more especially with regard to the allotment of the iron as metal, as oxide, or as sulphide. L. J. S.

**Mineral Water from Deutsch-Jassnik, Moravia.** M. GLÄSER (*Tsch. Min. Petr. Mitt.*, 1912, [i.e. 1913], 31, 659—662).—Detailed analyses are given of the water from two springs. They show 1.3056 and 2.8801 grams  $\text{Ca}(\text{HCO}_3)_2$ , 22.6984 and 24.1074 grams free carbon dioxide respectively, together with small amounts of other substances, in 10,000 grams of water. L. J. S.

## Analytical Chemistry.

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**The Foundations of Acidimetry and Alkalimetry.** A. THIEL (*Ber. Deut. Pharm. Ges.*, 1913, 23, 578—596).—A criticism of the views put forward by Crato (*A.*, 1913, ii, 665). The author also gives an account of the interpretation, which is afforded by the ionic theory, of the behaviour of indicators in the volumetric estimation of acids and bases.  
H. M. D.

**Physico-chemical Volumetric Analyses.** DOMINGA C. LANZA (*Anal. Soc. Quim. Argentina*, 1913, 1, 200—214).—The course of neutralisation is followed by means of measurements of conductivity. Figures are quoted for a mixture of hydrochloric and acetic acids, sulphuric acid, zinc chloride, and morphine hydrochloride.  
G. D. L.

**Pyro-analysis of Drugs.** L. ROSENTHALER (*Ber. Deut. Pharm. Ges.*, 1913, 23, 577. Compare *A.*, 1911, ii, 948).—A piece of apparatus for use in this method is described. The drug is placed at the bottom of a test-tube, and covered with a layer of glass-wool; a tube, slightly smaller in diameter than the test-tube, is inserted in the latter, the lower end of the tube resting on the layer of glass-wool, whilst the upper end is connected with an exhaust pump. A piece of rubber tubing slipped over the tube forms an air-tight joint between the mouth of the test-tube and the tube. The sublimate formed collects in the tube when the air is exhausted from the apparatus.  
W. P. S.

***o*-Tolidine as a Reagent for the Colorimetric Estimation of Small Quantities of Free Chlorine.** J. W. ELLMS and S. J. HAUSER (*J. Ind. Eng. Chem.*, 1913, 5, 914—917).—A hydrochloric acid solution of *o*-tolidine yields a yellow coloration with small quantities of free chlorine, and the reaction may be used for the estimation of the latter in water which has been treated with the gas. The coloration develops in about three minutes, is permanent for at least thirty minutes, and is not affected by the presence of the salts usually present in drinking waters. One hundred c.c. of the water are treated with 1 c.c. of a 0.1% *o*-tolidine solution in 10% hydrochloric acid, and, after five minutes, the coloration obtained is compared with that produced by known quantities of chlorine under similar conditions. The coloration may be obtained in as small a quantity of chlorine as 0.005 part per million.  
W. P. S.

**Estimation of Chlorine in the Blood.** H. ROGÉE and C. FRITSCH (*Biochem. Zeitsch.*, 1913, 58, 175—176).—Polemical. A reply to Bang's criticisms of the authors' method (*A.*, 1913, ii, 872).  
S. B. S.



**Iodometric Estimation of Iodine Present as Iodide.** ERICH MULLER and GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 1913, 53, 20—28).—When excess of potassium iodate is added to an acid solution of an iodide, the iodine liberated conglomerates, and is difficult to titrate. By the following device accurate results can be obtained.

The solution to be tested is placed in a stoppered bottle, 10 c.c. of 10% sulphuric acid are added, and the liquid is covered with a layer of benzene. After adding excess of potassium iodate and thorough shaking, a solution of 4 grams of anhydrous borax in water is added, and finally 3 grams of potassium iodide (not strictly necessary, however). The iodine is now titrated by means of *N*/10-arsenious acid with constant shaking. Thiosulphate should not be employed.

L. DE K.

**Estimation of the Sulphates in Wine by a Physico-chemical Volumetric Method.** PAUL DUTOIT and MARCEL DUBOUX (*Bull. Soc. chim.*, 1913, [iv], 13, 1068—1074).—A reply to Bruno and Turquand d'Auzay (compare *Bull. Soc. chim.*, 1913, [iv], 13, 24), in which the authors reaffirm the accuracy of their physicochemical volumetric method for estimating sulphates in wines, by the use of barium hydroxide (compare A., 1908, ii, 781, 892).

W. G.

**Estimation of Total Sulphurous Acid in Wine.** L. LÉVY (*Ann. Falsif.*, 1913, 6, 595).—The method depends on the oxidation of sulphur dioxide by hydrogen peroxide. Fifty c.c. of the wine are mixed in a stoppered flask with 2 grams of barium peroxide; after eighteen hours' contact, hydrochloric acid is run in until bubbles of gas are no longer evolved, ammonium chloride is added, the mixture boiled, and the barium sulphate collected, ignited, and weighed. The quantity of sulphate present in the wine is estimated in a separate portion of the sample, and the difference between the two estimations is calculated into sulphur dioxide.

W. P. S.

**New Method for the Volumetric Estimation of Thiosulphate in the Presence of Sulphite.** J. BODNÁR (*Zeitsch. anal. Chem.*, 1913, 53, 37—41).—The process is based on the fact that thio-sulphates when treated with silver nitrate yield in the end silver sulphide and free sulphuric acid. After removing the excess of silver by means of sodium chloride the acidity can be determined by standard alkali.

Sulphites do not interfere.

L. DE K.

**Detection and Estimation of Minute Traces of Selenious Acid.** JULIUS MEYER and WILHELM VON GARN (*Zeitsch. anal. Chem.*, 1913, 53, 29—33. Compare A., 1913, ii, 948).—Into two cylinders are put 5 c.c. of the solution to be tested and 5 c.c. of a solution of selenious acid of approximately the same strength respectively; 70 c.c. of water are added, also a drop of gum arabic and 5 c.c. of

5% hydrochloric acid, and then the whole is diluted to 99 c.c. After adding to each tube 1 c.c. of potassium iodide solution and stirring vigorously, the colorations, which are due to iodine and to colloidal selenium, are, after five minutes, compared in a Krüss colorimeter. Addition of starch solutions may be useful.

L. DE K.

**Comparison of the Kjeldahl-Gunning-Arnold Method with the Kjeldahl and Gunning Methods of Estimating Nitrogen.** T. C. TRESCOT (*J. Ind. Eng. Chem.*, 1913, 5, 914—915).—The Kjeldahl-Gunning-Arnold method was found to yield more trustworthy results than the Kjeldahl or Gunning methods. W. P. S.

**Apparatus for Use in the Estimation of Nitrogen in Soils by Kjeldahl's Method.** ALBERT HUTIN (*Ann. Chim. anal.*, 1913, 18, 426—428).—Owing to the small quantity of nitrogen present in soils, a relatively large portion of the sample must be taken for the estimation, and the insoluble substances (sand, etc.) remaining after the digestion cause difficulties to arise in the subsequent distillation of the ammonia. It is, therefore, recommended that the acid digestion mixture should be transferred to a flask and steam-distilled after the addition of sodium hydroxide. The flask is closed with a rubber stopper, through which pass the stem of a tapped funnel, a tube for the introduction of superheated steam, a delivery tube which is connected with a condenser, and a tube reaching to the bottom of the flask; the outer end of the latter tube is connected with a pump, so that the contents of the flask may be withdrawn at the end of the distillation. W. P. S.

**Apparatus for Use in the Distillation of Ammonia in Kjeldahl's Method.** EMM. POZZI-ESCOT (*Bull. Assoc. Chim. Sucr. Dist.*, 1913, 31, 235—236).—A description of a still-head is given; it consists of an elongated bulb provided with a stem, which passes through the stopper of the distillation flask. This stem extends upwards into the bulb itself, and is then bent downwards in the form of a spiral. The vapours from the flask pass through the spiral, then enter the bulb, and leave the latter by a tube at the top. Any alkaline spray escaping from the flask is effectually collected at the lower part of the bulb, and returns with other condensed liquid to the flask, a narrow tube, leading from the bottom of the bulb and passing down the centre of the stem, being provided for this purpose. W. P. S.

**Iodometric Estimation of Arsenic in Iron and in Iron Ores after Precipitation with Hypophosphorous Acid.** L. BRANDT (*Chem. Zeit.*, 1913, 37, 1445—1447, 1471—1472, 1496—1498).—Of ores, 10 grams are mixed with 8 grams of potassium chlorate and 60 c.c. of strong hydrochloric acid, and the whole is heated until all but some siliceous matter is dissolved. After diluting with water, the filtrate is made up to about 120 c.c. Of iron or steel samples, 10 grams are dissolved in dilute nitric acid, and then

evaporated to dryness with addition of sulphuric acid; the residue is then dissolved in about 125 c.c. of dilute hydrochloric acid. In either case the solution is heated to boiling, and the iron reduced by adding sodium hypophosphite, which then also yields a deposit of metallic arsenic. For iron ores 20 grams, and for iron or steels 40 grams, will suffice. Towards the end another 35 c.c. of hydrochloric acid are also added.

The precipitate is collected on an asbestos filter. After washing, the filter and contents are removed and treated with 15 c.c. (or less) of a solution containing 6 grams of potassium iodate and 30 grams of potassium iodide in 500 c.c. Owing to a trace of free iodine always present, the arsenic dissolves, slowly at first, more rapidly afterwards, with liberation of iodine, which must then be at once titrated with thiosulphate. In the circumstances, 1 atom of iodine = 1 atom of arsenic.

L. DE K.

**Method of Forming Realgar and its Influence on the Separation of Arsenic from Tin.** H. CARON and D. RAQUET (*Ann. Chim. anal.*, 1913, 18, 432—434).—When a mixture of stannous sulphide and arsenic trisulphide is boiled with hydrochloric acid, the stannous sulphide is converted into stannous chloride, whilst the arsenic trisulphide is reduced to the disulphide and remains insoluble; the disulphide is also insoluble in ammonia. In the case of a precipitate containing tin, antimony, arsenic, and gold sulphides, it is recommended that the tin and antimony sulphides should be separated by boiling the mixture with hydrochloric acid; the insoluble portion is then oxidised with nitric acid, when the arsenic is obtained in solution whilst the gold sulphide still remains insoluble.

W. P. S.

**The Dehydration and Recovery of Silica in Analysis.** F. A. GOOCH, F. C. RECKERT, and S. B. KUZIRIAN (*Amer. J. Sci.*, 1913, [iv], 36, 598—604).—After a large number of experiments the authors recommend drying the silica, as recovered by evaporation on the steam-bath, at a temperature of 110°, before attempting to remove the soluble salts with dilute hydrochloric acid.

Half an hour's ignition over a Bunsen burner is then sufficient to drive off the last traces of water. Should there be a further tendency to lose weight when heated over the blast, this is not caused by water not yet expelled, but by alkali compounds, which should be removed by the usual treatment with sulphuric and hydrofluoric acids, and allowed for.

L. DE K.

**Elementary Analysis of Substances containing Nitrogen.** WALTER EICHORN (*Chem. Zeit.*, 1913, 37, 1465).—If the copper spiral used in elementary analyses is reduced in a current of hydrogen and allowed to cool in that gas, it retains sufficient hydrogen to affect seriously the analytical results. Allowing the spiral to cool in a stream of nitrogen does not improve matters much; it is necessary to heat strongly in nitrogen, after the reduction with hydrogen is complete, and then to allow to cool in nitrogen in order to obtain good results.

T. S. P.

**Thioacetic Acid as a Reagent.** NAZARIO ÁLVAREZ (*Anal. Soc. Quim. Argentina*, 1913, **1**, 122—128).—A solution of ammonium thioacetate is used as a source of hydrogen sulphide. The author claims that the nascent agent is more effective than the gas. In applying it, the thioacetate is added to a solution of the metal salts in excess of hydrochloric acid. G. D. L.

**Thioacetic Acid as a Reagent. Action on Salts of Rare Metals.** NAZARIO ÁLVAREZ (*Anal. Soc. Quim. Argentina*, 1913, **1**, 223—230).—Ammonium thioacetate in the presence of hydrochloric acid may replace hydrogen sulphide in its action on vanadic, molybdic, tungstic, selenious, and telluric acids, and on thalious sulphate, palladium chloride, ruthenium chlorate, and sodium iridio-chloride. G. D. L.

**A Simple Process for Nitrating Sodium Hydroxide Solutions.** ERNST ALTMANN (*Chem. Zeit.*, 1913, **37**, 1465).—The total alkali present, hydroxide and carbonate, is estimated by titrating the hot solution with standard sulphuric acid, using phenolphthalein as indicator. The amount of sodium hydroxide present is estimated by titration after precipitating the carbonate with barium chloride. T. S. P.

**Flame Reactions of the Alkali and Alkaline-earth Metals.** LUDWIG KOPA (*Chem. Zeit.*, 1913, **37**, 1506).—The author recommends a rod of graphite in place of the ordinary platinum wire for use in flame reactions (compare Kopa, A., 1913, ii, 722; Wedekind, A., 1912, ii, 382; 1913, ii, 578). The graphite is most readily obtained from an ordinary lead pencil; it does not break when quenched in cold water. T. S. P.

**Titration of Calcium and Magnesium in the Same Solution.** PAUL J. FOX (*J. Ind. Eng. Chem.*, 1913, **5**, 910—913).—The solution containing the calcium and magnesium is treated, while hot, with oxalic acid, and ammonia is added slowly until the solution is slightly alkaline in reaction. Ammonium arsenate is then added to the hot solution, followed by ammonia, until the ammonium magnesium arsenate commences to precipitate. After cooling, an excess of ammonia is added, and the precipitate is collected after fifteen hours and washed with dilute ammonia. The precipitate is now rinsed into a flask with water and dilute sulphuric acid; the acid solution is heated, and titrated with standardised potassium permanganate solution. The mixture is then cooled, 25 c.c. of diluted sulphuric acid (1 : 1) and 5 grams of potassium iodide are added, and the solution is titrated with thiosulphate solution until the coloration is light yellow; it is then placed in the dark for about five minutes, and the titration completed. W. P. S.

**The Rapid Analysis of Bronzes.** KONRAD SCHENK (*Chem. Zeit.*, 1913, **37**, 1464).—The bronze is dissolved in nitric acid, and the tin estimated as dioxide, the impurities in which are determined

in the usual way by fusion with sodium carbonate and sulphur, etc. Copper and lead are estimated in the filtrate by the usual electrolytic rapid methods, after which the iron and any aluminium are precipitated as hydroxides. The filtrate from the iron is evaporated to dryness after the addition of a few c.c. of sodium hydroxide, in order to remove ammonium salts, and the residue again evaporated with concentrated sulphuric acid to remove nitric acid. The residue is dissolved in water, a large excess of sodium hydroxide added, and the zinc estimated electrolytically, using a rotating cathode.

T. S. P.

**Microchemical Detection of Aluminium.** F. RATHGEN (*Zeitsch. anal. Chem.*, 1913, 53, 33—37).—A particle of the alumina material is heated in a small platinum crucible with  $\frac{1}{8}$ — $\frac{1}{4}$  c.c. of crystallised ammonium fluoride, and 4—5 drops of strong sulphuric acid, and the whole is very gradually evaporated to dryness and then heated for a moment to redness. When cold, the mass is detached, if necessary, with the aid of a drop of water, and then examined under the microscope. Aluminium is easily recognised by the colourless corundum-like hexagons, which, however, may be slightly coloured by iron or chromium. Four micro-illustrations are given.

L. DE K.

**Estimation of Alumina in Bauxite.** W. TRAUTMANN (*Zeitsch. angew. Chem.*, 1913, 26, 702—703).—0.5 Gram of the finely powdered substance is fused in an open nickel crucible with an excess of sodium peroxide and a little hydroxide. The fusion is dissolved in a little water, diluted to about 500 c.c., and filtered into a litre flask. The undissolved mass is ignited, and again fused with the soda mixture, then dissolved in 20 c.c. of water, and without filtering added to the main solution. When cold, the liquid is diluted up to the mark, and after shaking, portions of 100 c.c. are filtered off. The solution is supersaturated with hydrochloric acid, and then boiled with a slight excess of ammonia. The precipitate, after being washed once with water containing a little ammonia and ammonium nitrate, is rinsed from the filter and redissolved in nitric acid, and then again precipitated by ammonia, using the same filter for collecting the alumina. After washing with the above liquid, the precipitate is at once heated in a platinum crucible until the ash is white. In order to free it from traces of silica, it is heated with 2 c.c. of hydrofluoric and 15 drops of sulphuric acid, and after expelling the acids, heated over the blow-pipe so as to render the alumina non-hygroscopic and to remove the last traces of sulphuric acid.

L. DE K.

**Use of Diphenylcarbohydrazide as Indicator in the Titration of Iron by the Dichromate Method.** L. BRANDT (*Zeitsch. anal. Chem.*, 1913, 53, 1—20).—The solution of ferric chloride containing large excess of hydrochloric acid is reduced in the ordinary manner with stannous chloride, the excess of which is then removed by mercuric chloride. After adding the usual solution of manganese sulphate containing free sulphuric acid and also phosphoric acid, 5 c.c. of the above indicator are added, and the liquid titrated with

standard potassium dichromate until the colour, reddish-violet at first, gradually passes into a pure green.

The indicator is prepared by dissolving 0.1 gram of *s*-diphenyl-carbohydrazide in 35 c.c. of concentrated acetic acid and diluting up to 100 c.c.; the solution does not keep well, rarely more than a week.

L. DE K.

**Colorimetric Estimation of Small Quantities of Manganese in Water.** L. HARTWIG and H. SCHELLBACH (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 439—442).—A method, depending on the oxidation of the manganese by ammonium persulphate in the presence of silver nitrate, is recommended as being more rapid than a similar method described by Schowalter (A., 1913, ii, 880) and more trustworthy than that proposed by Haas (*ibid.*, ii, 437). Fifty c.c., or more, of the water are treated with 0.5 c.c. of nitric acid evaporated to above one-half the original volume; after cooling, a quantity of silver nitrate more than sufficient to precipitate the chlorides is added, followed by 10 c.c. of a 10% ammonium persulphate solution. The mixture is heated on a water-bath until the silver chloride has settled completely, then heated to boiling, cooled, and the coloration obtained compared with that exhibited by known quantities of permanganate diluted with a solution prepared by boiling for twenty minutes 2 litres of water after the addition of 40 grams of ammonium persulphate and 12 c.c. of a 1% silver nitrate solution.

W. P. S.

**Estimation of Manganese, Vanadium, and Titanium in the Presence of One Another in Pig-iron and Steel.** C. W. WRIGHT (*Chem. News*, 1913, **108**, 248—249).—A quantity of 1.1 grams of the sample is dissolved in 35 c.c. of nitric acid, D 1.2, the solution is filtered, and the filtrate is heated after the addition of sodium bismuthate; sulphurous acid is then added, the solution is cooled, treated with an excess of sodium bismuthate, and filtered, the filter and residue being washed with 3% nitric acid. An excess of *N*/10-ferrous sulphate solution is added to the filtrate, followed by the addition of *N*/20-permanganate solution. As long as there is an excess of ferrous sulphate the permanganate solution, introduced at the rate of 2 or 3 drops per second, is decolorised immediately, but when the oxidation of the vanadium commences there is a distinct retardation in the disappearance of the pink coloration. The reading is now taken, and the titration is continued until a permanent pink colour is obtained; in case of doubt, the operation may be repeated any number of times by again adding ferrous sulphate and titrating with permanganate solution. The quantities of manganese and vanadium present are then found by calculation. The solution is now transferred to a graduated cylinder, hydrogen peroxide is added, and the coloration obtained is compared with a standard prepared by similarly treating pig-iron or steel free from titanium or vanadium, and adding to the solution a quantity of vanadium exactly equal to that found in the sample, hydrogen peroxide, and a definite volume of a standard titanium solution.

W. P. S.

**The Estimation of Chromium as Chromic Oxide.** G. ROTHHAUG (*Zeitsch. anorg. Chem.*, 1913, **84**, 165—189).—Precipitation of chromic salts with ammonia and ignition of the precipitate yield high results. The precipitate must be ignited at first in a closed crucible, as it becomes incandescent, with violent projection of particles, at 420—680°, according to the coarseness of the material. The average excess of weight found, starting with pure chromic sulphate solution, is 0.75% Cr. Ammonium sulphide gives a mean excess of 1.60%, and potassium iodide and iodate +1.02% Cr. The results are the same whether hard glass or platinum vessels are used. The error is lessened by shortening the preliminary heating to thirty seconds, and then transferring to an electric furnace, but chromic acid is always formed to a small extent.

Washing the precipitate extracts chromic acid, and repeated ignition, followed by washing, yields further quantities of chromic acid. Alkalis and lime are shown to be absent, and the solution contains a chromic chromate. The formation of this compound is a maximum at 300°, and is observable even at 100°. The quantity produced falls rapidly to 400°, and very gradually after that point. The reaction is  $5\text{Cr}_2\text{O}_3 + 9\text{O} \rightleftharpoons 2\text{Cr}_2(\text{CrO}_4)_3$ , and it is probable that solid solutions are formed.

The chromic acid in the washings may be estimated by Moulin's colorimetric method with diphenylcarbazide (A., 1904, ii, 368), whilst the same method, applied after oxidation with hydrogen peroxide, gives the total chromium. The composition of the chromic chromate,  $\text{Cr}_2(\text{CrO}_4)_3$ , has been determined in this way.

Ignition of the hydroxide in hydrogen gives completely accurate results.  
C. H. D.

**Sensitive Reaction of Molybdenum and Tungsten in Presence of Mercury.** ENM. POZZI-ESCOT (*Bull. Soc. chim.*, 1913, [iv], **13**, 1042).—In the author's previous note on this subject (A., 1913, ii, 532), the words tungstate and molybdate should be interchanged whenever they occur.  
T. A. H.

**Estimation of Titanium by Titration.** EDMUND KNECHT (*Zeitsch. angew. Chem.*, 1913, **26**, 734—735).—A claim for priority over Neumann and Murphy (A., 1913, ii, 1079); compare Knecht (A., 1907, ii, 654) and Hibbert (A., 1909, ii, 351).  
T. S. P.

**Apparatus for the Melting Points of Substances of Indefinite Melting Point.** A. P. BJERREGAARD (*J. Ind. Eng. Chem.*, 1913, **5**, 938—940).—The apparatus consists of a block of iron having one face inclined at an angle of 45° to the horizontal. A number of grooves, 0.5 in. wide and 0.25 in. in depth, are provided down this face, and samples of the material to be tested are pressed into the upper part of the grooves; two step-like cuts are made across the tops of the ridges between the grooves, the material filling the upper step. Heat is applied to the bottom of the block, and is so regulated that the temperature of the block, as determined by a thermometer inserted in a mercury cup at the top, is raised

10° in about every 100 seconds. The inclined face is covered with a glass plate. The temperature at which the material is liquid enough to flow from the upper to the lower step-like cut is taken as the melting point. The apparatus may be used for such substances as pitch, asphaltum, etc.

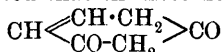
W. P. S.

**An Anomalous Reaction of Resorcinol.** EDWIN F. HICKS (*J. Amer. Chem. Soc.*, 1913, 35, 1891—1893).—From the author's experiments it appears that the commonly accepted idea that resorcinol can be titrated as a dibasic acid with alkali hydroxides, using Poirrier's blue as an indicator, is erroneous.

If an aqueous solution of resorcinol is titrated with a standard solution of alkali hydroxide, neutrality to the indicator is attained when a 1—1½ molecular proportion of the alkali has been added; after keeping for ten to fifteen minutes the alkali in the neutralised solution can be titrated back with a mineral acid, the liberated resorcinol being without effect on the indicator.

Even when resorcinol is kept in 0.1 molar solution for three hours with a decimolecular proportion of alkali hydroxide, the solution is found to be alkaline to the indicator, and the whole of the alkali can be titrated before acidity is restored.

The author inclines to the view that alkali induces in resorcinol a change to some non-phenolic and possibly tautomeric substance; extraction of the solutions with ether yielded nothing but ordinary resorcinol. It is suggested that the ketonic formula



possibly represents the less acidic substance.

D. F. T.

**Modification of the Fehling-Soxhlet Volumetric Method.** OTTORINO CARLETTI (*Boll. chim. farm.*, 1913, 52, 747—748).—The end-point in the titration of reducing sugars by this method may be accurately determined by taking advantage of the fact that cuprous potassium cyanide does not react with phenolphthalin, whilst cupric potassium cyanide gives with it a red coloration. The phenolphthalin reagent is made by mixing phenolphthalein (1 gram), potassium hydroxide (10 grams), zinc dust (5 grams), and water (100 c.c.), and boiling until decolorised. In the titration, the sugar solution is run into Fehling solution, and when reduction is almost complete, a drop of the liquid is withdrawn, mixed with a drop of the phenolphthalin reagent, and the mixture treated with two or three drops of potassium cyanide (10%). When the end of the titration is reached, this test will show no coloration, whilst as long as cupric salt is present, a red coloration will be obtained.

R. V. S.

**Influence of the Metals Present in Urine on the Velocity of the Reducing Tests for Dextrose.** GERTRUD WOKER and ELISABETH BELENCKI (*Pflüger's Archiv*, 1913, 155, 45—67).—The presence of mercury in urine retards the Nylander test for dextrose, and affects also other tests. Serum preparations containing mercury behave very irregularly. The indication of dextrose in urine by the usual reduction methods is affected also by the presence of



arsenic, iron, potassium iodide, and salicylic acid. The effect on the different methods is not quantitatively the same. Urine is considered to contain two substances, the one accelerating the interaction of dextrose with methylene-blue, bismuth nitrate, or mercuric chloride, the other retarding the reaction with alkaline copper sulphate or silver nitrate. The velocity of reduction of dextrose is in either case a function of the urine concentration. E. F. A.

**Velocity of Reduction of Methylene-blue by Dextrose and Lævulose and its Application to Urine Analysis.** J. F. MUSTER and GERTRUD WOKER (*Pflüger's Archiv*, 1913, 155, 92—96).—In presence of alkali hydroxides, methylene-blue is much more rapidly reduced by lævulose than by dextrose, and a method is based on this difference for detecting and discriminating between these two sugars in urine. E. F. A.

**Gabriel Bertrand's Method of Sugar Estimation.** M. ROSEBLATT (*Biochem. Zeitsch.*, 1913, 57, 335—336).—A reply to Sonntag (A., 1913, ii, 800). S. B. S.

**The Micro-method of Sugar Estimation.** IVAR BANG (*Biochem. Zeitsch.*, 1913, 57, 300—312).—The author has introduced certain modifications into the method previously described by him (A., 1913, ii, 446). He employs 1 c.c. of the copper solution instead of 3 c.c., and he has reduced the amount of acid used in the coagulation of the protein, which can be effectively done by substituting hydrochloric for acetic acid. The solution now employed for coagulating the blood is made up of the following mixture: 1360 c.c. saturated potassium chloride solution + 640 c.c. water + 1.5 c.c. 25% hydrochloric acid. *N*/200-Iodine solution can now be used for titration, and this is made from 5 c.c. *N*/10-hydrochloric acid + 1—2 c.c. 2% potassium iodate solution + 2 grams potassium iodide + water up to 100 c.c. In summer this solution should be titrated every twenty-four hours. An improved pincette for holding the flask during the reduction process is also described. Titration with the iodine solution is carried out until the blue starch colour remains permanent for thirty to sixty seconds. Various other new details are given by the author. In the micro-method the results of blood sugar analyses are usually slightly higher than those obtained by the macro-method. This can be accounted for by the fact that the solution containing the sugar decolorises a small amount of iodine before reduction by the copper solution. This amount is nearly constant. A subtraction of 0.015% from the total gives the correct result. S. B. S.

**Detection of Sucrose in Urine.** ADOLF JOLLES (*Biochem. Zeitsch.*, 1913, 57, 420—422).—The author has previously shown that dextrose solutions on treatment with alkali are rendered optically inactive. The estimation of the change in the polarisation after such treatment will give a measure of the amount of dextrose present. Change of polarisation produced by inversion will give

the measure of the sucrose present. By employing both methods of treatment, sucrose can be detected with certainty in the presence of dextrose. S. B. S.

**New Method for Estimating Crude Fibre.** HANNIS STIEGLER (*J. Landw.*, 1913, **61**, 399—426).—The amount of substance employed varies from 1·5 to 3 grams, according to the amount of fibre present. The finely-powdered substance is added to 20 c.c. of water in a 300 Soxhlet milk-sterilising bottle, treated with 60 c.c. of hydrochloric acid (D 1·19), well shaken, and left for ten minutes. Boiling water (to 200 c.c.) is then added, and the flask immersed in boiling water for an hour, a slow current of air being drawn through it all the time. When the heating is completed the residue is allowed to settle, and the acid liquid drawn off through a tube closed with a plug of glass-wool. The latter is then removed from the tube and placed in the bottle containing the residue. This is next neutralised, treated with 50 c.c. of potassium hydroxide solution (5%) and boiling water (to 200 c.c. as before), and again heated, for half an hour, in a water-bath. The hot solution is filtered through a porcelain Gooch crucible with a disc of ignited asbestos paper covered with ignited and washed asbestos. The fibre and the glass-wool are washed successively with hot water (500 c.c.) and alcohol, and then left in contact with ether for about half an hour. After filtering off the ether the crucible is heated for two hours at 100—105°, weighed, ignited, and again weighed. N. H. J. M.

**Titrimetric Estimation of Potassium Xanthate.** BROR HOLMBERG (*Ber.*, 1913, **46**, 3853—3859).—The estimation depends on the fact that free xanthic acid rapidly decomposes in solution into carbon disulphide and alcohol. The xanthate solution is treated with an excess of standard hydrochloric acid, the mixture allowed to remain about ten minutes until the decomposition of the xanthic acid is complete, and the excess of free mineral acid titrated with alkali.

A volumetric method for the estimation of mercury, depending on the formation of an insoluble mercuric xanthate, is also described; the solution of the mercury salt (which must be present in the mercuric condition) is treated with potassium xanthate, and the excess of the latter determined in the manner just described. The estimation can be carried out in the presence of chlorides, bromides, and sulphates, but if iodides are present the mercuric xanthate must be filtered off before the excess of potassium xanthate is determined.

It is claimed that mercury can be estimated in this manner more rapidly and more conveniently than by any other method. The author confirms the observations of previous workers that aqueous solutions of potassium xanthate are not very stable, but finds that the solid salt can be kept in a dry atmosphere without undergoing change. F. B.

**Estimation of Lactic Acid in Wine.** THEODOR ROETTGEN (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 437—439. Compare A., 1911, ii, 942; 1912, ii, 1005).—Results of experiments on the estimation

of lactic acid in wine and in the dry residue of the same show that the dry residue (total solids) of wine contains the whole of the lactic acid, and is practically free from volatile acids. Comparative estimations of lactic acid by the methods described by Kunz and Möslinger showed that the processes are equally trustworthy.

W. P. S.

**Estimation of Hydroxybutyric Acid.** PHILIP A. SHAFFER and W. McKIM MARRIOTT (*J. Biol. Chem.*, 1913, 16, 265—280).—The method of estimating hydroxybutyric acid by oxidising it to acetone with chromic acid gives uniformly about 90% of the theoretical values; the values must therefore be corrected by an addition of 10% of the amount formed. The results obtained by the oxidation method were compared with those obtained by Black's ether extraction method.

A procedure for the isolation and purification of hydroxybutyric acid in the form of *calcium zinc hydroxybutyrate*,  $\text{CaZn}(\text{C}_4\text{H}_7\text{O}_3)_4$ , m. p.  $200^\circ$  (decomp.), is described.

W. D. H.

**Estimation of  $\beta$ -Hydroxybutyric Acid in Blood and Tissues.** W. McKIM MARRIOTT (*J. Biol. Chem.*, 1913, 16, 293—298).—Shaffer's method is applicable to blood and tissues, provided proteins are removed (by sodium acetate); paired glycuronic acids, dextrose, and protein remnants are then precipitated by basic lead acetate and ammonia. Full details of distillation, etc., both for large and small quantities of blood are given. By applying the nephelometer for the estimation of acetone occurring as such, or as acetoacetic acid, or to that obtained by oxidation of  $\beta$ -hydroxybutyric acid, it is possible to make a complete analysis with only 2—5 c.c. of blood.

W. D. H.

**General Method for the Estimation of Fixed Acids in Vegetable Substances.** EMM. POZZI-ESCOT (*Bull. Assoc. Chim. Sucr. Dist.*, 1913, 31, 225—230).—Oxalic, tartaric, lactic, citric, malic, and succinic acids may be estimated in the presence of each other by means of the following method, which is a combination of processes described previously by the author (compare A., 1908, ii, 740, 904, 993, 1078). *Oxalic Acid*.—The solution containing the mixed acids is neutralised with ammonia, ammonium chloride and acetic acid are added, and the oxalic acid is precipitated as calcium oxalate or as barium oxalate; the oxalate is separated, dissolved, re-precipitated, and then titrated with permanganate solution in the usual way. The filtrates from the oxalate precipitate are mixed, treated with sulphuric acid to remove calcium or barium salts, and then diluted to a definite volume. The solution is used for the estimation of the other acids. *Tartaric Acid*.—This acid is precipitated from a portion of the solution as magnesium tartrate after the addition of 50% of alcohol to the solution; the precipitate is collected, washed with alcohol, ignited, and the tartaric acid calculated from the weight of magnesia obtained. *Lactic Acid*.—Another portion of the solution is treated with a large excess of

an alcoholic barium bromide solution and alcohol, when all the acids are precipitated with the exception of lactic acid. After filtration, the solution may be evaporated, acidified with sulphuric acid, and titrated, first to neutrality to Congo-red, and then to phenolphthalein, the latter titration giving the quantity of lactic acid. Or, the solution is evaporated to dryness, the residue calcined, and the resulting barium carbonate titrated. *Citric Acid*.—The barium precipitate obtained in the separation of the lactic acid is freed from barium by means of sulphuric acid, and then treated with an excess of lead acetate in acetic acid solution, when lead citrate and tartrate together with lead sulphate are precipitated, whilst lead malate and succinate remain in solution. After the lead has been removed from the precipitate as sulphide, the citric and tartaric acids are precipitated as their barium salts, the latter being collected, ignited, and the barium carbonate titrated. The quantity of tartaric acid found previously is deducted from the result to give the citric acid. *Malic and Succinic Acids*.—The solution containing the lead salts of these acids is treated with hydrogen sulphide, the lead sulphide is separated, and in one-half of the solution the two acids are estimated together by double titration, whilst the succinic acid is estimated in the other half of the solution by precipitation as its barium salt after the malic acid has been oxidised with permanganate (compare A., 1908, ii, 993).

W. P. S.

**Reaction of Nopic Acid (Reaction Characteristic of Oxalic Acid).** BERNABÉ DORRONSORO and OBDULIO FERNÁNDEZ (*Anal. Fis. Quim.*, 1913, 11, 441–443).—The coloration with resorcinol and sulphuric acid supposed by Fernández to be caused by nopic acid derived by oxidation of the terpenes by means of alkaline permanganate (A., 1910, ii, 1119), is shown to be due to oxalic acid, the sodium salt obtained in the oxidation being that of oxalic and not of nopic acid.

G. D. L.

**Modification of Jonescu's Test for the Detection of Benzoic Acid.** P. FLEURY (*J. Pharm. Chim.*, 1913, [vii], 8, 460–461).—This test, which depends on the conversion of benzoic acid into salicylic acid by the action of hydrogen peroxide, is very sensitive when carried out in the following way: To 10 c.c. of an aqueous benzoic acid solution are added, successively, three drops each of dilute ferric chloride solution, dilute hydrogen peroxide solution, and 3% ferrous sulphate solution. A violet coloration commences to appear in about thirty seconds, and reaches its maximum in about ten minutes; a distinct coloration is obtained with 0.2 mg. of benzoic acid. The mixture should not be heated, as the oxidation of the benzoic acid then proceeds too far, and the characteristic violet coloration is not obtained.

W. P. S.

**Detection of Vegetable Fats in Animal Fats.** M. KLOSTERMANN (*Zeitsch. Nahr. Genussm.*, 1913, 26, 433–437).—A method of isolating cholesterol and phytosterol by means of digitonin (com-

pare A., 1913, ii, 885) is described. One hundred grams of the fat are saponified with alcoholic potassium hydroxide solution, and, after dilution, the fatty acids are separated by the addition of hydrochloric acid; 250 c.c. of ether are then added, the ethereal solution of the fatty acids is separated from the aqueous portion, and washed three times with water. The ethereal solution is mixed with 250 c.c. of light petroleum and 25 grams of sodium chloride, shaken, filtered, and the filtrate is treated with 1 gram of digitonin dissolved in 20 c.c. of alcohol. After thirty minutes the crystals which separate are collected, washed with ether, dried, and boiled with acetic anhydride until completely dissolved. The excess of acetic anhydride is evaporated, the residue dissolved in 50 c.c. of alcohol, and 25 c.c. of water are added slowly to the solution. The crystalline precipitate is collected, washed with 70% alcohol, dissolved in ether, the solution is evaporated to dryness, and the residue is crystallised twice from alcohol, the m. p. being then determined. Pure lard yields crystals, m. p.  $110^{\circ}$ , whilst in the case of lard containing 2.5% of rape oil the crystals have m. p.  $118^{\circ}$ . Butter gives crystals having m. p.  $113^{\circ}$ , which is raised to  $115^{\circ}$  when the butter contains 2.5% of cocoanut oil. The crystals obtained from pure rape oil or cocoanut oil have m. p.  $126-128^{\circ}$ .

W. P. S.

**Estimation of Acetone.** W. McKIM MARRIOTT (*J. Biol. Chem.*, 1913, **16**, 281—288).—The Messinger method (A., 1889, 90) gives correct results. The Scott-Wilson method gives accurate results only when certain modifications of the original procedure are made; it is applicable to very minute quantities of acetone. In distilling a very dilute acetone solution, all the acetone may be collected in the distillate within ten minutes.

W. D. H.

**Nephelometric Estimation of Minute Amounts of Acetone.** W. McKIM MARRIOTT (*J. Biol. Chem.*, 1913, **16**, 289—292).—When the quantity of acetone is too small for estimation by the Scott-Wilson method, as, for example, in small amounts of blood, the estimation may be accurately made nephelometrically; the opalescence observed is produced by adding the acetone to a silver-mercury cyanide solution

W. D. H.

**Microchemical Detection of Myrosin.** K. PECHE (*Ber. Deut. Bot. Ges.*, 1913, **31**, 458—462).—When sections of the rind of white, or, better, black, radish are placed in a solution of potassium myronate (10% or less) saturated with barium chloride, white globules, presumably of barium sulphate, are deposited on some of the protein cells; with strontium chloride the precipitate is granular, whilst with calcium chloride well-formed needles of calcium sulphate are formed, after some time, both in and outside the sections. The sulphates are produced by the joint action of the glucoside and the alkaline earth.

On the assumption that the allyl group of the mustard oil is the only substance present which reacts with osmic acid (tannins have not been detected, and the presence of fats and oils in the rind of

radish is improbable), the glucoside may be localised by slightly heating a washed section in 1% osmic acid. N. H. J. M.

**The Fate of Protein Digestion Products in the Body. II. Estimation of Amino-nitrogen in the Tissues.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, 16, 187—196).—The amino-acids are extracted from the tissues with hot water. Uncoagulated proteins are precipitated by alcohol; alcohol and ammonia (present in the extract) are removed by concentration in a vacuum, and the amino-nitrogen estimated by nitrous acid. The action is rapid, and is only slightly increased after hydrolysis with hydrochloric acid; this indicates that the bulk of the amino-acids are free.

W. D. H.

**Estimation of Amino-acid-Nitrogen in Urine.** S. R. BENEDICT and J. R. MURLIN (*J. Biol. Chem.*, 1913, 16, 385—388).—The method previously published by the authors for modifying the formaldehyde titration gives low results, and it was found that certain amino-acids are in part removed by the preliminary treatment with lead. The procedure now recommended consists in adding phosphotungstic acid to dilute urine; three hours later the clear fluid is poured off, and phenolphthalein and barium hydroxide added until it turns pink; after an hour it is filtered, and the filtrate neutralised; it is then titrated with neutral formaldehyde to a deep red colour. The result is corrected by deducting the amount of  $N/10$ -sodium hydroxide necessary to produce the same colour in an equal quantity of water free from carbon dioxide with the same amount of formaldehyde.

W. D. H.

**A Delicate Test for Albumin in Urine.** OTTO MAYER (*Zeitsch. angew. Chem.*, 1913, 26, 639—640; *Pharm. Zentr.-h.*, 1913, 54, 1205—1208).—The author recommends that, in the examination of urines for albumin, the following reactions should be carried out in the cold; (a) a mucin test, (b) a protein test with a slight modification of Jolles's reagent. For quick approximate estimations, 5—10 c.c. of urine are floated in a conical glass on the same volume of a reagent, made by dissolving 5 grams of mercuric chloride, 5 grams of citric acid, and 40 grams of salt in 500 c.c. of water. At the end of 1.5 minutes, a well-defined, white ring appears at the junction of the liquids, when 0.001% of albumin is present. Stronger urines are diluted, after preliminary tests, until the same time is required for the development of the ring.

J. C. W.

**Estimation of Protein in Urine by the Centrifugal Method.** CASIMIR STRYZYKOWSKI (*Zeitsch. physiol. Chem.*, 1913, 88, 25—37).—In estimating the amount of protein in urine after adding Esbach's reagent, and centrifugalising, the depth of the precipitate varies with the temperature and with the specific gravity of the urine. The method may be made exact by the use of a standard centrifuge, standard sedimenting tubes, a constant temperature, and by bringing up the specific gravity of the urine to a standard level (D 1.030); this is best done by the addition of zinc sulphate.

W. D. H.

## General and Physical Chemistry.

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**Refractive Index of Gas Mixtures.** S. VALENTINER and O. ZIMMER (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1301—1316).—The authors have measured the refractive indices of mixtures containing hydrogen and carbon dioxide, and also hydrogen, helium, and neon. In the latter mixtures the proportion of helium to neon was constant, a mixture of these two gases containing 27.8% of helium being used in the preparation of the gases submitted to investigation. The refractivity data were obtained with the aid of a Zeiss interferometer.

The results indicate that the refractivity of mixtures of hydrogen and carbon dioxide is slightly less than that calculated according to the mixture rule. In the case of the mixtures of hydrogen, helium, and neon, the deviations from the mixture rule values are within the limits of possible experimental error. H. M. D.

**Mixed Liquid Crystals.** PAUL GAUBERT (*Compt. rend.*, 1913, **157**, 1446—1448. Compare A., 1911, ii, 949; 1912, ii, 109, 510).—The author has extended his study of the variation in birefracton of an optically negative, crystalline liquid on addition of a substance giving optically positive liquid crystals, to mixtures of substances capable of mixing in all proportions. The two substances studied were cholesteryl propionate and ethyl anisylideneaminocinnamate, the results are shown in a table and graphs, the measurements being made at 100° for the rays *B*, *C*, *D*, *E*, *F*. The rotatory power is found to increase considerably with the birefracton of the mixture. W. G.

**Spectroheliographic Investigation of the Arc Light.** OTTO OLDENBERG (*Zeitsch. wiss. Photochem.*, 1913, **13**, 133—172).—An apparatus is described by means of which the author has obtained monochromatic reproductions of the arc light on photographic plates. By impregnating the carbons with metallic salts it was possible to examine the behaviour of well-known series lines and bands.

In the case of sodium, the photographic records show that the principal and second subordinate series of lines are mainly emitted by the peripheral layers of the arc, whilst the first subordinate series is due to emission from layers nearer the axis. Lithium behaves similarly to sodium, but the observations with aluminium, magnesium, and calcium indicate that these behave quite differently from the alkali metals.

The monochromatic reproductions show, further, that there are two distinct types of bands. In the case of the carbon and cyanogen bands, the intensity diminishes from the centre to the edge of the arc, whilst all the other bands examined are characterised by greater intensity at the edge of the arc. In view of the very

considerable difference between the monochromatic photographs of bands and lines, it is suggested that this method may be made use of in doubtful cases to determine the character of a particular emission. H. M. D.

**Influence of the Constituents of the Crystal on the Form of the Spectrum in the X-Ray Spectrometer.** W. H. BRAGG (*Proc. Roy. Soc.*, 1914, [A], 89, 430—438).—It has been observed that the relative intensities of the different parts of an X-ray spectrum may be altered very considerably by changing the crystal which is employed in the spectrometer, and an account is given of experiments which have been made to determine the origin of this effect.

According to the observations of Barkla, every metal emits characteristic rays, which can only be excited by rays characteristic of metals which are of higher atomic weight. These observations have also shown that homogeneous X-rays are strongly absorbed by any substance in which they can excite the rays characteristic of that substance. As a consequence of these relations, the connexion between the atomic weight of an absorbing screen and its power of absorbing X-rays of given quality exhibits marked discontinuities, and it is shown that the operation of this factor through the absorbing action of the atoms of which the crystal is composed, gives rise to the variations in the relative intensities of the different parts of the spectrum. H. M. D.

**A Second Spectrum of Neon.** THOMAS RALPH MERTON (*Proc. Roy. Soc.*, 1914, [A], 89, 447—451).—A comparison has been made of the spectra obtained with a weak discharge from an induction coil and with the same discharge when a small Leyden jar and a spark-gap of about 2 mm. were introduced into the circuit. In the more refrangible region, the jar-discharge spectrum was found to consist of a large number of lines which are not present in the ordinary neon spectrum, whilst the strongest of the ordinary neon lines were only just visible. The wave-lengths of most of these lines were measured from photographs taken with the grating spectrograph, but some of the lines in the green are so feeble that it was found necessary to obtain photographic records with very long exposure on the prism spectrograph.

The wave-length data agree with those recorded by Liveing and Dewar (*A.*, 1901, ii, 213), although about 50% of the lines given by these authors have not been observed.

The experiments indicate that neon, like argon, krypton, and xenon, is capable of giving two different spectra, according to the manner in which it is electrically excited. H. M. D.

**The Band Spectrum of Aluminium and its Presence in the Flame Spectra of Certain Minerals.** ARNAUD DE GRAMONT (*Compt. rend.*, 1913, 157, 1364—1368).—The author has discovered a sixth absorption band in the spectrum of aluminium, much more refrangible and much weaker than the other five. It lies between  $\lambda$  4330.5 and  $\lambda$  4462.6, becoming degraded towards the red. Work-



ing with an oxy-acetylene flame, the author finds that, in the case of pure substances, the true aluminium spectrum is only obtained when using the metal itself or its haloids, the oxygen compounds not giving the spectrum as described. He has also studied a large number of minerals, and examined them carefully for halogens, and finds that, for them, the above rule does not hold good, but that the spectrum is more probably controlled by the constitution of the mineral.

W. G.

**Absorption of Inorganic Salts in the Ultra-violet.** T. RETSCHINSKY (*Ann. Physik*, 1913, [iv], 42, 1580—1588).—The ultra-violet absorption of lithium chloride, lithium bromide, sodium chloride, sodium bromide, sodium iodide, and potassium iodide has been examined in aqueous solutions of varying concentration. All these salts show a strong absorption maximum in the extreme ultra-violet beyond  $\lambda = 220 \mu\mu$ . In the case of lithium bromide there is also a weaker absorption band between 255 and  $280 \mu\mu$ , and some evidence of a further band at about  $300 \mu\mu$ . The former band is much less clearly marked in the case of sodium bromide, but both salts behave the same in regard to the limiting wave-length of ultra-violet transmission. The chlorides and bromides conform to Beer's law, but slight deviations have been found in the case of the iodides, in that the absorption increases with the concentration of the solution when the product of this concentration and of the thickness of the absorbing layer remains constant.

The absorption curve is shifted towards greater wave-lengths when the temperature is raised to  $100^\circ$  in the case of sodium chloride, lithium bromide, sodium bromide, and potassium iodide, but no shift is observed with lithium chloride.

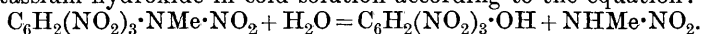
When the limiting absorption of the dissolved salts is compared with that found for the molten salts (A., 1908, ii, 910), it is found that the straight lines which represent the influence of temperature in the case of the molten salts pass through the points which correspond with the limiting absorption in aqueous solution at  $20^\circ$  and  $100^\circ$ . In making this comparison, the concentrations of the solutions were chosen so as to give the same number of absorbing molecules in the two cases.

H. M. D.

**Absorption Spectra of Nickel Derivatives of Primary Aliphatic Nitroamines.** A. P. N. FRANCHIMONT and H. J. BACKER (*Rec. trav. chim.*, 1913, 32, 321—324. Compare T., 1912, 101, 2256; A., 1913, i, 833).—The nickel derivatives of methyl- and ethyl-nitroamines have been prepared, and their absorption spectra compared with that of nickel nitrate. The amine derivatives are prepared by treating freshly precipitated nickel hydroxide with aqueous solutions of methyl- and ethyl-nitroamines respectively. It is shown that the colour of the nickel nitroamines resembles that of nickel nitrate much more than the colour of the corresponding derivatives of copper and cobalt resembles that of their nitrates. Nickel methylnitroamine crystallises with  $6H_2O$ , and possesses a bluish-green colour; it loses its water on remaining over sulphuric

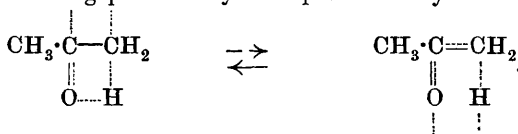
acid, and becomes intensely green. The anhydrous salt is more easily soluble in water than the crystallised salt. All three salts in  $N/2$ -solution have maxima of absorption at  $1/\lambda=2850$  and *ca.*  $1/\lambda=2000$ , whilst the nitrate has a third band at 3810. The absorption curves for the methyl- and ethyl-nitroamine derivatives coincide over practically their whole length, and the absorption is complete in the ultra-violet. J. F. S.

**Spectrographic Examination of the Colour of Picrylalkyl-nitroamines with Alkalis.** A. P. N. FRANCHIMONT and H. J. BACKER (*Rev. trav. chim.*, 1913, 32, 325—333).—The absorption spectra of alcoholic solutions of picrylmethylamine and picrylmethylnitroamine have been examined both alone and in the presence of potassium hydroxide. A solution  $N/5000$  of picrylmethylamine exhibits two absorption bands with their heads at  $1/\lambda=2390$  and 2875; there is a maximum of transmission at 2600 and at 3490. On adding a slight excess of potassium hydroxide both bands persist, but the head of the first is shifted to  $1/\lambda=2420$ . Picrylmethylnitroamine exhibits general absorption, but on the addition of alkali two bands appear at  $1/\lambda=1975$  and 2350. On allowing the alkaline solution to remain for twenty-four hours the character of the absorption spectrum is entirely changed, and on measurement is found to be that of potassium picrate, thus showing that picrylmethylnitroamine is hydrolysed by a slight excess of potassium hydroxide in cold solution according to the equation:



$N/200$ -Solutions of picrylmethylamine and picrylmethylnitroamine have about the same colour, but on dilution the colour of the picrylmethylamine is only slightly diminished, whilst that of picrylmethylnitroamine entirely disappears. J. F. S.

**Selective Absorption of Ketones.** GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON (*Proc. Roy. Soc.*, 1914, [A], 89, 414—418).—It is suggested that selective absorption of ultra-violet rays by ketones is caused by intramolecular vibrations due to the alternate formation and breaking down of unstable ring systems, and that the momentary formation of these is effected through the agency of free partial valencies which make their appearance on the atoms of the compound under certain conditions. In the case of acetone, the two alternating phases may be represented by the formulæ:



and the selective absorption is attributed to the electronic disturbances which accompany this intramolecular oscillation.

The semicarbazones of acetone and its homologues exhibit only general absorption, and this is also in agreement with the above hypothesis if it is assumed that the attraction between hydrogen and nitrogen is not sufficiently strong to cause the appearance of free partial valencies.

The theory can be extended to other groups of ketones, of which diacetyl [dimethyl diketone] and acetylacetone may be taken as examples.

H. M. D.

**Absorption of the Ultra-violet Rays by Alkaloids of the Morphine Group and by Phenanthrene.** M. GOMPEL and VICTOR HENRI (*Compt. rend.*, 1913, 157, 1422—1425).—A study of the ultra-violet absorption spectra of phenanthrene, morphine, codeine, and apomorphine, with a view to throwing some light on their relative constitutions. The absorption curve of phenanthrene can be divided into three regions: (1) between  $\lambda$  3800 and 3050, in which region  $\epsilon$  varies between 200 and 600, and there are five absorption bands; (2) between  $\lambda$  2990 and 2700, where  $\epsilon$  varies between 2000 and 10,000, and there are two absorption bands, one strong ( $\lambda$  2925) and the other weak ( $\lambda$  2810); and (3) the region between  $\lambda$  2700 and 2144, where  $\epsilon$  varies between 10,000 and 135,000, and there is a very intense band at  $\lambda$  2503.

Morphine and codeine present almost identical absorption curves having one single broad absorption band at  $\lambda$  2850, where  $\epsilon=1600$ . The curve then passes to a minimum at  $\lambda$  2620, and finally rises steadily to  $\lambda$  2195, where  $\epsilon=20,000$ .

The curve for apomorphine resembles that of phenanthrene much more closely, except that the intense band at  $\lambda$  2503 is missing. The authors therefore suggest that this band is produced by the double linking between the carbon atoms 9 and 10, this being missing in apomorphine.

apoMorphine can be detected spectrographically at a dilution of 0.01 mg. per c.c., whilst for morphine and codeine the extract must contain at least 0.1 mg. per c.c.

W. G.

**Photographic Determination of the Fluorescence Spectra of the Chlorophyll Pigments.** CH. DHÉRE (*Compt. rend.*, 1914, 158, 64—67).—An examination of the fluorescence spectra of  $\alpha$ - and  $\beta$ -chlorophyll, carotin, and the xanthophylls. Both  $\alpha$ - and  $\beta$ -chlorophyll show only one band of fluorescence, the axis of which is very slightly displaced towards the red as compared with that of the corresponding absorption band, this displacement being greater in the case of the  $\beta$ - than the  $\alpha$ -variety. In the case of carotin a slight green fluorescence is obtained, the band of which is distinct from  $\lambda=500 \mu\mu$  to  $560 \mu\mu$ . The xanthophylls show no visible fluorescence. The examination was made of solutions of the pigments in anhydrous ethyl ether, and photographs are given for  $\alpha$ - and  $\beta$ -chlorophyll.

W. G.

**Influence of Intramolecular Relative Vibration on the Intensity of the Absorption and Fluorescence of Valency Electrons.** J. STARK and P. LIPP (*Zeitsch. physikal. Chem.*, 1913, 86, 36—50).—A theoretical paper, in which the general statement is deduced: If of two substances, *A* and *B*, each containing similar atoms with similarly bound valency electrons, the number of collisions between the valency electrons with atom groups or other

molecules is greater in the case of *B* than that of *A*, then the absorption bands of *B* due to the valency electrons will be stronger than those in the case of *A*, and the fluorescence of *A* will be stronger than that of *B*. In other words, an increase in the number of collisions between valency electrons and atom groups or molecules increases the light absorption and weakens the fluorescence. The fluorescence and absorption spectra of a number of substances are considered on the basis of the above statement, and shown to be in accord with it.

J. F. S.

**Deductions from the Valency Theory. IV. Intramolecular Oscillations.** J. STARK (*Zeitsch. physikal. Chem.*, 1913, **86**, 51—60. Compare preceding abstract).—A theoretical paper, which considers intramolecular vibrations on the basis of the Stark valency hypothesis and Planck's radiation theory. It is shown that in an aggregate of a large number of molecules only very few valency electrons oscillate about their position of rest, and that the larger number of the valency electrons have no vibration of their own apart from that of the atoms to which they are attached. At moderate temperature the valency electrons can only be made to oscillate of themselves by the absorption of light energy of the same frequency as the oscillation. If these oscillations are not damped by intramolecular collisions, they take on a large amplitude, which makes itself visible in fluorescence. It is shown that in an aggregate of molecules a portion of the atoms possess a marked thermal vibrational energy at ordinary temperatures. The results of these deductions are applied to various chemical processes, such as tautomerism.

J. F. S.

**Experiment on Rotatory Polarisation in Liquids.** E. TALBOT PARIS and ALFRED W. PORTER (*Phil. Mag.*, 1914, [vi], **27**, 91—95).—A comparison has been made between the rotations of the plane of polarisation produced by a long column of a solution of sucrose when the light was emitted (1) from a constant source, (2) from an intermittent source, in the form of a platinum-mercury spark. Special experiments showed that the duration of the spark was less than  $3 \times 10^{-6}$  second. The means of several observations show that the rotations differ by less than one minute in  $500^\circ$ , which is within the limit of experimental error. The result shows that the incident light has no directive action on the molecules of sucrose in the solution.

H. M. D.

**Non-influence of Oxygen on Certain Photochemical Reactions.** MARCEL BOLL and VICTOR HENRI (*Compt. rend.*, 1914, **158**, 32—34).—A criticism of Bodenstein's theory (compare A., 1913, ii, 1039), explaining the disagreement of certain photochemical reactions with Einstein's law of photochemical equivalence (compare *J. Phys.*, 1913, **3**, 277). The authors show that this theory does not apply to the hydrolysis of the chloroplatinic acids (compare A., 1913, ii, 745) or the decomposition of oxalic acid in the presence of uranyl nitrate (compare A., 1913, ii, 652), these two reactions not being retarded by oxygen.

W. G.

**The  $\gamma$ -Rays of Polonium, Radium, and Radioactinium.** A. S. RUSSELL and J. CHADWICK (*Phil. Mag.*, 1914, [vi], 27, 112—125).—Ionium, radio-thorium, polonium, radium, and radioactinium expel, in addition to  $\alpha$ -rays, a minute quantity of  $\gamma$ -radiation, and this is probably generally true of all  $\alpha$ -ray-giving substances. For these  $\gamma$ -rays to be detected, the quantity of substance required is such that it must give off as many  $\alpha$ -particles per second as 1 mg. of radium. Ionium and polonium emit a still smaller amount of  $\beta$ -radiation also, of intensity about 10% of that of the  $\gamma$ -radiation. A detailed account is given of the separation of polonium, radium-*D* and -*E* from old radium, in a form suitable for experiment. In the final stage the active material is volatilised either in air or hydrogen in a porcelain tube on to a surface kept cool by contact with an inner tube in which water circulates. Polonium is volatilised in air at 900°, but to volatilise radium-*E* a temperature above 1100° is required, although in hydrogen 900° suffices.

For polonium the  $\gamma$ -radiation emitted is of one type with  $\mu/d = 215(\text{cm.})^{-1}$ , which comes from the polonium itself, independently of the material on which it is supported. But on copper, although not on aluminium, platinum, or lead, a characteristic radiation is excited in addition, which is probably in the *L* series. From radium the intensity of the  $\gamma$ -rays, measured through 1 mm. of aluminium, was from 1 to 1.5% of that of the radium in equilibrium with its short-lived products. In addition to the known soft  $\beta$ -rays, some hard  $\beta$ -rays with  $\mu(\text{Al, cm.})^{-1} = 20$  were observed, which were probably due to the radium itself, and not to its products. Their intensity was some 4% of that of the soft  $\beta$ -rays, and 2.5 times that of the  $\gamma$ -rays. In the latter three types were recognised, with  $\mu/d(\text{cm.})^{-1}$  in aluminium, 130, 6, and 0.1 respectively.

For radioactinium, two types of  $\gamma$ -rays, with  $\mu/d$  about 8 and 0.1, were found. This  $\gamma$ -radiation contributes about 25% of the total  $\gamma$ -radiation of actinium in equilibrium with its products. Results given in a previous preliminary communication on a new product in the actinium series are withdrawn. F. S.

**$\delta$ -Rays from Gases.** NORMAN CAMPBELL (*Phil. Mag.*, 1914, [vi], 27, 83—91).—The theory is considered of conduction through an ionised gas when the pressure is so low that the free path of the electrons liberated is not small compared with the distance between the electrodes, and the number of ions made in the gas is not large compared with the number of  $\delta$ -rays liberated from the electrodes. The view taken is based on the work of Franck and Hertz (*A.*, 1913, ii, 548), that an electron colliding with a molecule of helium or hydrogen is reflected with little loss of energy, and that with a molecule of oxygen, or other element with strong affinity for the electron, probably the electron is not reflected, but adheres to the molecule. Some earlier measurements in air and hydrogen are considered in light of the theory, and, although not capable of quantitative explanation, they are in general accord with it, and show that the  $\delta$ -rays from ionised gases are probably emitted with

velocities of the same order of magnitude as those emitted from metals. F. S.

**The Ionisation in Various Compounds of Carbon, Hydrogen, and Oxygen by Homogeneous X-Radiation.** H. MOORE (*Phil. Mag.*, 1914, [vi], 27, 177—187).—A long cylindrical chamber of aluminium, lined internally with paper, to minimise the ionisation (chiefly corpuscular) due to the radiation from the walls, was filled with a mixture of hydrogen and the vapour of various liquids—methyl formate, ethyl ether, ethyl formate, methyl acetate, benzene, ethyl acetate, ethyl alcohol—at their saturation pressure at 0°. The secondary X-radiation from copper was employed as the ionising radiation. It was found impossible to obtain any “atomic ionisation” values which would satisfy the results; the values for an atom of carbon and for an atom of oxygen (that for hydrogen being negligible), obtained from one pair of compounds, gave errors as great as 25% when applied to the others. It was found that the discrepancy is due to the different ionisation produced by a corpuscle, liberated from the molecule or atom of the gas or vapour, when absorbed by different gases. Further experiments showed that the real “atomic” effect is the liberation of these corpuscles from the atoms of the X-rays. The absorption of the X-rays, resulting in the liberation of corpuscles, is atomic, and is the same for a given atom, whether in combination or not. The ionisation produced, however, is a secondary effect, the ionisation resulting by the absorption of the liberated corpuscular radiation in the gas being dependent on the chemical nature of the gas. Knowing the “corpuscular factor,” the ionisation in the various gases and vapours could be calculated from the composition of the gas from fixed values for the atomic corpuscular radiations of oxygen and carbon, in most cases with good agreement with the experimental results. F. S.

**Registration of the Emanation Content of the Underground Air at Potsdam by the Benndorf Electrometer.** K. KÄHLER (*Physikal. Zeitsch.*, 1914, 15, 27—31).—A zinc cylinder, 1.5 metres deep and 0.45 metre in diameter, open at the bottom, was sunk into the earth, and an inner electrode connected with the recording electrometer. A continuous register of the leak due to emanation in the cylinder was taken from late summer, 1910, to early summer, 1912. It was found that the vertical movements of the air, including the changes of barometric pressure, had the greatest effect on the emanation content of the air and on the escape of emanation from the ground. Sunshine also favoured the escape of emanation. The daily variations have no influence on atmospheric conductivity, but possibly the yearly variation has an influence. F. S.

**A Determination of the Variation with Altitude of the Radium Emanation Content of the Atmosphere.** J. R. WRIGHT and O. F. SMITH (*Physikal. Zeitsch.*, 1914, 15, 31—39).—These measurements were carried out by the coconut charcoal method

in Manila, for two places, one 5 metres and the other 2460 metres above sea-level, on Mount Pauai. The individual measurements of the emanation content varied widely in accordance with the changes in meteorological conditions. Rainy weather and high wind velocities lowered, whilst settled weather with low wind velocities favoured, the emanation content. For the low station the mean content was  $82.5 \times 10^{-12}$  curie per cubic metre, about four times greater than the mean content,  $19.2 \times 10^{-12}$  curie per cubic metre, on the mountain. F. S.

**An Alleged Separation of the Radium-*D* from the Lead in Active Lead by means of Grignard's Reaction.** CHARLES STAEBLING (*Compt. rend.*, 1913, 157, 1430—1432).—The author has repeated the work of Hofmann and Wölfl (compare A., 1907, ii, 521), and has been unable to obtain any evidence in support of their views, his results being entirely negative. W. G.

**The Existence of Uranium-*Y*.** FREDERICK SODDY (*Phil. Mag.*, 1914, [vi], 27, 215—221).—The effects observed by Antonov (A., 1911, ii, 844; 1914, ii, 17) of an abnormal decay of the soft  $\beta$ -rays of uranium- $X_1$  have been obtained from all uranium- $X$  preparations, however chemically separated, in which the time of re-accumulation of the uranium- $X$  from the uranium was short. The barium sulphate method of separation, which Antonov found gave uranium- $X$  free from uranium- $Y$  and decaying normally, gave decay curves identical with those of the other preparations. The conclusion is formed that if uranium- $Y$  has an existence separate from that of uranium- $X_1$ , it must be *isotopic* with it, that is, occupies the same place in the periodic table, and is chemically identical with it. This requires that both uranium- $X_1$  and - $Y$  should be formed from either uranium-*I* or -*II* in a dual change, in which, in both modes,  $\alpha$ -rays are expelled, and that initially the slope of the soft  $\beta$ -ray recovery curve of pure uranium preparations must be considerably steeper than that due to uranium- $X$  alone. Under conditions when the  $\alpha$ -rays of uranium are completely absorbed, the soft  $\beta$ -rays produce only one-tenth of the effect of the hard  $\beta$ -rays, and the point is difficult to establish. Evidence of the increased slope in the recovery curve was obtained, however, which, although slight, was of the right order of magnitude. The whole of the results are in agreement with the view that uranium- $Y$  is the parent of actinium in a branch series, starting from either uranium-*I* or uranium-*II*, claiming some 8% of the atoms, on the assumption that the atoms of uranium- $X_1$  and uranium- $Y$  produce equal ionisations on disintegration. Since, however, the product of uranium- $Y$  in group IV by a  $\beta$ -ray change must be in group V, a further  $\alpha$ -ray change must occur before actinium, in group III, can be produced. Attempts to detect an  $\alpha$ -radiation from uranium- $X$  and - $Y$  separated as rapidly as possible from uranium, were negative. F. S.

**Dependence of the Photo-electricity of Metals on the [Surrounding] Gas.** GEORG PAECH (*Ann. Physik*, 1914, [iv], 43, 135—164).—The dependence of the photo-electric activity of platinum

on the nature of the surrounding gaseous medium has been examined in a similar manner to that which was adopted by Ullmann in a previous series of experiments on the photo-electric behaviour of zinc (*Ann. Physik*, 1910, [iv], **32**, 1—48). In both cases the surrounding gas has a considerable influence on the photo-electric activity, and from the data obtained with hydrogen, air, carbon dioxide, and water vapour it is evident that the activity of the two metals is similarly affected by a given change in the surrounding gas.

From observations in which small quantities of the vapours of methyl alcohol, acetone, chloroform, benzene, and water were admixed with air, it has been found that the photo-electric effect is much larger than in pure dry air, and that the difference increases with the dielectric constant of the admixed vapour.

Other experiments were made, in which the metal was in contact with pure ammonia, methyl ether, and ethylene vapours. With ammonia the photo-electric effect was five times, with methyl ether 2·5 times, and with ethylene 1·8 times as great as with dry air. These results also support the view that the photo-electric effect is influenced by the nature of the gas which is in contact with the active metal.

H. M. D.

**Relation between the Conductance and the Viscosity of Electrolytic Solutions and its Bearing on the Theory of these Solutions.** CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1914, **36**, 35—65).—A study has been made of the conditions under which corrections for viscosity may be applied to conductivity values, and the results are interpreted in the light of the ionic theory. The influence of a change in viscosity on the speed of an ion in a solution varies with the nature of the process by means of which the viscosity change is brought about. In general, such a change is effected by: (1) a change in concentration, due either to the addition of a new substance or of a further amount of one already present in solution; (2) a change in pressure; or (3) a change in temperature. Consideration is given to the relation between the change of ionic velocity and the change of viscosity as brought about in each of these three different ways, and the results obtained are based on the figures recorded by various workers in this field.

It is shown that in the case of aqueous solutions exhibiting negative viscosity, the conductivity may be corrected for viscosity in direct proportion to the fluidity change, and that the same is probably true for viscosity change due to external pressure. Corrections for viscosity cannot, as a rule, be made in the case of aqueous solutions exhibiting a positive viscosity, although sometimes correction may perhaps be effected by considering the influence of viscosity on the individual ions.

The change in the true transference numbers of electrolytes with concentration is due to the different effect of viscosity on the speed of the two ions. The viscosity change due to change in concentration in non-aqueous solutions is positive, and much greater than it is in water for inorganic electrolytes. The velocity of the ions in



non-aqueous solutions changes much less than the fluidity of the solutions, although, at high concentrations, a marked influence results. Correction for viscosity is not possible in these cases, and up to  $N$ -concentrations is in many cases unnecessary.

It is pointed out that the influence of viscosity on the speed of the ions depends on the relative dimensions of the ions and molecules to which viscosity change is due. The characteristic relations observed in aqueous solutions are partly due to the complexity of the liquid water molecules.

At higher temperatures the velocities of different ions in aqueous solutions tend to reach a common limit, indicating that the ions are becoming of approximately the same size. The dimensional changes observed cannot be accounted for on the assumption that the larger ions become smaller at higher temperatures, but it is suggested that, as the temperature rises, the smaller ions increase in size owing to increasing hydration.

It is shown that the view, that the high speed of the hydrogen and hydroxyl ions is related to the fact that these ions are ions of the solvent itself, is erroneous.

E. G.

**Electrical Conductivity in Hydrocarbons, their Halogenated Derivatives, Esters, and Bases. Part I. (cont.).** P. WALDEN (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 987—996).—Further conductivity measurements have been made (compare this vol., ii, 21) of solutions of various substituted ammonium salts in aniline, quinoline, methylaniline, acetic acid, sulphuryl chloride, ethyl formate, methyl acetate, and methyl benzoate. Consideration of the results obtained and of those previously described (*loc. cit.*) leads to the following conclusions.

Beginning with benzene, toluene, and carbon tetrachloride, which have dielectric constants of 2.2—2.3, all solvents are capable of giving salt solutions with measurable electrical conductivity, and must be regarded as ionising media. The magnitude of the molecular conductivity depends essentially on (1) the nature of the electrolyte, binary salts especially giving conducting solutions, and (2) the concentration of the electrolyte, which with faintly ionising solvents must be relatively great in order that the conductivity may be appreciable.

In correspondence with the slight ionising power and extremely low dielectric constants of these media, the ionic concentration and the molecular conductivity are only small. In passing from the more concentrated ( $V$  equal to or less than 1) to the more dilute of these salt solutions, the conductivity curve follows one of three courses, according to the nature of the solvent: (1) the molar conductivity  $\lambda_v$  first rises to a maximum, generally at  $V=1-2$ , and then falls rapidly, no minimum having been yet observed; (2)  $\lambda_v$  attains a maximum, and then a minimum, and subsequently increases again; the dilution corresponding with the minimal or transition point varies with different solvents, and the value of the minimum ranges from about 30 to 500; (3)  $\lambda_v$  shows continual increase. With tetraisoamyl- or tetrapropyl-ammonium iodide, case (1) is realised with solvents having dielectric constants of

about 2, case (2) when  $\epsilon$  lies between 4.95 (chloroform) and 8—10 (dichloromethane, ethyl bromide, quinoline, *s*-dichloroethane), and (3) when  $\epsilon$  is greater than 9 or 10. With another binary salt having a lower ionising tendency than the above iodides, for instance, tripropylammonium chloride, the typical curve (2) may be observed when the value of  $\epsilon$  for the solvent is greater than 9.

Curve (2), showing successively an increase, a decrease, and an increase of the conductivity, represents the general or typical form. The lengths of its first and second branches depend on the choice of solvent and solute. In some circumstances the minimum may approach the maximum so closely that branch 2 virtually disappears and branch 3 becomes a continuation of branch 1, so that the curve exhibits no apparent maximum or minimum.

Comparison of the values of  $\lambda$  ( $V=20$ ,  $t=25^\circ$ ) for tetraisoamylammonium iodide in the different solvents with the dielectric constants and viscosities of the latter shows that, in general: (1) in solvents with approximately equal values of  $\eta$ , the greatest molecular conductivity corresponds with the greatest dielectric constant; (2) in solvents with approximately equal dielectric constants the molecular conductivity is the greater the smaller the viscosity of the solvent; (3) the molecular conductivity is therefore a function of the dielectric constant,  $\epsilon$ , and of the fluidity  $f(1/\eta)$ , that is,  $\lambda_v = F(\epsilon, f)$ . The value of the minimum shows similar dependence.

Solutions of good salt-like electrolytes in solvents of high ionising power obey the Nernst-Thomson law, according to which the extent of the electrolytic dissociation increases with the dielectric constant of the solvent; further, the molecular conductivity increases with the fluidity. Hence, with such solvents, the dependence of the molecular conductivity on the viscosity and the dielectric constant is similar to that holding with those of low ionising properties. Between the latter, which are often termed insulators, and solvents which readily ionise electrolytes, there is then no fundamental difference.

T. H. P.

**Some Solvents with Small Dielectric Constants.** A. SACHANOV and J. PRSCHEBOROVSKI (*Zeitsch. Elektrochem.*, 1914. 20, 39—41). —It was previously shown (Sachanov, A., 1912, ii, 730) that solvents with small dielectric constants bring about a decreased molecular conductivity of the dissolved substance on dilution. With the object of testing this point further, the conductivity of a number of salts in solutions of *o*-toluidine (*DC* 6.0), benzylamine (*DC* 5.2), chloroform (*DC* 4.7), bromal (*DC* 7.5),  $\alpha$ -bromobutyric acid (*DC* 7.2), and isobutyric acid (*DC* 2.6) were determined. The specific conductivities of these solvents are less than  $1 \times 10^{-7}$ . The molecular conductivities of solutions in these solvents decrease on dilution, and it is shown that the relationship  $\lambda v^n H/h = \text{constant}$  holds for all concentrations; in the case of dilute solutions where  $H=h$  (approx.) the expression becomes  $\lambda v^n = \text{const.}$ , where  $\lambda$  is the molecular conductivity,  $v$  the dilution, and  $n$  a constant,  $H$  the viscosity of the solution, and  $h$  that of the solvent. In the cases

examined the value found for this expression is very constant. The authors' expression is compared with a similar expression of Kraus and Bray (A., 1913, ii, 914), which is shown to reduce to the same form.

J. F. S.

**Calculation of the Electrical Conductivity in Very Dilute Aqueous Solutions.** SVANTE ARRHENIUS (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 42, 1—12).—The author discusses the question of the correction which must be applied to the conductivity values for dilute aqueous solutions in order to eliminate the influence of the solvent. On the assumption that the conductivity of the solvent is due to carbonic acid, it is shown that the methods usually adopted in the case of acids and salts are theoretically justified, provided that the acids are stronger than acetic acid, and that the salts in question are salts of strong acids. On the other hand, if the salts are salts of weak acids, the correction to be applied is less than that represented by the conductivity of the solvent. The theoretical correction depends, as a first approximation, on the value of  $k/c$ , where  $k$  is the ionisation-coefficient of the acid, and  $c$  is the concentration of the salt, and a table is given in which the correction is expressed in terms of the actual conductivity of the solvent, such numbers being recorded for a series of values of  $k/c$ .

By reference to the conductivity measurements of Kohlrausch and Maltby for very dilute solutions of sodium chloride and sodium nitrate, it is shown that the variation of the conductivity at the highest dilutions is in agreement with the requirements of the mass law. For both salts, the ionisation-coefficient  $k = \alpha^2/(1-\alpha)v$  is equal to 0.024, and the view is expressed that at sufficiently great dilutions the ionisation of all electrolytes is in accord with the law of mass action.

H. M. D.

**Affinity Measurements in Aqueous Alcoholic Solutions.** H. EULER and K. BLONDAHL (*Arkiv. Kem. Min. Geol.*, 1913, 4, No. 40, 1—8).—The authors have determined the affinity constants of phenol and guaiacol in 80% aqueous-alcoholic solution by measurements of the conductivities of solutions of their ammonium salts (compare Euler and Bolin, A., 1909, ii, 374; Hägglund, A., 1912, ii, 120, 910). The values are respectively  $3.1 \times 10^{-12}$  and  $2.4 \times 10^{-12}$ , corresponding with the fact that the dihydroxybenzenes are very little more dissociated than phenol (Euler and Bolin, *loc. cit.*).

The ratio of the dissociation constants of the compounds salicylic acid, acetic acid, *p*-nitrophenol, and phenol in water to that in 80% alcohol varies between 15 and 77; experiments with phosphoric acid indicated that its dissociation is affected in a similar way, probably to a greater extent, by alcohol.

T. S. P.

**Dissociation Constants of Organic Acids.** JAMES KENDALL (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 38, 1—27).—A general formula for the ionisation of acids has been given in a previous paper (T., 1912, 101, 1275), and further measurements of the

electrical conductivity of acids have been made in order to test the formula more completely. The acids previously examined have been investigated in more concentrated solutions, and measurements have also been made for salicylic acid and some of its derivatives.

The results obtained afford further confirmation of the view that the ionisation constant is subjected to the influence of two disturbing factors, one of which (the total concentration influence) causes the constant to diminish as the concentration increases, whilst the other (the ionic concentration influence) gives rise to an increase in the constant with increasing concentration.

In the case of very dilute solutions of salicylic acid and its derivatives, it is found that the ionisation constant increases to a small extent with increasing dilution. This property is characteristic of dibasic acids, and it is supposed that the proximity of the carboxyl group to the phenolic group increases the strength of the latter to such an extent that the acid behaves as a weak dibasic acid. In agreement with this, it is found that salicylic acid and its derivatives cannot be titrated at all sharply with phenolphthalein as an indicator.

The theoretical significance of the equation

$$m^2/(1-m)v_i = k + c(1-m)/m$$

is not apparent, but the presence of the expression  $(1-m)$  as a factor on the right-hand side of the equation seems to point to the activity of the non-ionised acid as being the cause of the variation in the constant.

It is also shown that the author's equation may be regarded as a special form of the general equation put forward by Bray and Kraus (A., 1913, ii, 914).

H. M. D.

**Piezoechemical Studies. XII. The Influence of Pressure on Affinity. III.** G. TIMOFÉEV (*Zeitsch. physikal. Chem.*, 1913, **86**, 113—128. Compare A., 1905, ii, 678; 1911, ii, 15).—The influence of pressure on the *E.M.F.* of the elements:

(a) Ag—AgCl—KCl 0.1*N*—HgCl—Hg;

(b) 7% Zn amalgam—35.03% ZnCl<sub>2</sub> solution—AgCl—Ag; (c) 7% Zn amalgam—65.59% ZnCl<sub>2</sub> solution—AgCl—Ag; (d) 7% Zn amalgam—65.59% ZnCl<sub>2</sub> solution—HgCl—Hg has been determined over a range of pressure 1—1500 atmospheres and at 25°. The influence of pressure can be represented by the expression

$$E_{\pi} - E_0 = \pi(v_1 - v_2),$$

in which  $E_{\pi}$  and  $E_0$  represent the *E.M.F.* at pressures  $\pi$  and 1 atmosphere respectively, and  $v_1$  and  $v_2$  the volumes of reacting substances before and after the change.

J. F. S.

**Calibration Tables for Copper-constantan and Platinum-platinrhodium Thermoelements.** L. H. ADAMS (*J. Amer. Chem. Soc.*, 1914, **36**, 65—72).—Owing to the fact that thermo-elements are becoming more extensively used for measuring high temperatures, two tables have been constructed with the object of obviating trouble in converting micro-volts into degrees. Each table gives the temperature and temperature-difference for every 100 micro-

volts, the cold junction being maintained at  $0^{\circ}$ . The table for each of the two elements is intended for use in conjunction with a deviation curve determined by calibration of the particular element with three or more of certain fixed points given at the foot of each table.

E. G.

**Behaviour of Wehnelt Electrodes in Different Gases.** KARL FREDENHAGEN (*Physikal. Zeitsch.*, 1914, 15, 19—27. Compare Gehrts, A., 1913, ii, 1005).—The influence of oxygen, nitrogen, and hydrogen on the efficiency of the Wehnelt cathode has been investigated by measurements at  $945^{\circ}$ ,  $1085^{\circ}$ , and  $1235^{\circ}$ , and in a few cases at  $1340^{\circ}$ . The results obtained are presented in the form of curves, which show the connexion between the current and the applied potential up to 200 volts. In all cases the current-potential curves were determined for different pressures of the gas present.

These curves indicate that nitrogen diminishes the efficiency of the oxide electrode, but has little influence on the variation of the effect with temperature. In presence of oxygen, the efficiency of the electrode is found to be diminished to a very much greater extent, and at the same time the temperature-coefficient of the effect is reduced, especially at the higher oxygen pressures. In contrast with the behaviour of nitrogen and oxygen, hydrogen is found to increase the activity of the electrode, and in this case the current-potential curves for the different temperatures lie very close together. A few experiments have also been made with methane, coal-gas, and cyanogen. The two former behave like hydrogen, whilst cyanogen reduces the activity of the electrode to a much greater extent than oxygen. The change produced by the cyanogen in the oxide electrode is permanent, and the activity is not restored even when the electrode is strongly heated in an atmosphere of oxygen. It is supposed that the change is due to the formation of calcium cyanamide.

The observations are interpreted in terms of the theory of the Wehnelt electrode, which has been put forward in a previous paper (*loc. cit.*).

H. M. D.

[Electrodes of the Third Type.] FRIEDRICH AUERBACH (*Zeitsch. physikal. Chem.*, 1914, 86, 243—246).—A criticism of the methods employed by Spencer (A., 1913, ii, 596) in the calculation of the ionic solubility product  $L=[\text{Cu}^{++}][\text{IO}_3']^2$  for cupric iodate. It is shown that the agreement between the values obtained from different combinations of electrodes is determined by algebraic relationships. From Spencer's data (compare also A., 1912, ii, 1129) the author finds  $L=1.47 \times 10^{-7}$ . In view of the magnitude of the solubility of cupric iodate, it is not permissible to calculate this solubility directly from the ionic solubility product.

H. M. D.

**A Scheme for the Dissociation of Ternary Electrolytes.** RUD. WEGSCHEIDER (*Zeitsch. Elektrochem.*, 1914, 20, 18).—Polemical against Drucker (A., 1913, ii, 1015). The author shows that

Drucker's statements are too wide if he applies the generally adopted meaning to the word "electrolyte," but if the term "electrolyte" is distinguished from the term "half-electrolyte" the conclusions arrived at by Drucker are tenable. J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. I. Alloys of Nickel and Iron Deposited at the Ordinary Temperature.** R. KREMANN, C. TH. SUCHY, and R. MAAS (*Monatsh.*, 1913, **34**, 1757—1809).—All the experiments were made using a current density of one ampere per sq. dcm. at the cathode.

Iron may be deposited from solutions of a ferric salt (0.5-*M* ferric ammonium sulphate), the current yield being 3.9%, if it is assumed that the  $\text{Fe}^{+++}$ -ions are directly deposited. If nickel sulphate (0.6-*M* solution) is also present in solution, the current yield is increased, agreeing with the assumption that in the simultaneous deposition of two metals which form solid solutions, the deposition of these metals is facilitated by the mutual depolarising effect of the metals.

In all the following experiments the electrolyte consisted of a solution of ferrous and nickel sulphates in varying proportions. It was found that the ratio ( $R_1$ ) of nickel to iron in the alloy was considerably smaller than the ratio ( $R_2$ ) of the metals in the solution; also,  $R_1$  gradually increased with  $R_2$ . The character of the deposit depended on the nature of the cathode; with a carbon cathode the deposits were smooth and adherent, whilst with iron cathodes they were irregular and scaly; in all cases they were brittle, owing to occlusion of hydrogen. When a combined nickel-iron anode was used, chiefly iron went into solution. A slight alteration of the current density had scarcely any influence on the composition of the deposit.

The addition of potassium oxalate to the electrolyte increased the ratio  $R_1$ , in accordance with the fact that nickel forms more highly complex ions with oxalate-ions than does iron.

Attempts to coat sheet iron with adherent deposits of an iron-nickel alloy from a neutral electrolyte were unsuccessful, owing to the formation of large quantities of a cathode sludge and to the fact that the expansions of sheet iron and the alloy deposited are different. The alloy was also very brittle because of its hydrogen content, and in different experiments carried out under the same conditions the composition of the alloy varied. The formation of the cathode sludge could be prevented by the addition of sulphuric acid to the electrolyte, but in solutions 0.2*N* with respect to the acid no deposition of metal took place.

In the last series of experiments, citric acid was added to the electrolyte. It was found that the acid was used up during the electrolysis, and at the same time the alloy deposited contained carbon, which varied from 0.5 to 1.1%; the higher the concentration of the citric acid the greater the carbon content of the alloy. With increase in value of the ratio  $R_2$  the carbon content of the alloy increased to a maximum and then fell. When the concen-

tration of the citric acid was kept constant, the ratio  $R_2$  increased with the ratio  $R_1$ , although not in proportion.

The addition of citric acid to the electrolyte almost completely did away with the formation of cathode sludge, and it was possible to deposit alloys 4—5 mm. in thickness on a carbon anode; the alloys were brittle.

The metallographic investigation of the alloys deposited showed that they were analogous in structure to, and in some cases identical with, alloys prepared by thermal methods. In some cases structures similar to those occurring in meteorites were observed. A structure which was characteristic of the electrolytic alloys consisted of concentric layerings (sphaerolites). The cross-section of the deposits had a distinctly lamellar appearance, which only disappeared on heating to a white heat.

The hardness of the various electrolytic alloys was measured by the sclerometric method. Both nickel and iron, when deposited from acid baths, are softer than when deposited from neutral baths. The alloys obtained from acid baths are harder than would correspond with the rule of mixtures. The authors are of the opinion that the hardness of the electrolytic deposit depends on the fineness of the structure, and not on the presence of hydrogen; the finer the structure the harder the alloy.

T. S. P.

#### Magnetic Properties of the Alkali Metals in Combination.

PAUL PASCAL (*Compt. rend.*, 1914, 158, 37—39).—By measuring the molecular-coefficients of magnetisation of the haloid salts, and the nitrates, sulphates, and carbonates of the alkali metals, knowing the values of the part contributed by the acidic ions, the author has calculated the atomic coefficients of magnetisation of these metals. The values obtained increase with increase in atomic weight. By plotting the logarithms of these coefficients against the atomic weights, he finds that the points for lithium, sodium, and potassium lie on a straight line, and for potassium, rubidium, and caesium on another straight line. Comparing these figures with those obtained for hydrogen and silver, hydrogen comes on the first line and silver on the second line.

W. G.

**The Shape of Molecules.** T. SVEDBERG (*Arkiv Kem. Min. Geol.*, 1913, 4, No. 39, 1—5).—It has been shown by Cotton and Mouton (compare A., 1913, ii, 4) that certain isotropic substances, for example, nitrobenzene, become doubly refracting in a strong magnetic field. This is probably due to incomplete orientation of the molecules, but hitherto it has not been possible to detect any variation of the electrical conductivity of such substances according as the conductivity is measured along or across the lines of magnetic force. Such a variation should occur if the molecules show geometrical dissymmetry, since the resistance to migration should vary with the orientation of the molecule.

The author has found that such a variation takes place in the conductivity of anisaldazine. This substance forms an anisotropic liquid (liquid crystals) between 165° and 180°, and, in a magnetic

field, behaves as a strongly doubly refracting uniaxial crystal, the optical axis of which is parallel with the magnetic lines of force (compare Wartenberg, A., 1911, ii, 952; Mauguin, A., 1912, ii, 630).

Since the amount of ionisation, and consequently the conductivity, of anisaldazine is very small, an electrometric method of measurement had to be used for determining the conductivity. The results showed: (1) that the conductivity in a magnetic field is smaller than the ordinary conductivity; (2) that with the cell used the relative increase in resistance at right angles to the magnetic lines of force is about three times greater than parallel to the same; (3) that in a field of about 4500 Gauss the relative increase in resistance to the magnetic lines of force is of the order of 4%; (4) that the influence of the magnetic field is closely connected with the anisotropic condition of the anisaldazine, since it does not exist above  $180^{\circ}$  or below  $165^{\circ}$ . T. S. P.

**Expansion of Mixtures of Carbon Disulphide and Acetone.** J. VECINO Y VARONA (*Anal. Fis. Quim.*, 1913, **11**, 498—515).—The density at  $0^{\circ}$  and refractive index at  $14.58^{\circ}$  of acetone were found to be 0.81229 and 1.43528, and of carbon disulphide 1.29217 and 1.63149 respectively.

The coefficients of expansion of acetone and carbon disulphide were determined as  $148.1 \times 10^{-5}$  and  $117.53 \times 10^{-5}$  respectively.

Mixture of these liquids is attended by expansion in contradistinction to the usual rule, and similarly the thermal expansion does not follow the rule of mixtures, possibly on account of the formation of molecular compounds. G. D. L.

**Convenient Method for Calibrating Thermometers by means of Floating Equilibrium.** THEODORE W. RICHARDS and JOHN W. SHIPLEY (*J. Amer. Chem. Soc.*, 1914, **36**, 1—10).—In an earlier paper (A., 1912, ii, 599) it was shown that the "floating equilibrium" of a suitable solid float is exceedingly sensitive, and that the "floating equilibrium temperature" is almost a linear function of the concentrations. It was also shown that this method can be used to analyse solutions, and to calibrate thermometers.

The present paper deals with the application of this process to the standardisation of thermometers, and experiments are described which consist in determining the temperatures at which different aqueous solutions of sodium sulphate attain exactly the density of a given float. By plotting the floating equilibrium temperatures against the percentage composition of the solutions, an almost linear curve is obtained, and it is pointed out that this curve, when once established, will serve for the calibration of any thermometer at any time. The method is also serviceable for determining the coefficients of expansion of liquids with known floats, or the coefficients of expansion of floats with known liquids. E. G.

**Electrical Contact Vapour-pressure Thermoregulator.** ALEX. L. FIELD (*J. Amer. Chem. Soc.*, 1914, **36**, 72—76).—A new form of



vapour-pressure thermoregulator is described, which is not affected by changes of atmospheric pressure. It consists essentially of an upright U-tube, closed at both ends. One side of the tube contains a volatile liquid, the b. p. of which is near the desired temperature of the bath. Above the liquid is its saturated vapour, with or without admixture of air or other gas. The pressure exerted by the vapour, or the vapour and gas, supports a column of mercury which makes and breaks an electrical contact on the other side of the U-tube. This contact is made in an atmosphere of dry carbon dioxide.

This thermoregulator is light, easily adjustable, and has an observed sensitiveness of  $0.01$ — $0.005^\circ$ . It is adapted for use in liquid baths, is not affected by agitation of the liquid, and rapidly adjusts itself to changes of temperature of the bath. The regulator is therefore particularly adapted for the accurate control of the temperature of an ordinary thermostat. E. G.

**Specific Heat.** G. D. OSGOOD (*Zeitsch. Elektrochem.*, 1914, 20, 37).—A mathematical paper, in which the application of a curve, found in a thermodynamical investigation of the mass action equilibrium constant, is shown in connexion with a heat loss, as indicated from the magnetic hysteresis curves. J. F. S.

**Specific Heat of Solids.** II. H. VON JÜPTNER (*Zeitsch. Elektrochem.*, 1914, 20, 10—18. Compare A., 1913, ii, 921).—A mathematical paper, in which an expression is evolved by means of which the atomic heat of solid substances between the temperatures  $T = \beta v'$  and  $T = 0.394\beta v'$  can be calculated. An expression of the form:

$$(C_v)_{T=\beta v'}^{T>\beta v'} = 3Re^{-\beta v'/T}$$

is deduced for the mean atomic heat of solids between  $T = \beta v'$  and higher temperatures. A series of tables are given by means of which the true and mean atomic heats and heat capacities between  $T = 0.394\beta v'$  and any higher temperature may be calculated. It is shown that the heat capacity at temperatures below  $T = 0.394\beta v'$  is so small that it for most purposes may be neglected. J. F. S.

**Specific Heat of Grey Tin and the Richarz Rule.** ALBERT WIGAND (*Zeitsch. Elektrochem.*, 1914, 20, 38—39).—The specific heat of the two forms of tin have been re-determined by the author, and it is shown that grey tin has a smaller value than white tin. This is in accord with the measurements of Bronsted (A., 1912, ii, 897). The previous values for grey tin obtained by Wigand (A., 1907, ii, 70) are shown to be due to the presence of oxide. These results are discussed in connexion with the van't Hoff-Thomsen rules and the Richarz rule, the latter of which states that in the case of allotropic substances the form with the higher specific heat has the smaller density. This rule is not followed in the case of tin. J. F. S.

**An Inversion Point for Liquid Carbon Dioxide in Regard to the Joule-Thomson Effect.** ALFRED W. PORTER (*Proc. Roy. Soc.*, 1914, [A], 89, 377—378).—According to the experiments of Jenkin and

Pye (A., 1913, ii, 753), the Joule-Thomson effect for liquid carbon dioxide shows a change in sign at  $-20^{\circ}$  to  $-30^{\circ}$ . Assuming that the change in pressure may be treated as a differential, it is shown that the inversion point must correspond with a minimum (or maximum) value of  $v/T$ , where  $v$  is the specific volume at  $T^{\circ}$  (absolute). Three sets of experimental data, corresponding with a mean pressure of 500 pounds per square inch, concur in giving a minimum value of  $v/T$  at about  $-24^{\circ}$ , which agrees fairly closely with the result of direct observation. The result is of special interest, in that it implies that liquid carbon dioxide in this region behaves approximately like a perfect gas, its volume being nearly proportional to the absolute temperature. H. M. D.

**Latent Heat of Fusion of Ice.** H. C. DICKINSON, D. R. HARPER, and N. S. OSBORNE (*Chem. Zentr.*, 1913, ii, 2025; from *J. Franklin Inst.*, 1913, 176, 453—454).—The latent heat of fusion of ice has been determined (1) by allowing a mass of 100—200 grams to melt in a calorimeter, and (2) by measurement of the energy in form of an electric current necessary to fuse a mass of about 500 grams placed in a calorimeter. As mean of ninety-two experiments performed with a great variety of samples of ice, the number 79.63 cal. per gram is found. H. W.

**Occurrence of an Upper Critical Point of Mixing at the Co-existence of Two Mixed Crystal Phases.** A. SMITS and C. A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 557—564).—The freezing-point and melting-point curves for binary mixtures of potassium and sodium chlorides are continuous, and exhibit a minimum at about  $664^{\circ}$ . During the cooling of a solidified mixture of the two salts, changes occur, whereby the homogeneous isomorphous mixture is converted into two co-existing mixed crystal phases. These phases are identical in composition at  $407^{\circ}$ , but as the temperature falls, they diverge to an increasing extent until at the ordinary temperature the one consists of practically pure potassium chloride and the other of pure sodium chloride. This mixture affords, therefore, an instance of an upper critical mixing point.

In order to ascertain whether the observed phenomena are due to the formation of a compound, experiments have been made with two mixtures containing respectively 20 and 60 mols. % of potassium chloride. The two mixtures were melted and allowed to cool, the rate of cooling between  $370^{\circ}$  and  $340^{\circ}$  being very slow. The mixtures were then powdered, and agitated with a little water for two hours at  $25^{\circ}$ , the saturated solutions obtained being then analysed. The analyses show that the same solution was obtained for both solid mixtures, and from this the conclusion is drawn that the phenomena of mixing in the solid state are not due to the formation of a compound of the two salts. H. M. D.

**The Basicity of Acids.** G. WYROUBOFF (*Ann. Chim. Phys.*, 1913, [viii], 30, 633—634. Compare A., 1909, ii, 740).—A reply to Cornec (compare A., 1913, ii, 840). W. G.

**Properties of Liquids as Functions of the Critical Constants.**  
**JAMES KENDALL** (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 29, 1—28).—It is shown that the heat of vaporisation and the specific volume can be expressed as simple functions of the critical constants, and by reference to the experimental data of Young (A., 1910, ii, 271) the validity of these relations is demonstrated for the ordinary range of temperatures.

For the heat of vaporisation, the equation obtained is

$$Q = k(T_c - T)^n,$$

in which  $Q$  is the latent heat,  $T$  the temperature,  $T_c$  the critical temperature,  $k$  a constant characteristic of the liquid under examination, and  $n$  a constant which has the same value, 0.386, for all normal liquids. By combination of this equation with Trouton's rule, it assumes the form  $MQ = 20.7T(1 - T/T_c)^n$ , in which  $M$  is the molecular weight of the liquid.

For the specific volume of liquids, the equation obtained is:

$$\sqrt[3]{d} - \sqrt[3]{d_c} = k_1(T_c - T)^{\frac{1}{2}},$$

in which  $d$  is the density of the liquid at  $T^\circ$ ,  $d_c$  the critical density, and  $k_1$  a constant which depends on the nature of the liquid. The variation of the density of the saturated vapour with the temperature is represented by a similar formula:

$$\sqrt[3]{d_c} - \sqrt[3]{D} = k_2(T_c - T)^{\frac{1}{2}},$$

in which  $D$  is the density of the saturated vapour at temperature  $T$  and  $k_2$  is a constant characteristic of the substance.

The densities of liquids at absolute zero have been calculated from the first of these two equations, and it is found that the values obtained in this way are in good agreement with those found by Guldberg by extrapolation. The ratio of the density at absolute zero to that at the critical temperature is approximately the same for all normal liquids, with an average value of 3.75, which is identical with the value obtained by Guldberg. With the aid of this relation,  $d_0/d_c = 3.75$ , the equation connecting the specific volume of the liquid with the temperature may be simplified, in which case it reduces to the form  $\sqrt[3]{d/d_c} - 1 = 0.553(1 - T/T_c)^{\frac{1}{2}}$ , and this equation is found to be approximately satisfied by all normal liquids. By combination of the above equations with that of Mills for the heat of vaporisation, the relation:

$$Q = 0.0431833P(V - v) + k_1\mu(T_c - T)^{\frac{1}{2}} + k_2\mu(T_c - T)^{\frac{1}{2}}$$

is obtained, in which  $P$  is the vapour pressure,  $V$  the volume of 1 gram of saturated vapour,  $v$  that of 1 gram of liquid, and  $\mu$  is a constant characteristic of the liquid. According to this, the equation  $Q = k(T_c - T)^{0.386}$  is an interpolation formula, in which the exponent has a value intermediate to the values which are characteristic of the second and third terms of the previous equation. At low temperatures, this equation assumes the form:

$$Q = RT/M + k_1\mu(T_c - T)^{\frac{1}{2}} + \mu\sqrt[3]{d_c}.$$

In this equation the condition  $dQ_0/dT = 0$  is satisfied if the relationship  $k_1\mu M/3T_c^{\frac{1}{2}} = R$  holds. This is found to be the case for normal liquids.

H. M. D.

**Heat of Vaporisation of Associated Liquids.** JAMES KENDALL (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 36, 1—14).—The formula for the heat of vaporisation of normal liquids, given in a previous paper (preceding abstract), has been applied to a number of associated liquids. In the case of normal liquids the value of  $n$  in the equation  $Q = k(T_c - T)^n$  is equal to 0.386, but it is found that the exponent must have its value changed if a formula of this type is to afford values in agreement with those derived from experiment.

If the heats of vaporisation of water, acetic acid, and methyl, ethyl and propyl alcohols are plotted against the temperature  $(T_c - T)$ , it is found that water approximates most nearly to the normal type, whilst acetic acid is the most abnormal. The alcohols occupy an intermediate position. An explanation of the difference in behaviour is put forward, in which the changes in molecular complexity on vaporisation and the accompanying heat changes are taken into consideration.

H. M. D.

**New Relations between the Physical Properties of Liquids.** DANIEL TYRER (*J. Physical Chem.*, 1913, 17, 717—736).—A large number of empirical relations have been found connecting the latent heat of vaporisation, surface tension, density, and other physical properties of liquid substances. From an examination of these relations by reference to the data for a number of chemically dissimilar substances, it appears that the three following equations are satisfied within the limits of experimental error. In these equations  $l$  is the internal heat of vaporisation,  $d_l$  the density of the liquid,  $d_v$  that of the saturated vapour,  $T$  the absolute temperature,  $T_c$  the critical temperature,  $T_s$  the boiling point,  $d_s$  the density of the liquid at  $T_s$ ,  $\gamma$  the surface tension,  $m$  the molecular weight,  $C, C' \dots$  constants which are independent of temperature, but vary with the nature of the liquid,  $k, k' \dots$  constants which are independent both of the temperature and the nature of the liquid. The three relations in question are:

$$ml = C(T_c - T)^{\frac{1}{2}} / (d_l^{\frac{1}{2}} + d_v^{\frac{1}{2}}),$$

$$\gamma^{\frac{1}{2}} = C' d_l^{\frac{1}{2}} (d_l^{\frac{1}{2}} - d_v^{\frac{1}{2}}), \text{ where } C' = k T_s^{\frac{1}{2}} / m^{\frac{1}{2}} \cdot d_s^{\frac{1}{2}}, \text{ and}$$

$$\gamma d_s^{\frac{1}{2}} / l (d_l - d_v)^{\frac{1}{2}} = k'. \text{ The equation:}$$

$$(T_c - T) d_l / l (d_l - d_v) = C'' = k'' m / d_s^{\frac{1}{2}}$$

holds equally well provided the temperature is not less than 60° below the critical temperature, and the relation

$$ml = k''' \sqrt{T_c(T_c - T)}$$

has a similar validity if the temperature is more than 80° removed from the critical temperature. The other relations given by the author are approximate in character, and the divergences met with when these are applied to actual data cannot be accounted for on the basis of experimental error.

H. M. D.

**Relation between the Boiling Point and Composition of a Mixture of Ethyl Iodide and Ethyl Alcohol.** SARAT CHANDRA JANA and JITENDRA NATH SEN GUPTA (*J. Amer. Chem. Soc.*, 1914, 36, 115—118).—A study has been made of the b. p.'s of mixtures of ethyl iodide and ethyl alcohol, and it has been found that these are much lower than the b. p. of either of the two components. A

mixture containing 26.69% of ethyl iodide has b. p.  $70.2^{\circ}$ . As the proportion of ethyl iodide is increased, the b. p. gradually falls until a minimum is reached with a mixture consisting of 87% of ethyl iodide and 13% of ethyl alcohol. This mixture distils at  $61.2^{\circ}$  as a homogeneous liquid. On further increasing the proportion of ethyl iodide, the b. p. rises again; when 97.63% of ethyl iodide is present, the b. p. is  $64.0^{\circ}$ . The results of the investigation are plotted as a curve.

E. G.

**General Comparison of Vapour Pressures.** J. M. CRAFTS (*Compt. rend.*, 1913, 157, 1403—1405).—By means of the formula  $T - T' = (T'' - T''')C$ , where  $T$  and  $T'$  are the boiling points of any substance at pressures  $P$  and  $P'$ , and  $T''$  and  $T'''$  are the boiling points of a standard substance at the same pressures,  $C$  being a constant, it is possible in most cases to calculate all other vapour pressures of a substance. In the case of hydrogen, chlorine, water, alcohols, and acids the formula needs to be modified to:

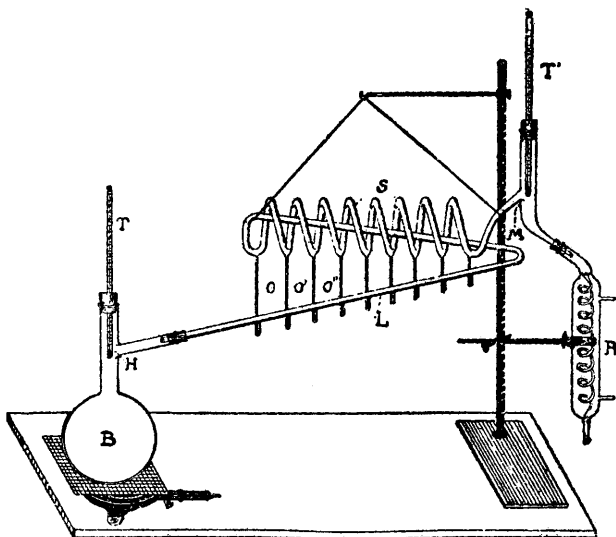
$$T - T' = (T'' - T''')[C \mp c(t' - t)],$$

where  $c$  is another constant.

The standard substance used is naphthalene, and a table is given showing the results for a considerable number of substances, and giving the values of  $C$  and  $c$ . The value of  $t' - t$  increases by unity from zero for each  $20^{\circ}$  difference between  $T''$  and  $T'''$  for naphthalene.

W. G.

**Chenard's Tube for Fractionation by Adiabatic Condensation.** E. HILDT (*Bull. Soc. chim.*, 1914, [iv], 15, 37—41).—The



apparatus is shown in the diagram. Partial condensation takes place in the spiral  $S$ , owing, according to the author, to the cooling of the vapour brought about by the work done in expanding against the external pressure. The liquid thus condensed is

returned by the tubes  $O$ ,  $O'$ ,  $O''$ , etc., to the tube  $L$ , and hence to the flask.

Using this apparatus, the first four fractions of 40 c.c. obtained in the distillation of 1500 c.c. of a 12.5% alcohol consisted of 91% alcohol. T. S. P.

**The Temperature of Sublimation.** J. JOLY (*Phil. Mag.*, 1914, [vi], 27, 1—14. Compare A., 1913, ii, 556).—Further experiments have been made to determine the approximate temperature at which sublimation occurs when different minerals are heated to a gradually increasing temperature in contact with air. The new observations have reference to minerals containing antimony, arsenic, sulphur, tellurium, bismuth, selenium, and lead, and it is shown that the temperature of sublimation may be utilised in the classification of the members of these different groups. H. M. D.

**Laboratory Apparatus for the Continuous Evaporation of Large Volumes of Liquid in a Vacuum.** WILLIAM A. DAVIS (*J. Agric. Sci.*, 1913, 5, 434—436).—A simple apparatus is described with sketch, by means of which large volumes of alcoholic plant extracts, which are liable to froth, can be evaporated continuously, and the distillate recovered, if desired, in fractions. When once started, the distillation can be left to itself, except when the liquid in the flask has to be renewed.

The apparatus consists of an ordinary distilling flask, the side-tube of which is bent upwards, and passes into a short, wide tube, which serves as a froth trap. The latter is connected with the top of an upright condenser, the lower end of which is fitted to a cylindrical funnel (with tap), which is connected below with a pump flask, and above with a large reservoir to ensure a steady vacuum. The vacuum is obtained by means of an ordinary water-pump, a safety valve (Hutchinson, A., 1911, ii, 933) being inserted between the pump and the apparatus. N. H. J. M.

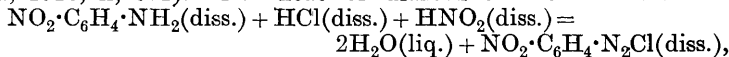
**Heat of Formation of Hydrogen from Hydrogen Atoms.** IRVING LANGMUIR (*Phil. Mag.*, 1914, [vi], 27, 188—189. Compare A., 1912, ii, 826).—Further measurements of the loss of heat from electrically-heated tungsten wires in hydrogen at pressures ranging from 1 to 760 mm. have shown that the value of 130,000 cal. for the heat of formation of hydrogen molecules from hydrogen atoms is much too large. The new experimental evidence indicates a value of 75,000 to 80,000 cal., which is much closer to the value calculated by Bohr from his theory of the constitution of atoms and molecules (A., 1913, ii, 689, 943, 1045). H. M. D.

**The Determination of Heat of Formation from Electromotive Force [Measurements].** LUISE WOLFF (*Zeitsch. Elektrochem.*, 1914, 20, 19—22).—The electromotive force and temperature-coefficients of the *E.M.F.* have been measured for the cells:  
 (1)  $\text{Ag}|\text{AgCl}|n\text{HCl}|\text{Cl}_2|\text{Pt}$ , (2)  $\text{Hg}|\text{HgCl}|n\text{HCl}|\text{Cl}|\text{Pt}$ ,  
 (3)  $\text{Ag}|\text{AgCl}|n\text{HCl}|\text{HgCl}|\text{Hg}$ ,

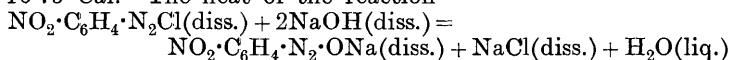
and from the values obtained, the heat of formation of silver chloride and mercurous chloride and the heat of reaction of the change  $2\text{Ag} + \text{Hg}_2\text{Cl}_2 = 2\text{Hg} + 2\text{AgCl}$  have been calculated. The chlorine electrode was fed by chlorine largely mixed with air to reduce the secondary reactions. The heat of formation of silver chloride is found to be 30612 cal.,  $\text{Hg}_2\text{Cl}_2$  31827 cal., and the heat of the reaction between silver and calomel  $-2\cdot1324$  cal. A comparative table is given of the corresponding values found by Halla, Thomsen, Brönsted, Korev, and Braune. J. F. S.

**The Heat of Formation of Some Compounds of Cupric Chloride with Ammonium Chloride.** A. BOUZAT and ED. CHAUVENET (*Compt. rend.*, 1914, 158, 40—42).—The authors have determined the heats of solution of anhydrous cupric ammonium chloride,  $\text{CuCl}_2\cdot 2\text{NH}_4\text{Cl}$ , and the hydrate with  $2\text{H}_2\text{O}$ , obtained in the blue or the green form. The anhydrous double chloride is best prepared by warming the hydrate in an atmosphere of hydrogen chloride and chlorine, or heating it at  $100^\circ$  in a current of dry chlorine. W. G.

**Thermochemical Studies of Diazo- and Azo-compounds. VI. Diazo-derivatives of the Three Nitroanilines.** V. SVENTOSLAVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1739—1765. Compare A., 1910, ii, 691).—The heat of diazotisation of *m*-nitroaniline,



in aqueous hydrochloric acid is  $+24\cdot19$  Cal., and in acetic acid  $+16\cdot75$  Cal. The heat of the reaction



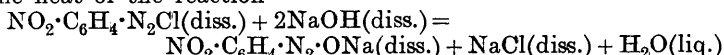
has been measured in three ways: (1) starting from the anti-salt,  $+11\cdot20$  Cal.; (2) starting from the amine,  $+11\cdot04$  Cal.; (3) starting from the diazonium chloride,  $+11\cdot58$  Cal. The agreement between these numbers, in conjunction with the fact that the last method excludes the possibility of the formation of traces of *syn*-diazo-salt, demonstrates that the action of sodium hydroxide, even in dilute solution, on *m*-nitrobenzenediazonium chloride consists in the quantitative isomerisation of the *m*-nitrobenzenediazonium into the *anti*-diazo-salt.

Measurements of the amounts of heat developed in the coupling of *m*-nitrobenzenediazonium chloride with  $\beta$ -naphthol show that the process proceeds quantitatively, independently of whether the  $\beta$ -naphthol or the diazonium salt is in excess.

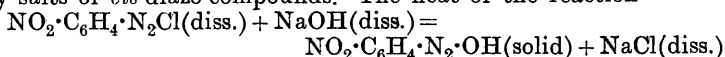
The value,  $+18\cdot89$  Cal., previously given (A., 1910, ii, 691) for the heat of diazotisation of *p*-nitroaniline is incorrect, owing to an error in the calculation of the amount of sodium hydroxide used in one of the control experiments. In aqueous solution the value for the reaction



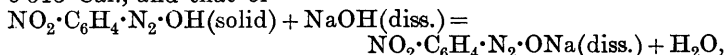
is now found to be +19.722 Cal. in aqueous solution and +18.36 Cal. in acetic acid, or, allowing for the heat of solution of *p*-nitroaniline in acetic acid, namely, -4.47 Cal. (*loc. cit.*), +13.89 Cal. The heat of the reaction



is +13.77 Cal., or if the sodium hydroxide is taken in large excess, +14.724 Cal., so that the salt  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{ONa}$  undergoes hydrolysis, but to an extent inconsiderable in comparison with that shown by salts of *cis*-diazo-compounds. The heat of the reaction

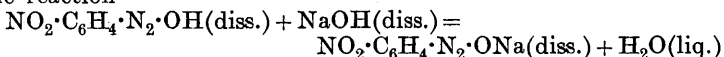


is 6.513 Cal., and that of

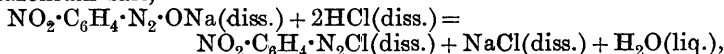


+6.991 Cal.; the sum of these two values, +13.50 Cal., agrees satisfactorily with the number given above, +13.77 Cal. Hence, the product,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{OH}$ , precipitated by the action of the first molecule of sodium hydroxide does not undergo any subsequent profound change, but these results are insufficient to show that its structure is that of a *trans*-diazonium hydroxide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \overset{\text{N}}{\underset{\text{N} \cdot \text{OH}}{\text{N}}}$ ,

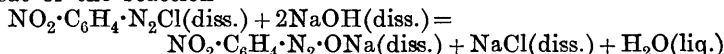
since it might equally well be the nitrosoamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NO}$ . But, if it is assumed that the heat of solution of the precipitate differs little from that of the nitroaniline, 3.74 Cal., the heat of the reaction



will be 3.74 + 6.99 = 10.73 Cal.; and the heat of the same reaction taking place under such conditions that the compound undoubtedly has the structure of a *trans*-diazo-hydroxide, has already been determined to be +10.37 Cal. (*loc. cit.*). Comparison of the heats of solution of *p*-nitrobenzenediazonium chloride in 12.7% hydrochloric acid, -1.363 Cal., and in water, -3.00 Cal., indicates hydrolysis in the aqueous solution. The *trans*-salt,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{ONa}$ , after repeated crystallisation from 95% alcohol, contains  $2\text{H}_2\text{O}$ , and not  $1\text{H}_2\text{O}$ , as was stated by Schraube and Schmidt (A., 1894, i, 237). Its transformation in 12.7% hydrochloric acid into diazonium salt,



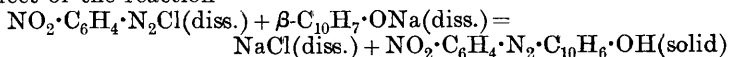
is accompanied by the development of 15.48 Cal., and from this the heat of the reaction



is +11.92 Cal. The difference between the latter number and that determined above, +13.77 Cal., is owing to hydrolysis and decomposition of the *trans*-salt at the beginning of the reaction, to the unevenness of the process of isomerisation, and to the difficulty experienced in making use of concentrated hydrochloric acid as a calorimetric liquid; 13.77 Cal. is the more probable value, and

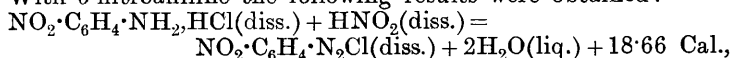


13.63 Cal., instead of 15.48 Cal., for the reverse change. The heat effect of the reaction

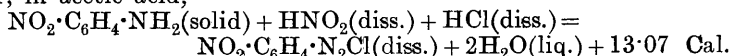


is +38.69 Cal., which should differ from 26.21 Cal., the heat developed by the same reaction in 95% acetic acid, by approximately the heat of neutralisation of acetic acid, namely, 13.30 Cal.; the actual difference is 12.48 Cal.

With *o*-nitroaniline the following results were obtained:



or, in acetic acid,



For the isomerisation of the diazonium salt into *trans*-diazo-salt by the action of excess of sodium hydroxide, the amount of heat developed, +13.78 Cal., agrees exactly with that found with the corresponding para-derivative.

These results, in conjunction with some of those previously obtained, show that, for aniline, *p*-toluidine,  $\alpha$ -naphthylamine, and *m*- and *p*-nitroanilines, the sum of the heats of diazotisation, isomerisation into diazo-hydroxide, and coupling is constant, 48.44–49.35 Cal. For *o*-toluidine, benzidine, and dianisidine, the heat of neutralisation by hydrochloric acid, necessary to the calculation, is unknown.

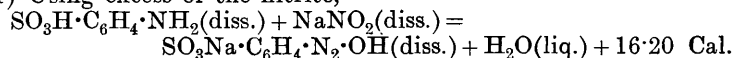
T. H. P.

## Thermochemical Studies of Diazo- and Azo-compounds.

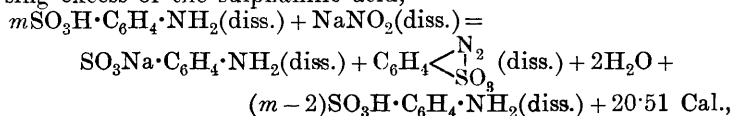
### VII. Supplementary Data for Diazobenzenesulphonic Acid.

V. SVENTOSLAVSKI and A. MANOSZON (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1765–1770).—The following reactions have been investigated:

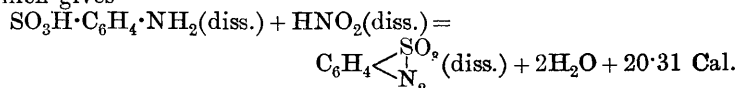
(1) Using excess of the nitrite,



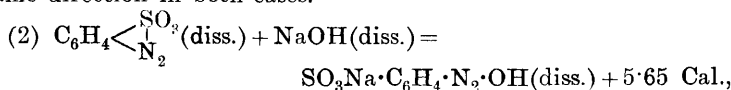
Using excess of the sulphanilic acid,



which gives



The agreement of these results with those previously obtained (A., 1910, ii, 588) shows that the process proceeds quantitatively, independently of whether the nitrite or the sulphanilic acid is in excess, and that the process of diazotisation proceeds in one and the same direction in both cases.



and  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_3 \\ | \\ \text{N}_2 \end{smallmatrix} (\text{diss.}) + 2\text{NaOH}(\text{diss.}) =$

$\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{ONa}(\text{diss.}) + \text{H}_2\text{O}(\text{liq.}) + 10.15 \text{ Cal.};$   
 hence  $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{OH}(\text{diss.}) + \text{NaOH}(\text{diss.}) =$

$\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{ONa}(\text{diss.}) + \text{H}_2\text{O}(\text{liq.}) + 4.50 \text{ Cal.}$

If a large excess of sodium hydroxide is used, the heat of formation of the pseudo-salt,  $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{ONa}$ , is 6.18 Cal., the mean between this value and 4.50 Cal. approximating closely to the value 5.46 Cal. previously given (*loc. cit.*). T. H. P.

**Simple Form of Micro-balance for Determining the Densities of Small Quantities of Gases.** F. W. ASTON (*Proc. Roy. Soc.*, 1914, [A], **89**, 439—446).—A simple form of quartz micro-balance (compare Steele and Grant, A., 1909, ii, 876) is described, in which a small quartz bulb, of about 0.3 c.c. capacity, fused to the end of one arm is balanced by a fixed counterpoise, consisting of a piece of quartz rod, attached to the end of the other arm. With this arrangement the pressure necessary to bring the beam to zero affords a measure of the density of the gas in the balance case. This consists of a cell, about 3 mm. wide, made of thick glass plates, accommodation for the bulb being provided by an attached glass tube, which is closed by a glass plug pushed in as far as possible without actually touching the bulb itself. The case is connected by a short capillary tube to the gas-admission apparatus and pump through one stop-cock, and to the manometer through another. The total volume of the balance case, manometer, and tubes through which the gas is admitted is only a few c.c., so that the quantity of gas necessary for measurements at a pressure of about 100 mm. of mercury is only about 0.5 c.c.

In making measurements with the micro-balance, the gas, of which the density is required, is admitted into the balance case and manometer, and the pressure is raised until the bulb rises and the knob at the extremity of the counterpoise appears on the field of a fixed reading microscope. The pressure is then carefully adjusted until the knob reaches some definite arbitrary zero, when the pressure is read off. The gas is now pumped out, and the operation repeated with a gas of known density. The ratio of the densities is then given by the inverse ratio of the pressures. The determination can be performed in a few minutes, with an accuracy of 0.1%.

It is suggested that the instrument may conveniently be applied to the measurement of pressure in gases of known density.

H. M. D.

**The Relationships between the Co-volume  $b$  and the Critical Constants.** L. GAY (*Compt. rend.*, 1914, **158**, 34—36).—The author has determined the values of the ratios  $V_c/b$  and  $R\theta/\pi b$  (compare A., 1913, ii, 1027) for a number of other substances, inorganic and organic, gaseous and liquid.

For the ratio  $R\theta/\pi b$ , the inorganic substances give values con-

cordant with that already found, namely, 13.84 (*loc. cit.*). The alcohols, aniline, benzonitrile, and water, however, give results differing somewhat widely, and this the author considers is due to their polymerisation.

The ratio  $V_c/b$ , for which the value 3.65 had previously been obtained, needs to be increased to 3.95 for the difficultly liquefiable gases such as nitrogen and argon. The other substances give values closely approximating to 3.65.

W. G.

**Piezometric Analysis.** JEAN TIMMERMANS (*Bull. Acad. Roy. Belg.*, 1913, 810—830).—A method of studying the changes which occur in condensed systems is described. This depends on the observation of the changes in volume which take place when the compressed system is allowed to return very slowly to the condition which it assumes under ordinary atmospheric pressure, the temperature being maintained constant during the process. If the pressure readings are plotted against time, piezometric curves are obtained, which are in many ways analogous to the well-known cooling curves of thermal analysis.

The nature of the piezometric curves which are to be expected for the various types of changes which occur in one or two component systems is examined and discussed in detail. H. M. D.

**Viscosity of Binary Mixtures.** JAMES KENDALL (*Medd. K. Vet. Nobelinst.*, 1913, 2, No. 25, 1—16).—It is shown that the viscosity of binary mixtures of non-associating, chemically indifferent liquids can be satisfactorily represented by the formula  $\eta = \eta_1^{n_1} \cdot \eta_2^{n_2}$  or  $\log \eta = n_1 \log \eta_1 + n_2 \log \eta_2$ , in which  $\eta$  is the viscosity of the mixture,  $n_1$  and  $n_2$  the molar fractions of the two components in the mixture, and  $\eta_1$  and  $\eta_2$  the viscosities of these components.

The formula has been applied to the observations of Thorpe and Rodger, Linebarger, Dunstan, and Getman, and it is found that the average percentage deviation between the calculated and observed viscosity is smaller than that afforded by any of the formulæ which have been previously put forward.

In the case of dilute solutions, the viscosity  $\eta$  may be expressed in terms of that of the solvent  $\eta_0$  by the formula  $\eta = A^x \cdot \eta_0$ , in which  $A$  is a constant and  $x$  the molar concentration of the solute with reference to a fixed weight of solvent. This formula may be derived from the previous formula by assuming that one of the components of the mixture is present in large excess. It is shown that the viscosities of aqueous solutions of sucrose and carbamide and of benzene solutions of octyl hydrogen phthalates can be satisfactorily represented by the second formula over very considerable ranges of concentration.

It should be noted that the above logarithmic formulæ only differ from those put forward by Arrhenius (*A.*, 1888, 236) in the manner in which the composition of the binary mixture is expressed.

H. M. D.

**Viscosity of Calcium Chloride Solutions.** FREDERICK SIMEON (*Phil. Mag.*, 1914, [vi], 27, 95—100).—The viscosity of a series of concentrated aqueous solutions of calcium chloride has been measured at 15° and 20°. The liquid was made to pass at constant pressure through a horizontal tube, about 30 cm. long and 0.4 mm. in diameter. Curves are drawn connecting the viscosity with the concentration, and it is found that these curves are not in agreement with Tucker's recent measurements (*A.*, 1913, ii, 378) of the fluidity at 16.77°. The curve representing Tucker's data intersects the author's curve for 20° at a high concentration. H. M. D.

**Is Poiseuille's Law Valid for Suspensions.** M. ROTHMANN (*Pflüger's Archiv*, 1914, 155, 318—348).—A form of viscometer is described by means of which it is possible to make continuous measurements of the rate of flow of a liquid through a capillary tube when the driving pressure is increased at a steady rate. One end of the horizontal capillary is attached to a wider glass tube serving as reservoir, whilst the other end is connected to a second glass tube of uniform diameter and also perfectly cylindrical. The position of the liquid meniscus in this tube affords a measure of the volume of the liquid which has passed through the capillary. This position is recorded on a photographic film which moves with constant speed in a direction perpendicular to the capillary tube. In the case of a liquid which obeys Poiseuille's law, the record obtained on the film for the movement of the liquid in the wider horizontal tube will be represented by a parabolic curve. This result was actually obtained in experiments with a mixture of glycerol and water. A parabolic curve was also obtained with frog's blood and with dog's blood (diluted with serum in the ratio 1:10) when a capillary tube of a diameter equal to  $465\mu$  was employed. In both these cases, quite different curves were obtained, however, when a tube of much smaller diameter ( $100\mu$ ) was used. The evaluation of these curves by a graphic method indicates that the viscosity diminishes as the pressure increases. The rate of diminution of the viscosity with increasing pressure is much greater in the case of the frog's blood, which fact is doubtless connected with the much larger size of the corpuscles. In the matter of the number of the corpuscles, the two liquids were practically identical, the dilution of the dog's blood with serum in the above-mentioned ratio being such as to make the liquids strictly comparable in this respect.

The experiments indicate that Poiseuille's law is not valid for liquid suspensions moving through narrow capillary tubes. For such liquids, the viscosity depends on the driving pressure, and also on the ratio of the diameter of the suspended particles to the diameter of the capillary.

From an examination of the available observations relating to the circulation of blood in the living organism, the author arrives at the conclusion that this does not occur in accordance with the Poiseuille's law. H. M. D.

**The Laws of Absorption of Carbon Monoxide by Blood in vitro.** MAURICE NICLOUX (*Compt. rend.*, 1913, 157, 1425—1428. Compare A., 1913, ii, 1071; and Douglas, Haldane, and Haldane, A., 1912, i, 591).—The percentage of hæmoglobin combined with carbon monoxide in blood placed in contact with a mixture of carbon monoxide and oxygen can be determined by the equation  $y = 100x / x(1 - K) + 100K$ , where  $y$  is the percentage of hæmoglobin combined with the carbon monoxide and  $x$  the percentage of carbon monoxide in the gaseous mixture, referred to their respective pressures in the mixture, and  $K$  is a constant. The author has verified this law in the case of pig's blood and has obtained very concordant values for  $K$  on varying the values of  $x$ . Hæmoglobin in blood, therefore, when in contact with mixtures of carbon monoxide and oxygen combines with the two gases in proportions defined by their respective pressures in the mixture, and regulated by the law of mass action. The same holds good if air is substituted for oxygen, it being necessary then to consider only the oxygen in the air.

W. G.

**Adsorption from Solutions.** A. M. WILLIAMS (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 27, 1—23).—Experiments have been made on the adsorption of acetic acid by blood charcoal from aqueous solutions and on the adsorption of acetic acid and water from the vapour in contact with acetic acid solutions of varying concentration.

It is pointed out that both solute and solvent may be adsorbed, and when this occurs, the methods usually adopted for the measurement of the adsorption lead to erroneous conclusions, for neither the volume of the solution nor its mass can be regarded as constant. It is therefore suggested that the concentration of the solution should be referred to a constant weight of solvent.

In cases where the adsorption equilibrium is the same, independently of whether adsorption takes place from solution or from the vapour phase in contact with it, it is shown that the amounts of solvent and solute adsorbed may be calculated. In terms of this double adsorption, it is possible to give a simple explanation of the phenomena of "negative" and "anomalous" adsorption.

Observations at great dilutions seem to show that the value of  $n$  in the exponential adsorption equation  $a = kc^n$  becomes a whole number or a simple fraction.

H. M. D.

**Utilisation of Diffusion Processes in the Preparation of Pure Substances.** JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1914, 36, 16—19).—The formation of large particles of slightly soluble substances can be secured by causing the separation of the substance to proceed very slowly and by so selecting the temperature and composition of the medium as to have the substance as soluble as possible. The simplest way of carrying out such a process is to fill, with a suitable liquid, a large vessel at the opposite sides of which are placed two small evaporating dishes containing the solid substances. The vessel is protected from violent fluctuations of tem-

perature in order to prevent the disturbing effect of convection. By this means, large hexagonal prisms of calcium hydroxide can be obtained from calcium chloride and sodium hydroxide at the ordinary temperature. Large crystals of barium sulphate have been obtained in a similar manner at 100°, which were practically free from the impurity occluded by this salt when precipitated in the usual way.

Another method is described in which solutions of the interacting substances are placed in flasks provided with syphon tubes which dip into the main mass of liquid. Each solution is transferred very slowly, since air is only admitted into each flask through a second tube which is drawn out to a very fine capillary.

The crystals obtained in this way are of great purity, and are, therefore, very suitable for the determination of physico-chemical constants.

E. G.

**Molecular Complexes in Solutions and the Distribution of Certain Substances between Benzene and Water.** F. BUBANOVIĆ (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 33, 1—29).—By means of measurements of the changes which occur in the freezing points of solutions of ethyl alcohol, acetic acid, and chloral hydrate in benzene when successive small quantities of water are added to the solutions, it has been found that each of these substances forms hydrates by combination with the added water. From these data and the molecular association of the three substances in anhydrous benzene solution, it has been found possible to deduce approximately the composition of the hydrates. The calculations indicate that ethyl alcohol in the more dilute solutions forms the hydrate  $6\text{EtOH}\cdot\text{H}_2\text{O}$ , whilst in solutions which contain a larger proportion of alcohol, the hydrate  $8\text{EtOH}\cdot\text{H}_2\text{O}$  appears to be formed. In the case of acetic acid and chloral hydrate, the complex molecules formed correspond with the formulæ  $4\text{CH}_3\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$  and  $4\text{CCl}_3\cdot\text{CH}(\text{OH})_2\cdot\text{H}_2\text{O}$ .

The solubility of water in benzene solutions of the above three substances has also been determined. The results show that the increase in the solubility is proportional to the square of the quantity of ethyl alcohol associated with a definite quantity of benzene, whilst the increase of the solubility in the case of acetic acid and chloral hydrate solutions is proportional to the first power of the quantities of these substances.

Other experiments have been made on the ratio of distribution of alcohol, acetic acid, and chloral hydrate between benzene and water. These show that all three substances form complex molecules in the benzene solution.

H. M. D.

**Solubility of Crystals on Different Faces.** J. LEBRUN (*Bull. Acad. Roy. Belg.*, 1913, 953—979).—A solution of sodium nitrate (containing 48·55 grams of salt per 100 c.c.) dissolved from the faces (1011), (0001), and ( $\bar{1}\bar{2}\bar{1}0$ ) of a crystal of sodium nitrate, 11·8, 10·8, and 10·7 mg. per sq. cm. per minute respectively. A solution of magnesium sulphate (33·10 grams  $\text{MgSO}_4$  per 100 c.c.)

dissolved from the faces (001), (010), (110), and (111) of a crystal of magnesium sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), 3.7, 3.5, 3.5 and 3.7 mg. per sq. cm. per minute respectively. The amount of material in mg. per sq. cm. per day dissolved from different faces of a quartz crystal by hydrofluoric acid of concentration I (9.718 grams) and II (20.169 grams HF per 100 c.c. of solution) is as follows:

	I.	II.
Base (0001) .....	7.2	18.76
Prism of second order (11 $\bar{2}$ 0) ...	1.15	4.37
Prism of first order (10 $\bar{1}$ 0) .....	1.17	4.41
Direct rhombohedron (10 $\bar{1}$ 1) ...	0.97	3.7
Fused quartz .....	—	70.0

L. J. S.

**Solubility Differences on Crystal Surfaces.** ALBERT RITZEL (*Zeitsch. physikal. Chem.*, 1913, **86**, 106—108).—Polemical against Kuessner (A., 1913, ii, 932; compare also Ritzel, A., 1911, ii, 488).

J. F. S.

**Modifications of the Form of Crystals of Some Substances Artificially Coloured during their Growth.** PAUL GAUBERT (*Compt. rend.*, 1913, **157**, 1531—1533. Compare A., 1906, ii, 152, 343; 1910, ii, 4; Marc, A., 1911, ii, 193, 258).—Colouring matters dissolved in aqueous solutions of various salts, from which crystallisation is proceeding, enter regularly into the crystals during the growth, not only modifying their faces, but also causing the formation of macles.

W. G.

**Retger's Rule as a Criterion of Isomorphism.** W. STORTENBEKER (*Rec. trav. chim.*, 1913, **32**, 210—225).—A theoretical paper in which the various means of testing isomorphism are discussed. It is shown that there is nothing, or at most very little, in modern work which is incompatible with the view that the properties of isomorphous mixtures are a continuous linear function of the composition; this is most markedly seen in the case of the specific volume of isomorphous mixtures.

J. F. S.

**The Action of Hydroxyl Ions on Clays and Kaolins.** II. PAUL ROHLAND (*Biochem. Zeitsch.*, 1913, **58**, 202—204. Compare A., 1912, ii, 1150; 1913, ii, 412).—Very small hydroxyl ion concentrations have no influence on the sedimentation of kaolin emulsions. If the concentration is increased, the sedimentation effect is also increased up to a certain maximum point. Increase of the hydroxyl concentration above this point generally slowly diminishes the sedimentation.

S. B. S.

**Equilibrium in Ternary Systems.** X. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 540—552. Compare A., 1913, ii, 851; this vol., ii, 41).—A theoretical paper in which the author discusses the nature of the equilibria in ternary systems characterised by constancy of both temperature and pressure.

H. M. D.

**Equilibria in the System, Sulphuric Acid, Ammonium Sulphate, and Lithium Sulphate at 30°.** G. C. A. VAN DORP (*Zeitsch. physikal. Chem.*, 1913, 86, 109—112. Compare Dorp, A., 1910, ii, 698; and Schreinemakers and Cocheret, A., 1906, ii, 424; 1907, ii, 23).—The equilibrium relations of the four-phase system water, sulphuric acid, ammonium sulphate, and lithium sulphate have been determined and the results plotted on a projected spatial co-ordinate system. The following hitherto unknown compounds were isolated:  $(\text{NH}_4)_2\text{SO}_4, 3\text{Li}_2\text{SO}_4, 4\text{H}_2\text{SO}_4$ ;

$2(\text{NH}_4)_2\text{SO}_4, 2\text{Li}_2\text{SO}_4, 4\text{H}_2\text{SO}_4$ ; and  $3(\text{NH}_4)_2\text{SO}_4, \text{Li}_2\text{SO}_4, 4\text{H}_2\text{SO}_4$ .

J. F. S.

**Neutral Salt Action.** BOHDAN DE SZYSZKOWSKI (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 41, 1—55. Compare A., 1907, ii, 238; 1908, ii, 761; 1910, ii, 703).—The experiments described were carried out in order to determine the influence of strong electrolytes on the affinity constants of weak acids. It is shown that this influence may be calculated from observations on the distribution of the acids between benzene and water containing varying amounts of a strong electrolyte. The acids used were benzoic and salicylic, with sodium chloride as the electrolyte, and the concentration of this was varied from 0.1 to 1*N*.

If the values of the affinity constants of the acid are plotted as a function of the sodium chloride concentration, the curve for benzoic acid is found to rise from  $6.0 \times 10^{-5}$  in pure water to a maximum value of  $8.2 \times 10^{-5}$  at about 0.5*N*. As the concentration of the sodium chloride is further increased, the affinity constant falls, and in 1*N*-solution its value is only  $4.1 \times 10^{-5}$ .

In the case of salicylic acid, a similar type of curve is obtained, the affinity constant increasing from  $1.02 \times 10^{-3}$  in water to a maximum value of about  $1.65 \times 10^{-3}$  in 0.25*N*-solution, then falling to  $1.00 \times 10^{-3}$  in 1*N*-sodium chloride solution.

The results obtained for a particular concentration of the strong electrolyte are independent of the concentration of the acid, and this fact affords strong support to the interpretation which is placed on the experimental data. In order to account for the maximum in the value of the affinity constant at a definite salt concentration, it is supposed that the ionisation of the acid is subjected to the influence of two opposite factors. On the one hand, the ions tend to increase the ionisation of the weak acid, whilst the undissociated salt molecules tend to reduce the ionisation. The maximum affinity constant can obviously be explained on the basis of this hypothesis, for the action of the ions will preponderate in the more dilute solutions, and that of the undissociated molecules will be the more important in more concentrated solutions.

Measurements of the solubility of benzoic and salicylic acids in water containing variable amounts of sodium chloride have given results which support the above view. In this connexion, it may be noted that the solubility of salicylic acid in 0.1*N*-sodium chloride solution is somewhat greater than it is in pure water.

The later portions of the paper are concerned with the explana-



tion of the deviations from the mass law which are exhibited by strong electrolytes, and the view is expressed that such deviations are merely due to effects comparable with that which has been examined by the author. When it is possible to apply the necessary correction for such neutral salt effects, it will probably be found that the mass law is applicable to the ionisation of all electrolytes.

H. M. D.

**The Combustion of Gaseous Mixtures and the Velocities of Reaction.** TAFFANEL (*Compt. rend.*, 1914, 158, 42—45).—A mathematical discussion of results already published (compare A., 1913, ii, 1039).

W. G.

**Influence of Hydrogen Ion and of Neutral Salts on Colour Changes and Reaction Velocities among Dyes of the Triphenylmethane Series.** H. C. BIDDLE (*J. Amer. Chem. Soc.*, 1914, 36, 84—104).—It has been shown in an earlier paper (A., 1913, ii, 312) that the action of an excess of an acid on a rosaniline dye or its carbinol base leads to an equilibrium between the coloured and the colourless forms which is largely dependent on the concentration of the hydrogen ions of the acid.

A further study of this change has proved that the velocity of the reaction leading to this equilibrium is a function of the diminishing concentration of the  $H^+$  ion. The rate of the reaction differs from that of the conversion of the cinchona alkaloids into their toxins (Biddle and Rosenstein, A., 1913, ii, 492) in being independent of the nature of the acid and being consequently a function of the molecular concentration of the acid. The velocity increases as the temperature rises, the rate of increase becoming greater with diminishing concentration of the  $H^+$  ion. Neutral salts increase or decrease the rate of the reaction in presence of a weak acid in accordance with their effect in diminishing or increasing the degree of dissociation of such an acid. The neutral salt effect gives rise to a change of colour and a diminution of the velocity of the reaction corresponding precisely with the results produced by an increasing concentration of the  $H^+$  ion. It has been found that, within certain limited ranges, the rate of reaction may be used as a dynamic method for determining the concentration of the  $H^+$  ion.

E. G.

**Expression of the Velocities of Transformation of Physico-chemical Systems as a Function of the Affinity.** R. MARCELIN (*Compt. rend.*, 1913, 157, 1419—1422. Compare A, 1911, ii, 27).—A mathematical discussion of such expressions in the case of diffusion, evaporation, sublimation, and solution, based on the hypothesis that a physico-chemical complex in process of transformation is constituted by two systems, which evolve in opposite senses; the progressive system increases in mass, whilst the regressive system diminishes. The observed velocity  $v$  is the resultant of the velocities of these systems.

W. G.

**Reactions of Vibriolysins.** SVANTE ARRHENIUS [with THORVALD MADSEN and YUTAKA TERUUCHI] (*Medd. K. Vet. Nobelinstitut*, 1913, 2, No. 39, 1—39).—Experiments have been made to determine the nature of the processes which are involved in the absorption of vibriolysin by blood corpuscles, coagulated serum-albumin and animal charcoal, and also in its neutralisation by anti-vibriolysin.

In the case of the blood corpuscles, the rate of absorption can be represented by the formula for a unimolecular reaction, an equilibrium condition being reached in which the concentration of the vibriolysin in the corpuscles is 286 times that in the surrounding solution. The ratio of distribution in the equilibrium condition has been found to remain constant when the concentration is varied in the ratio 1:25. The velocity of absorption increases very rapidly with the temperature, the velocity becoming 4·7 times as great for a rise of 10°.

The dynamic experiments with charcoal show that vibriolysin is decomposed by this substance, and the data would appear to indicate that each particle of carbon is only capable of decomposing a definite quantity of the lysin per unit of time. In many respects, the change offers a close resemblance to reactions in which enzymes are involved. The influence of temperature on the change is relatively small, a rise of temperature of 10° increasing the velocity only in the ratio 1:1·5.

The neutralisation of vibriolysin by anti-vibriolysin takes place in accordance with the formula for a bimolecular reaction if the concentrations of the reacting substances are reckoned from the equilibrium condition. This behaviour is closely similar to that which has been observed in the neutralisation of tetanolyisin.

With regard to the absorption of the lysin in coagulated serum-albumin, it is found that the process leads to a condition of equilibrium, and that the rate of change is approximately in agreement with the bimolecular formula. The amount absorbed in the equilibrium condition is proportional to the square-root of the concentration of the surrounding solution, and it seems probable, therefore, that the phenomenon is one of absorption. It differs, therefore, completely from the changes which are involved in the absorption of vibriolysin by blood corpuscles and in the neutralisation by anti-vibriolysin. Although the decomposition of the lysin is the chief characteristic in the action of animal charcoal, it is possible that the decomposition is preceded by adsorption. H. M. D.

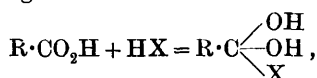
**The Influence of Foreign Substances on the Activity of Catalysts. III. Platinum as Hydrogen Carrier.** C. PAAL and E. WINDISCH (*Ber.*, 1913, 46, 4010—4016).—In continuation of previous experiments (compare A., 1913, ii, 1043), the catalytic behaviour of platinum deposited on various metal powders and insoluble compounds has been investigated; the particular reaction used was the reduction of cotton-seed oil by hydrogen.

The platinised metals were prepared by shaking the metal powder with an aqueous solution of chloroplatinic acid; in the case of magnesium an aqueous-alcoholic solution was used. The products

were washed with water, alcohol, and ether, excepting platinised magnesium, where washing with water was omitted, and then dried in a vacuum. The amount of platinum deposited was 2·5% of the weight of the metal. The compounds were coated with 2·5% of platinum by suspending them in an alkaline solution of chloroplatinic acid and subsequent reduction with hydrazine.

Only magnesium and nickel have no effect on the catalytic activity of the platinum; aluminium, cobalt, and bismuth diminish the activity very considerably, whilst iron, copper, zinc, silver, tin, and lead do away with it completely. Magnesium oxide and carbonate have no effect, whereas basic lead carbonate and basic bismuth nitrate make the platinum passive. T. S. P.

**Catalytic Esterification by the Wet Method.** F. BODROUX (*Compt. rend.*, 1913, 157, 1428—1430).—A theoretical discussion of the nature of the action in the catalytic esterification of acids by means of inorganic acids (compare this vol., i, 10). The author suggests that an intermediate additive compound is formed by the organic and inorganic acids as follows:



where HX represents an inorganic acid.

W. G.

**Size and Constitution of the Atoms.** ADOLF HEYDWEILLER (*Ann. Physik*, 1913, [iv], 42, 1273—1286. Compare A., 1913, ii, 645, 919).—The diameters of molecules can be calculated from the mean free path in the gaseous condition, and also from the molecular refractivity. A comparison of the results obtained in the case of the monatomic inert gases shows that satisfactory agreement is obtained only in the case of xenon. With falling atomic weight, the divergence between the numbers increases, and in the case of helium the ratio of the values reaches 1·5:1.

The values obtained for the diameters of the molecules of hydrogen and chlorine from viscosity data are respectively 2·176 and  $3\cdot693 \times 10^{-8}$  cm. The diameters of the hydrogen and chlorine ions as deduced from refractivity data are  $1\cdot663 \times 10^{-8}$  cm. and  $2\cdot765 \times 10^{-8}$  cm. respectively. The ratio of the numbers for hydrogen is 0·764, and for chlorine 0·749. On the assumption that the hydrogen (or chlorine) atoms fuse together to form a spherical molecule, the ratio of the atomic to the molecular diameter would be 0·794. If, on the other hand, the atoms remain isolated, the ratio of the atomic to the effective molecular diameter would be 0·774. Both these numbers are in fair agreement with the above ratios for hydrogen and chlorine, and afford support for the author's view that atomic dimensions can be accurately calculated from refractivity data.

The constitution of the atom is discussed in reference to the author's steric theory (*loc. cit.*), and evidence is obtained which suggests that the number of electrons in the atom is about a hundred times as large as the steric number. According to this, the hydrogen atom would contain about 500 electrons. H. M. D.

**Theory of the Electrical and Chemical Forces in the Atom.** A. БЫК (*Ann. Physik*, 1913, [iv], 42, 1417—1453).—A theoretical paper, in which the author discusses the constitution of the atom and the nature of the forces which come into play in atomic systems. The theory is applied in the calculation of molecular dimensions, values being obtained for the diameters of the molecules of the alkali metals, the halogens and compounds of carbon, sulphur, and chlorine, which are in accordance with those derived from experimental data. The heats of dissociation of chlorine, bromine, iodine, sulphur, and phosphorus are also deduced from a formula in which electro-magnetic data only are involved, the values obtained being in all cases in fair agreement with the thermal data recorded in the literature.

A further conclusion to which the author's theory leads is that the forces operating within the atom give rise to a definite atomic configuration in the case of the atoms of carbon compounds and complex inorganic compounds, but that such a condition of atomic equilibrium is not characteristic of the atoms of electrolytes.

H. M. D.

**Calculations of Frequency and Certain Relations between Elastic and Thermal Constants of Solid Elements.** C. E. BLOM (*Ann. Physik*, 1913, [iv], 42, 1397—1416).—The various formulæ which have been put forward for calculating the frequencies of atomic vibration are compared by reference to the values obtained for a large number of metals. The values are not in agreement, and it is not possible to decide which of the formulæ gives the best results.

The formula comparison suggests that the quantities  $1/K$ ,  $T_s/V$ ,  $R/3\alpha V$ , and  $C_v/3\alpha V$  are proportional to one another,  $K$  being the compressibility,  $T_s$  the absolute melting temperature,  $V$  the atomic volume,  $R$  the gas constant,  $C_v$  the atomic heat at constant volume, and  $\alpha$  the coefficient of linear expansion. If this proportionality is assumed, a number of relations can be shown to hold between the elastic and thermal constants; these relations have been obtained previously, in some cases empirically and in others by theoretical deduction.

The atomic frequencies show a periodic variation with the atomic weight, a relation which is not surprising in view of the periodic connexion between the elastic properties and the atomic weight, and of the fact that the atomic frequencies are closely related to the cohesive forces.

Although the frequency formulæ are not in general applicable to compounds, certain relations which these formulæ suggest are to be found between the elastic and thermal properties in certain cases. For oxides of the type RO it is shown that there is a parallelism between the hardness and the atomic heat. H. M. D.

**Linking of Atoms, particularly those of Carbon.** A. F. HOLLEMAN (*Rec. trav. chim.*, 1913, 32, 175—183).—The author evolves a theory of the linking of atoms which combines some of

the views of Werner with those of Stark. Making use of Stark's idea of valency electrons, it is shown how the linkings can move their relative positions on the surface of the atoms. The hypothesis is made use of to explain the Walden inversion, racemisation, and the Baeyer strain theory. It is shown that easy formation of double linkings cannot be directly explained on the present hypothesis. The theory is examined in the case of other atoms; the positions of the valency electrons at opposite ends of a diameter of the oxygen atom are regarded as producing a strain in the carbonyl group, which explains the ease with which the carboxyl group enters into combination. The isomerism of oximes is explained if the quinquivalent character of nitrogen is admitted. The equilibrium positions of the valency electrons for elements of valencies one to six are deduced. J. F. S.

**Mechanical Processes of Combination.** NATHANIEL T. BACON (*J. Physical Chem.*, 1913, 17, 762—768).—A theoretical paper in which an attempt is made to explain certain reactions between gases and solids by the assumption that condensed layers of gas molecules are formed at the surface of the solid in consequence of the imperfect elasticity of the molecules. H. M. D.

**The Electron Theory and the Conception of Valence.** P. DE HEEN (*Bull. Acad. Roy. Belg.*, 1913, 667—679).—The author considers that the electron theory does not furnish any satisfactory explanation of the behaviour of elements of variable valency. H. M. D.

**Automatic Mercury Pump.** G. P. PAMFIL (*J. Chim. Phys.*, 1913, 11, 801—804).—A description of a mercury pump, the automatic action of which is maintained by the use of a water-pump. The reservoir into which the gases from the apparatus to be exhausted expand, and from which they are then expelled by the mercury, is relatively large, so that the rate of exhaustion is rapid. The pump contains an arrangement for collecting the exhausted gases for analysis. T. S. P.

**Simple Stirring Arrangement for Test-tubes.** H. E. SCHAUMBURG (*Chem. Zeit.*, 1913, 37, 1581).—A bulb, the diameter of which is about 1 mm. less than the internal diameter of a test-tube, is blown on the end of a piece of glass tubing. If this is immersed in the liquid in the test-tube and then moved rapidly up and down, taking care that the bulb does not come above the surface of the liquid, it acts as a very efficient stirrer. T. S. P.

**An Electric Vacuum Oven for High Temperatures.** JOHANNES WOLF and ERICH MÜLLER (*Zeitsch. Elektrochem.*, 1914, 20, 1—4).—An electric oven is described, which, by the use of carbon resistance tubes, gives a temperature of 2850°. The energy consumption for this temperature is 15 kilowatts, a quantity about 30% less than that consumed by other ovens of the same type.

The furnace is fitted with an arrangement for removing the experimental substance whilst it is at its highest temperature.

J. F. S.

**A Rapid Apparatus for Ether Extractions.** J. J. L. ZWIKKER (*Pharm. Weekblad*, 1914, 51, 21—23).—A new simple form of ether-extraction apparatus, in which the extraction vessel is immersed in a condenser, the ether vapour is carried by a bent tube to the lower end of it, and the condensed ether rises through the liquid to be extracted, and passes through a side-tube back into the heating flask.

A. J. W.

**A New Form of Extraction Apparatus and Reflux Condenser.** PROBODHA CHUNDRA CHATTOPADHYAY (*J. Soc. Chem. Ind.*, 1913, 32, 1145—1146).—The extractor consists of an outer glass jacket and an inner glass tube (thimble) of smaller diameter. The latter is provided with a series of holes at the top and with some near the middle; there is also a very small hole at the bottom of the thimble to allow the liquid to drain away completely when the extraction is finished. There is no syphon tube, as in the Soxhlet apparatus. The substance to be extracted is placed directly into the thimble, or else in a fat-free paper thimble, which is then placed in the glass thimble. During the extraction the liquid overflows continuously through the holes near the middle of the thimble.

In the reflux condenser the inner tube consists of a series of four bulbs with flat spirals interposed between the second and third, and between the third and fourth bulbs. The advantage of this arrangement is that a central draught, which is a drawback, even with double surface condensers, is prevented.

T. S. P.

**Experiments in Dyeing.** A. W. DAVISON (*J. Physical Chem.*, 1913, 17, 737—754).—The paper contains an account of a series of experiments on the dyeing of wool and cotton which were undertaken with the special object of collecting data which might be utilised in devising lecture experiments to illustrate the theory of dyeing. The experiments were made with basic and acid dyes, and the behaviour of these in alkaline, neutral, and acid solution was compared. Other observations have reference to the influence of the addition of sodium sulphate and the behaviour of lakes.

H. M. D.

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### Inorganic Chemistry.

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**Preservation of Hydrogen Peroxide by means of Acetanilide.** A. M. CLOVER (*Amer. J. Pharm.*, 1913, 85, 538—545) —The investigation has been undertaken with the object of determining the justification for using acetanilide as a preservative for com-

mercial hydrogen peroxide solutions, since it has been claimed that the usual instability of the latter is due to the presence of certain impurities introduced in the course of manufacture and that, if these impurities could be eliminated, a stable product would result.

The gradual decomposition of hydrogen peroxide solution in the presence of hydrochloric, sulphuric, phosphoric, or boric acid at different concentrations has been studied, whilst the effect of various salts (sodium chloride, potassium chloride, calcium chloride, sodium silicate, ferric chloride, and aluminium sulphate) alone and with acetanilide on solutions of hydrogen peroxide which have been made  $N/100$  in hydrochloric, sulphuric, and phosphoric acids respectively, has been investigated.

The author is led to the conclusion that pure hydrogen peroxide is a very unstable substance, and that its stability is greatly increased by the addition of small amounts of acid. Addition of salts of the alkali and alkaline-earth metals does not appear to have any marked effect. Of the acids used, phosphoric acid gave the best results at all concentrations, but the best preserved solution had lost nearly 30% in strength after seven months. In the presence of both acids and salts, the decomposition in those solutions containing acetanilide is only a small fraction of that in the corresponding solutions which do not contain the preservative. As to the mineral impurities, the salts of the alkali and alkaline-earth metals and all other salts used, except those of copper and iron, appear to have no influence whatever on the stability of the solutions when acetanilide is used. Traces of copper and iron have a very deteriorating effect, but this is prevented to a great extent by acetanilide. H. W.

**Ignition of a Glowing Splint of Wood in Oxygen Mixtures.** P. ANEMA (*Chem. Weekblad*, 1913, 10, 1056).—A mixture of air and oxygen containing 30% of the latter does not ignite a glowing splint of wood. A. J. W.

**Ignition of Glowing Match-Sticks and the Extinction of Their Flame in Mixtures of Oxygen and Nitrogen.** W. P. JORISSEN (*Chem. Weekblad*, 1913, 10, 1057. Compare preceding abstract).—The ignition limit is 28—29% of oxygen by volume, and the extinction limit about 16% of oxygen by volume. A. J. W.

**A Third Form of Sulphur. III.** A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1913, 86, 1—35. Compare A. 1913, ii, 580).—The third form of sulphur,  $S_\pi$ , has been further investigated. A method is devised by means of which the quantity of  $S_\pi$  may be estimated in a mixture of  $S_\lambda$ ,  $S_\mu$  and  $S_\pi$ . The transformation of  $S_\pi$  into  $S_\mu$  is investigated, and it is shown that the change  $S_\pi \rightarrow S_\mu$  is, at first, very rapid, but the velocity quickly decreases and becomes extremely small when there is only a small quantity of  $S_\pi$  present. The relative quantities of  $S_\lambda$ ,  $S_\mu$ , and  $S_\pi$  present in sulphur which has been heated to various temperatures are determined. The amount of  $S_\pi$  is at a maximum in sulphur which has been heated to  $180^\circ$ , and at this point the amount present is 6.5%. The quantity



of  $S_\mu$  increases as the temperature increases up to  $445^\circ$ , the greatest rate of increase being between  $170^\circ$  and  $180^\circ$ .  $S_\lambda$  decreases as the temperature increases; at  $180^\circ$ , the composition is given by  $S_\pi = 6.5\%$ ,  $S_\mu = 20.4\%$ , and  $S_\lambda = 73.1\%$ . The influence of the catalysts, sulphur dioxide, ammonia, and iodine on the equilibria  $S_\mu \rightleftharpoons S_\pi \rightleftharpoons S_\lambda$  is studied, and it is shown that ammonia increases the transformation of  $S_\pi$  more than it does that of  $S_\mu$ . The change  $S_\pi \rightarrow S_\mu$  takes place at the same rate in the presence of iodine as it does in the absence of iodine. The hard and soft varieties of  $S_\mu$  are considered together with  $S_\pi$ , and evidence advanced to show that  $S_\pi$  is, in all probability, contained in the soft variety of  $S_\mu$ , which is really a mixture of  $S_\pi$ ,  $S_\lambda$ , and  $S_\mu$  containing very little  $S_\lambda$ . A number of properties of sulphur, for example, coefficient of expansion, and viscosity are considered, and it is shown that the changes in these properties with temperature are more easily explained when three modifications of sulphur are admitted than when two only are considered. A table of the composition of various forms of solid sulphur is given; in most cases, the quantity of  $S_\mu$  is extremely small, but  $S_\pi$  is found in sulphur which has been melted, but not in that which has been crystallised. J. F. S.

**The Change of Sulphites into Sulphates.** ÉMILE SAILLARD (*Zeitsch. Ver. deut. Zuckerind.*, 1913, 1035—1043. Compare Titoff, A., 1904, ii, 113; Lange, A., 1912, ii, 550).—The change of sulphites into sulphates is retarded in sucrose solutions, the amount of retardation being the greater the greater the concentration of the sucrose. Rise in temperature increases the velocity of change.

Invert sugar has approximately the same effect as sucrose. Nitrogenous substances, for example, asparagine, aspartic acid, glutamic acid, and potassium lactate, also exert a retarding action, whilst sodium chloride has no effect. T. S. P.

**Active Nitrogen.** ERICH TIEDE and EMIL DOMCKE (*Ber.*, 1913, 46, 4095—4103).—In a previous communication (A., 1913, ii, 210), Tiede has stated that, when pure nitrogen is used, the active modification of Strutt cannot be obtained; this has been disputed by Koenig and Elöd (A., 1913, ii, 316) and by Strutt (A., 1913, ii, 316, 696). The authors now give an account of experiments in support of the statement of Tiede.

In the preliminary experiments, the apparatus was made completely of glass, no rubber joints being used; the various connexions were either fused together, or else cemented with marine glue. Taps were made tight with mercury, in order to prevent the use of any fat, and mercury vapour was prevented from diffusing into the apparatus by the interposition of vessels filled with gold leaf and cooled in liquid air. The nitrogen used was freed from oxygen by a combination of the copper method with that of Gehlhoff (A., 1911, ii, 487), and moisture and carbon dioxide were removed by appropriate absorbents. All parts of the apparatus were freed from adsorbed gases by heating during exhaustion. Under these

conditions, when it was certain that all oxygen had been removed, the phenomena described by Strutt could not be observed.

The final experiments were made with a smaller apparatus, completely of glass, which contained, fused on to it, two glass tubes containing, respectively, barium azoimide and silver oxide, from the former of which pure nitrogen is readily obtained by heating at  $170^{\circ}$ . After all parts of the apparatus had been freed from gas by repeated heating and exhausting, the barium azoimide being maintained at  $120^{\circ}$ , it was filled with pure nitrogen from the azoimide. There were then no signs of Strutt's phenomenon, but, if the silver oxide were heated in order to add oxygen to the contents of the apparatus, the characteristic glow was observed. The apparatus could then be cleaned from oxygen, filled with pure nitrogen, and again there would be no sign of Strutt's phenomenon.

The authors, therefore, conclude that the phenomena observed with so-called "active nitrogen" are due to traces of oxygen in the nitrogen.

T. S. P.

**Oxidation of Nitrogen during Electric Discharge.** FRANZ FISCHER (*Ber.*, 1913, 46, 4103).—The author maintains his opinion that the oxidation of nitrogen during electric discharges is preceded by an activation of the oxygen (compare Fischer and Hene, A., 1913, ii, 132, 317). The views of Koenig and Elöd (A., 1913, ii, 1049) are invalidated by the recent communication of Tiede and Domcke (compare preceding abstract).

T. S. P.

**Combustion of Air in the Voltaic Arc.** A. GORBOV and V. MITKEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1693—1697).—The authors criticise the manner in which the results of Saposhnikov, Gudima, and Kutovski (A., 1913, ii, 950) are expressed, the hourly volumes of air passing through the furnace being referred to varying numbers of kilowatts, whereas the important point is, not the absolute volume of air traversing the furnace per unit of time, but a magnitude indicating the amount of energy applied to such volume of air. Calculation from the results given by the above authors shows good agreement with the formulæ elaborated by the present authors (A., 1913, ii, 950).

T. H. P.

**Reduction of Hydronitric Acid [Azoimide]. II. Structures of the Trinitride Radicle.** J. W. TURRENTINE (*J. Amer. Chem. Soc.*, 1914, 36, 23—35. Compare A., 1912, ii, 448).—Further evidence is adduced in favour of the formula  $\text{H}\cdot\text{N}:\text{N}:\text{N}$  for azoimide (compare Turrentine and Moore, A., 1912, ii, 449). It is shown that Fischer's interpretation of the reaction yielding diazobenzeneimide (A., 1878, 305), on which is based the conception of the cyclic structure of the trinitride radicle, is erroneous. It is pointed out that this reaction is essentially an oxidation of hydrazine, and that Browne and Shetterly (A., 1907, ii, 863; 1908, ii, 373; 1909, ii, 233, 658), in their study of the oxidation of hydrazine, have failed to observe any reaction analogous to that proposed by Fischer.

E. G.

**The Intermediate Formation of Nitrogen Trioxide by the Action of Oxygen on Nitric Oxide. Behaviour of Nitrogen Trioxide towards Potassium Hydroxide.** GABRIEL KLINGER (*Zeitsch. angew. Chem.*, 1914, 27, 7—8).—Both Raschig and Lunge have shown that a mixture of nitric oxide and nitrogen dioxide dissolves in concentrated sulphuric acid quantitatively, as if it were the compound  $N_2O_3$ , whereas sodium hydroxide dissolves only about 85% of the mixture, relatively more of the dioxide dissolving than of nitric oxide. Raschig (A., 1905, ii, 700) gives an explanation of this which postulates the existence of the compound  $N_2O_3$  in the gaseous mixture, whereas Lunge (A., 1906, ii, 438) gives a different explanation, and denies the existence of nitrogen trioxide. The author points out that both explanations are unsatisfactory, and that it is probable that water is the disturbing factor when sodium hydroxide is used. Nitrogen trioxide would give nitrous acid with even traces of water, and this would be further oxidised to nitric acid by the excess of nitrogen trioxide, with evolution of nitric oxide, and thus cause the observed discrepancies.

In support of this theory, it is found that dry nitrogen trioxide is quantitatively absorbed by dry potassium hydroxide (compare A., 1913, ii, 619).

The question as to whether nitrogen trioxide is formed as an intermediate product when a mixture of nitric oxide and nitrogen dioxide is acted on by dry potassium hydroxide can be decided by measuring the ratio of the contraction which takes place to the volume of nitric oxide taken when a known mixture of nitric oxide with excess of oxygen is treated with the dry hydroxide. Experiments which were carried out agreed quantitatively with the intermediate formation of nitrogen trioxide, which was then absorbed by the potassium hydroxide, giving potassium nitrite. T. S. P.

**The Reaction of Metals and Alloys with Nitric Acid.** J. H. STANSBIE (*J. Soc. Chem. Ind.*, 1913, 32, 1135—1136).—Nitric acid dissolves copper, silver, mercury, and bismuth much more rapidly when the metals remain at rest in the acid than when they are rapidly rotated or the acid is stirred, owing to the fact that, in the former case, nitrous acid accumulates in the neighbourhood of the metal (compare A., 1913, ii, 982).

Similar results are obtained with alloys of copper and zinc, as long as they contain more than 48% of copper, the alloy dissolving as a whole. Below this percentage of copper, the zinc either dissolves faster in proportion than the copper, or precipitates that metal from solution, with the result that more copper dissolves in the stirred solutions than in the solutions at rest. A neutral solution of copper nitrate has no corrosive action on alloys containing more than 80% of copper. T. S. P.

**The Action of Carbonyl Chloride on Phosphates and Oxides.** J. RIBAN (*Compt. rend.*, 1913, 157, 1432—1433. Compare A., 1883, 287).—A claim for priority over Barlot and Chauvenet (compare this vol., ii, 49). W. G.

**Preparation of Solid Alkali Perborates from Boric Acid and Alkali Peroxides without the Use of Water as Solvent.** CHEMISCHE FABRIK REISHOLZ (D.R.-P. 262144).—Boric acid is mixed with the amount of ice necessary for hydration and the alkali peroxide is added. Examples are given of the preparation of sodium perborates of the formulæ,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{NaBO}_3 \cdot 10\text{H}_2\text{O}$ ,  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ , and  $\text{Na}_2\text{B}_4\text{O}_8 \cdot 10\text{H}_2\text{O}$ . J. C. C.

**Experimental Demonstration of the Variability of the Molecule and the Atom.** P. DE HEEN (*Bull. Acad. roy. Belg.*, 1913, 680—694).—Observations are described which seem to show that the sensitiveness of silver chloride to light can be varied by the action of reagents, although the physical condition of the chloride remains constant.

If the silver salt is triturated with a very concentrated solution of potassium hydroxide, washed with water, and boiled with nitric acid, it is found that the residual silver chloride is very much more sensitive to light than the original silver salt. A similar effect is obtained if the silver chloride is spread in a thin layer over the surface of a platinum cathode, and subjected to the action of a current for several days. If, on the other hand, the silver salt is subjected to the action of the current at the surface of the anode, its photo-sensitiveness is found to diminish. In this case, the action is less rapid, and the current must be passed for, at least, ten days.

In another series of experiments, a quantity of silver chloride was divided into three portions, one of which was subjected to the action of the current at the cathode, the second portion to the anodic action of the current, whilst the third was unacted on. The three portions of silver chloride were then reduced to metal, and the three samples of metallic silver re-converted into chloride by dissolving in nitric acid and precipitating with hydrochloric acid. The silver chloride obtained from the first sample of silver was found to be much less sensitive, and that from the second sample much more sensitive, to light than the chloride prepared from the third sample of silver.

The above facts are supposed to show that the silver chloride molecule can be modified by suitable treatment, and that the different forms of silver salt are to be regarded as derived from silver atoms which are not identical. In other words, the experiments afford evidence of transmutation of normal silver into its meta-elements. H. M. D.

**New Compounds of Nitrogen and Hydrogen with the Alkaline-earth Metals.** F. W. DAFERT and R. MIKLAUZ (*Monatsh.*, 1913, 34, 1685—1712).—The calcium used by the authors in their experiments was obtained pure by distilling the commercial article in an apparatus similar to that used by Guntz in the preparation of strontium (A., 1910, ii, 1064); the strontium and barium were obtained by distilling a mixture of the respective oxides with the equivalent quantity of aluminium powder (compare Guntz, A., 1906, ii, 669; 1910, ii, 1064).

The pure nitrides and hydrides of calcium, strontium, and barium are readily obtained by heating the respective metals in the pure gases. When the nitrides are heated in a current of hydrogen, compounds having the formulæ  $M''_3N_2H_4$  are formed (compare A., 1909, ii, 882), but only the calcium and strontium compounds could be obtained pure, since the barium compound, even at relatively low temperature, reacts with hydrogen in accordance with the equation,  $Ba_3N_2H_4 + H_2 = 3BaH_2 + N_2$ .

When hydrogen is passed over heated barium nitride, or, more correctly, over the impure compound,  $Ba_3N_2H_4$ , ammonia is formed. The barium hydride which is thereby produced is readily transformed back to the nitride by the action of nitrogen, so that a process is given for the fixation of atmospheric nitrogen.

When a mixture of equal volumes of hydrogen and nitrogen is passed over the heated alkaline-earth metals, or over their hydrides or nitrides, imides,  $M''NH$ , are produced, which, similarly to lithium imide (A., 1912, ii, 253), darken on exposure to the light. Calcium imide is most easily prepared, but it has not been obtained pure; the formation of barium imide is incomplete.

The following table, giving the temperatures at which reaction occurs with the various gases, shows that the tendency of the alkaline-earth metals to combine with nitrogen and hydrogen increases with the atomic weight, whilst the tendency of the nitrides to combine with hydrogen decreases with increase in atomic weight of the metal.

	N.	H.		H.
Ca .....	410°	300°	$Ca_3N_2$ .....	230°
Sr .....	380	215	$Sr_3N_2$ .....	270
Ba .....	260	170	$Ba_3N_2$ .....	300

T. S. P.

**Formation of Magnesium, Barium, and Strontium Compounds Analogous to Apatite and Wagnerite.** HANS WINTER (*Diss., Leipzig*, 1913, 1—46).—The phosphates and halogen salts were fused together in an electric oven and the equilibrium diagrams are given for several pairs. Barium chloride (m. p. 958°, D 3·789) is optically biaxial and positive, whilst barium fluoride (m. p. 1289°), strontium chloride (m. p. 874°, D 3·054), and strontium fluoride (m. p. 1400°) are all cubic in crystallisation. These do not form mixed crystals, but the double salts,  $BaCl_2 \cdot BaF_2$  (m. p. 1008°, D 5·931) and  $SrCl_2 \cdot SrF_2$  (m. p. 962°, D 4·616), both of which are tetragonal and optically negative. Magnesium fluoride and phosphate yield wagnerite,  $MgF_2 \cdot Mg_3P_2O_8$ , and only, doubtfully a compound corresponding with apatite (magnesium-fluorapatite). The barium and strontium compounds corresponding with wagnerite were not obtained, but the four apatites of the composition  $BaCl_2 \cdot 3Ba_3P_2O_8$ ,  $BaF_2 \cdot 3Ba_3P_2O_8$ ,  $SrCl_2 \cdot 3Sr_3P_2O_8$ , and  $SrF_2 \cdot 3Sr_3P_2O_8$ ; these were obtained in a crystallised condition, and their melting points, density, and refractive indices determined.

L. J. S.

**Allotropy of Zinc.** ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 565—568).—Experiments are described which show that zinc, which has been obtained by rapid cooling of the liquid metal, undergoes slow changes in respect of its density. The molten metal was poured into a cylinder of asbestos paper, cooled by a mixture of solid carbon dioxide and alcohol. The density of the solid was then found to be 7.130 at 25°. After heating for a fortnight at 100°, in a solution of zinc sulphate, the density was found to be only 7.102. These observations show that ordinary zinc is in a metastable condition, and that the modification which is formed at high temperatures changes only very slowly into that which is stable at the ordinary temperature. The stable form was probably obtained in an almost pure condition by Kahlbaum, Roth, and Siedler (*A.*, 1902, ii, 259).  
H. M. D.

**Atomic Weight of Cadmium by the Investigation of Cadmium Chloride and Cadmium Bromide.** ELTON L. QUINN and GEORGE A. HULETT (*J. Physical Chem.*, 1913, **17**, 780—798).—Weighed quantities of the carefully purified chloride or bromide were converted into sulphate by evaporating solutions of the salts to dryness, after the addition of the calculated quantity of sulphuric acid. The cadmium sulphate was then dissolved and subjected to electrolysis in an amalgamated platinum crucible which served as the cathode. As shown by previous experiments (Perdue and Hulett, *A.*, 1911, ii, 433), this method can be applied very conveniently in the case of metals, like cadmium, which are readily soluble in mercury, and sufficient evidence has already been obtained that the electrolytic method affords very exact results in the estimation of cadmium (compare also *A.*, 1911, ii, 397).

The results obtained with the chloride give for the atomic weight of cadmium,  $112.32 \pm 0.01$ , whilst the bromide results lead to the value,  $112.26 \pm 0.005$ . The mean of these is 112.29, which agrees very well with the value 112.30, obtained by Perdue and Hulett (*loc. cit.*) from the analysis of cadmium sulphate, and also with the results obtained by Laird and Hulett in their work on the cadmium coulometer (*Trans. Amer. Electrochem. Soc.*, 1912, **22**, 385), which lead to the value 112.31. The authors consider that these observations show that the atomic weight of cadmium is nearer 112.3 than the value of 112.4, which is accepted as the most probable value, according to previous measurements. H. M. D.

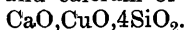
**Cadmium.** MANUEL VERES (*Compt. rend.*, 1914, **158**, 39—40).—Using the methods of Lepierre and Lachaud (compare *A.*, 1892, 943, 1282) and Klobb (compare *A.*, 1892, 941, 1399), the author has prepared a new double salt of cadmium sulphate and ammonium sulphate having the constitution  $2\text{CdSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ . It is obtained in microscopic crystals, yellow when hot, white when cold. It is very hygroscopic and has  $D^{22}_4$  3.11. It is very soluble in water, and from its solution, on evaporation, crystals of  

$$\text{CdSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$$

are deposited. The salt,  $2\text{CdSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ , is decomposed by warming with concentrated sulphuric acid at  $100^\circ$ , giving anhydrous cadmium sulphate in rhombic crystals.

W. G.

**Egyptian-Blue.** A. P. LAURIE, W. F. P. McLINTOCK, and F. D. MILES (*Proc. Roy. Soc.*, 1914, A, 89, 418—429).—Experiments have been made to determine the nature and conditions of formation of Egyptian-blue. According to Fouqué (*Bull. Soc. Mines*, 12, 36; *Compt. rend.*, 1889, 108, 325), this substance is a crystalline double silicate of copper and calcium of the formula



That the substance is really crystalline in character has been shown by the examination of a number of samples of real Egyptian-blue between crossed nicols.

In order to ascertain the conditions under which the compound is formed, a mixture containing 36 grams of quartz sand, 4 of fusion mixture, 8.6 of copper carbonate, and 7.2 of calcium carbonate was heated for several hours in an electric resistance furnace at temperatures ranging from  $760^\circ$  to over  $900^\circ$ . These experiments show that the temperature should be kept between narrow limits ( $830$ — $900^\circ$ ) if the blue compound is to be obtained. The mixture may, however, be heated to the temperature of the oxyhydrogen blow-pipe, provided that the mass is subsequently maintained for a considerable time at about  $850^\circ$ . If the temperature is too high or too low, the product is an olive-green glass.

Further experiments show that the formation of the blue compound is not dependent on the presence of sodium or potassium carbonate or other alkali salts, although if these are absent, the mass is so infusible that reaction takes place with great difficulty. On the other hand, if the amount of fusion mixture is increased very much above that corresponding with the mixture referred to above, the calcium copper silicate does not crystallise out of the mass, but remains in solution as a green glass.

From analyses of Egyptian-blue prepared by the authors it appears that in presence of an alkali, a little of the copper and calcium is replaced by the alkali metals. Apart from this, the analyses are found to correspond with the formula  $\text{CaO}, \text{CuO}, 4\text{SiO}_2$ .

H. M. D.

**Polymorphism of Mercuric Iodide.** MEINHARD HASSELBLATT (*Zeitsch. physikal. Chem.*, 1913, 86, 61—64).—Polemical against Smits (*A.*, 1910, ii, 400).

J. F. S.

**Mercuric Oxide.** GUY B. TAYLOR and GEORGE A. HULETT (*J. Physical Chem.*, 1913, 17, 755—761).—Mercuric oxide was prepared by heating carefully purified mercury in an atmosphere of oxygen at about  $420^\circ$  and a pressure of 2—3 atmospheres. The apparatus was arranged so that fresh supplies of oxygen could be admitted from time to time. It was found possible to obtain from 10 to 15 grams of the oxide in the course of an experiment, which lasted from five to seven days. The oxide was finally freed from all

traces of uncombined metal by heating to  $400^{\circ}$  in a rapid current of oxygen at atmospheric pressure.

The pure mercuric oxide obtained in this way was reduced to metal by heating with pure finely divided iron, the temperature being maintained at  $275$ — $300^{\circ}$  for two to three hours and then at about  $600^{\circ}$  for twenty-four to thirty-six hours. During the last half-hour the protruding end of the tube was cooled in ice, and the globule of condensed mercury transferred to a porcelain crucible and weighed.

Nine analyses of the oxide were made according to this method, the results agreeing exceedingly well with one another, and giving for the mean value of the percentage of mercury in the oxide  $92.6053 \pm 0.0008$ . This corresponds with an atomic-weight value for mercury of  $200.37 \pm 0.025$ .

This value is considerably smaller than that recently obtained by Easley and Brann (A., 1909, ii, 1013; 1910, ii, 957; 1912, ii, 257) from the analysis of mercuric chloride and bromide, namely, 200.62. If the higher value is correct, the lower value might be explained by the presence of a small quantity of a higher oxide. The authors consider, however, that the discrepancy calls for a further investigation of the atomic weight of mercury. H. M. D.

**The Alloys of Cerium with Silicon and Bismuth.** RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1913, 84, 323—339).—The fact that cerium combines with lead and tin with development of heat, forming several compounds, indicates that it does not belong to the same chemical family of the fourth group. It is now found that it combines with silicon at high temperatures with great violence. It has not been found possible to prepare alloys containing more than 70% of cerium, as combination does not take place until  $1400^{\circ}$ , and the heat developed brings about the destruction of the containing vessel, or, if carbon crucibles are used, there is a considerable production of cerium carbide, in which case the alloys rapidly disintegrate in air. Solid silicon floats on molten cerium, and at a sufficiently high temperature combines explosively.

Between 0 and 70% Ce the freezing-point curve has two branches, intersecting at  $1240^{\circ}$  and 53% Ce. The eutectic times indicate that the maximum on the curve must be at 83% Ce, corresponding with a compound,  $\text{CeSi}$ , melting above  $1500^{\circ}$ . This compound forms yellow, rounded crystallites, and the eutectic has a distinct lamellar structure. Free silicon crystallises in needles, which are harder than the compound. The alloys are brittle, very stable in air, and are not pyrophoric.

Cerium and bismuth combine with great development of heat. Porcelain tubes are rapidly corroded, but carbon tubes may be used, and the alloys are not seriously contaminated with carbide. The thermal effects are often small, and the micro-structure has been largely employed in determining the form of the diagram. The sections must be polished with wet alumina, but they oxidise very rapidly, and the polished surfaces cannot be preserved.



Four compounds are formed:  $\text{BiCe}_3$ ,  $\text{Bi}_3\text{Ce}_4$ ,  $\text{BiCe}$ , and  $\text{Bi}_2\text{Ce}$ . The compound  $\text{Bi}_3\text{Ce}_4$  melts at  $1630^\circ$ , and appears as a maximum on the freezing-point curve. It crystallises in polygonal grains.  $\text{BiCe}_3$  is formed at  $1400^\circ$ , and is softer than  $\text{Bi}_3\text{Ce}_4$ . It forms a eutectic with cerium at  $757^\circ$ .  $\text{BiCe}$  is formed at  $1525^\circ$  and  $\text{Bi}_2\text{Ce}$  at  $882^\circ$ , whilst the second eutectic point practically coincides with the melting point of bismuth.

All the alloys are more readily attacked by water than cerium. Between 25 and 75% Bi the action of water may even raise the alloys to incandescence.

C. H. D.

**The Resolution of Ytterbium into its Elements.** C. AUER VON WELSBACH (*Monatsh.*, 1913, **34**, 1713—1728).—In the resolution of ytterbium into its elements (compare A., 1908, ii, 591) the fractionation proceeds at first very slowly, but after a large number (200) of fractionations have been carried out there is a very marked increase in the rate of fractionation. This increase could be ascribed to the existence of an unknown element occurring between the elements aldebaranium and cassiopeium, but the spectroscopic examination afforded no definite evidence in this direction. The cause of the increased rate of fractionation is therefore, at present, inexplicable.

The atomic weights of aldebaranium and cassiopeium have been determined by a new method. The respective hydrated sulphates,  $\text{M}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , were dried in a platinum crucible in a vacuum desiccator; heating on a water-bath is not permissible in the case of cassiopeium sulphate. They were then dehydrated by careful heating, an excess of oxalic acid added, and the crucible two-thirds filled with water. The crucible and its contents were then heated on a water-bath to dissolve the excess of oxalic acid, after which the insoluble oxalates were collected, washed, and then converted into oxide. Any salt remaining in the mother liquor and washings was precipitated by making use of the fact that the ammonium oxalates of these metals are insoluble in a saturated solution of ammonium hydrogen oxalate, and allowed for. The results gave  $\text{Cp} = 175.00$ ,  $\text{Ad} = 173.00$ .

T. S. P.

**The Perchlorates of Aluminium, Chromium, and Magnesium.** R. F. WEINLAND and FR. ENSGRABER (*Zeitsch. anorg. Chem.*, 1913, **84**, 368—372).—*Aluminium perchlorate*,  $[\text{Al}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ , is a derivative of the hexa-aquo-base, and thus completely resembles the ferric compound (this vol., ii, 132). Its solution yields with sodium perchlorate a crystalline *sodium aluminotetraperchlorate*,  $[\text{Al}(\text{ClO}_4)_4]\text{Na} \cdot 12\text{H}_2\text{O}$ , which loses  $6\text{H}_2\text{O}$  over sulphuric acid.

Chromium yields two *perchlorates* of the hexa-aquo-base,  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$  and  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ , but no sodium chromiperchlorate. Both of these salts are bluish-green.

*Magnesium perchlorate*,  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ , is also a hexa-aquo-salt.

C. H. D.

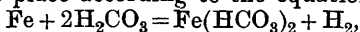
**The Critical Ranges of Pure Iron.** H. C. H. CARPENTER (*J. Iron Steel Inst.*, 1913, i, 315—326).—Electrolytic iron sheet, containing 99·967% of iron, gives cooling curves which are consistent with the view that the critical point  $Ar_2$  is merely the retarded termination of  $Ar_3$ . The point  $Ac_2$  is only faintly marked on the heating curves when dissolved gas has been removed. The results support the view of Benedicks (A., 1913, ii, 599) that  $\beta$ -iron is a solid solution of  $\gamma$ -iron in  $\alpha$ -iron (compare Müller, A., 1909, ii, 485; Burgess and Crowe, A., 1913, ii, 711). C. H. D.

**The Tenacity, Deformation, and Fracture of Soft Steel at High Temperatures.** WALTER ROSENHAIN and J. C. W. HUMFREY (*J. Iron Steel Inst.*, 1913, i, 219—271. Compare A., 1910, ii, 128).—Tensile tests with strips of soft steel in a very high vacuum indicate that the tenacity falls rapidly with increasing temperature from 600° to 730°; there is then a break in the curve, and the tenacity passes through a minimum between 800° and 900°, an entirely distinct curve, starting from a relatively high tenacity at 900° and then falling gradually, representing the  $\gamma$ -phase. The first break is considered to represent the  $\alpha \rightarrow \beta$  change. The influence of size of crystal grain and rate of loading on the results has also been determined, and the results are regarded as supporting the "amorphous cement" theory of the constitution of metals (Rosenhain and Ewen, A., 1913, ii, 119). C. H. D.

**Influence of Sulphur on the Stability of Iron Carbide in the Presence of Silicon.** W. H. HATFIELD (*J. Iron Steel Inst.*, 1913, i, 139—156).—Sulphur increases the stability of iron carbide (cementite) at high temperatures, entering in small quantity into the carbide. The influence of sulphur is not purely mechanical, through the formation of sulphide films. Its influence in cast iron is neutralised by the presence of manganese, which forms an insoluble sulphide, and of silicon, possibly owing to the formation of a silicon sulphide, although such a compound was not actually isolated. C. H. D.

**The Rusting of Iron in Water.** W. A. BRADBURY (*Chem. News*, 1913, 108, 307—308).—Two flasks were filled with well-boiled Manchester tap-water, some coils of bright iron binding wire added, and the flasks securely corked. No rusting took place, whereas rusting readily occurred in unboiled tap-water.

If rusting takes place according to the equation:



the ferrous hydrogen carbonate then being oxidised by oxygen present, hydrogen should be evolved. It was found, however, that no hydrogen was liberated when rusting took place in ordinary tap-water. This could be accounted for by the nascent hydrogen liberated being oxidised by the oxygen present in the water, or else by the hydrogen remaining dissolved in the water. This was tested by using water into which carbon dioxide had been passed for fifteen minutes. At first no hydrogen was evolved; the iron

remained quite bright, but ferrous iron was present in solution. After some days hydrogen was evolved, but the iron remained quite bright. Apparently no hydrogen was evolved until all the oxygen present in the water had been reduced; owing to the removal of this oxygen no rust could form, although a large quantity of iron was present in solution as ferrous bicarbonate.

These experiments confirm the view that rusting is due to dissolved oxygen and carbonic acid present in the water.

Contrary to what is usually supposed to be the case, magnesium chloride was found not to have a deleterious effect on iron.

T. S. P.

**New Method for the Preparation of Colloidal Ferric Hydroxide.** THEODORE COHEN (*J. Amer. Chem. Soc.*, 1914, **36**, 19—23).—Experiments are described which show that a colloidal solution of ferric hydroxide can be obtained by the hydrolysis of a ferric nitrate solution which takes place in a nitric acid solution containing copper; for example, if 3 grams of iron filings, containing copper as an impurity, are added to 10 c.c. of concentrated nitric acid and the solution is diluted, filtered, and dialysed, a deep red liquid is obtained, from which, on treatment with a little sulphuric acid or with the electric current, ferric hydroxide separates. A similar solution can be prepared by boiling a solution of ferric nitrate with copper filings or with zinc dust. E. G.

**Ferrous Sulphate and Its Hydrates.** R. DE FORCRAND (*Compt. rend.*, 1914, **158**, 20—23).—A study of the hepta-, tetra-, and monohydrates of ferrous sulphate and the anhydrous salt. The heptahydrate can be obtained perfectly pure and dry, by powdering an ordinary sample, and repeatedly pressing it between folds of filter-paper. The product thus obtained is quite stable in air at 15°. It neither oxidises, effloresces, nor deliquesces. It has heat of solution  $-4.323$  Cal. at 13.5°. The tetrahydrate has heat of solution  $+1.599$  Cal. at 13.5°, the monohydrate  $+7.538$  Cal. at 13.5°, and the anhydrous salt  $+14.901$  Cal. at  $+13.5^\circ$ . From these results, the author calculates for the monohydrate a b. p., 300°, for the tetrahydrate, b. p. 118.5°, and for the heptahydrate, 118.3°.

W. G.

**Salts of Ferri-phosphoric, -sulphuric, and -perchloric Acids.** R. F. WEINLAND and FR. ENSGRABER (*Zeitsch. anorg. Chem.*, 1913, **84**, 340—367).—An ammonium ferriphosphate has been obtained by Cohen (*A.*, 1907, ii, 552), and there is other evidence of a series of complex salts. Either ferric hydroxide or ferric chloride is mixed with an excess of phosphoric acid, and the complex alkali salts may then be obtained by the addition of alkali hydroxide, phosphate, or chloride. Definite proportions must be used, and the solutions must be heated for at least twenty-four hours, otherwise the products, although well crystallised, are not homogeneous.

*Sodium ferridiphosphate*,  $[\text{Fe}(\text{PO}_4)_2]\text{H}_2\text{Na}, \text{H}_2\text{O}$ , is obtained in pale pink crystals by heating a solution of ferric hydroxide in

phosphoric acid with sodium hydroxide ( $\text{Fe}:\text{P}:\text{Na}=1:24:8$ ) for three days on the water-bath. After six months at the ordinary temperature, it is obtained with  $3\text{H}_2\text{O}$ . The corresponding *ammonium* salt,  $[\text{Fe}(\text{PO}_4)_2]\text{H}_2\cdot\text{NH}_4$ , consists of pale pink, microscopic, hexagonal crystals. By using less ammonia, an acid *ammonium* salt,  $[\text{Fe}(\text{PO}_4)_2\text{H}_3]_3\text{NH}_3\cdot 7\text{H}_2\text{O}$ , may be prepared in light red, microscopic crystals. The *pyridinium* salt,  $[\text{Fe}(\text{PO}_4)_2]\text{H}_3\cdot\text{C}_5\text{NH}_5$ , is white.

*Sodium ferritriphosphate*,  $[\text{Fe}(\text{PO}_4)_3]\text{H}_5\text{Na}\cdot\text{H}_2\text{O}$ , is obtained when sodium phosphate or chloride is added to the solution of ferric phosphate instead of sodium hydroxide. Thus, a mixture in the proportions ( $\text{Fe}:\text{P}:\text{NaCl}=1:6:4$ ) yields the salt after heating for twenty-four hours on the water-bath. It is a very pale red, crystalline powder. A mixed *ammonium ferri-di- and tri-phosphate*,  $3[\text{Fe}(\text{PO}_4)_2]\text{H}_3\cdot[\text{Fe}(\text{PO}_4)_3]\text{H}_6\cdot 1\cdot 5\text{NH}_3\cdot 10\text{H}_2\text{O}$ , crystallises in the course of six months. With a large excess of ammonium chloride and a deficiency of phosphoric acid, an entirely different salt, of unknown constitution, is obtained as a greenish-yellow, microcrystalline powder. It has the empirical composition



All of these compounds are very sparingly soluble in water. It has not been found possible to prepare corresponding potassium salts.

Ferric phosphate, prepared by heating molecular proportions of ferric chloride or acetate with phosphoric acid for two days on the water-bath, is a pink, microcrystalline powder, and may be regarded as *ferric ferridiphosphate*,  $[\text{Fe}(\text{PO}_4)_2]\text{Fe}\cdot 5\text{H}_2\text{O}$ . It is very sparingly soluble in water and dilute acids, whilst the phosphates of variable composition, obtained by precipitating ferric solutions with alkali phosphates, dissolve readily in dilute acids.

*Ammonium ferridisulphate*,  $[\text{Fe}(\text{SO}_4)_2]\text{NH}_4$ , obtained on heating a solution of ferric ammonium alum with sulphuric acid for twenty-four hours, is a white, microcrystalline powder, sparingly soluble in water, and depositing ferric hydroxide rapidly on heating. The *potassium* salt,  $[\text{Fe}(\text{SO}_4)_2]\text{K}\cdot\text{H}_2\text{O}$ , and the *pyridinium* salt,  $[\text{Fe}(\text{SO}_4)_2]\text{H}\cdot\text{C}_5\text{NH}_5\cdot 2\text{H}_2\text{O}$ ,

have similar properties.

*Trisodium ferritrisulphate*,  $[\text{Fe}(\text{SO}_4)_3]\text{Na}_3\cdot 3\text{H}_2\text{O}$ , is a white, crystalline salt, as is the previously known ferridisulphuric acid,  $[\text{Fe}(\text{SO}_4)_2]\text{H}\cdot 4\text{H}_2\text{O}$ .

*Sodium ferritetra-perchlorate*,  $[\text{Fe}(\text{ClO}_4)_4]\text{Na}\cdot 6\text{H}_2\text{O}$ , forms large, pink, hygroscopic crystals. *Ferric perchlorate*,  $\text{Fe}(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$ , is to be regarded as a hexa-aquo-salt,  $[\text{Fe}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ .

C. H. D.

**Rinmann's Green.** ARVID HEDVALL (*Arkiv. Kem. Min. Geol.*, 1913, 5, No. 6, 1—27).—The author's further investigations (compare A., 1912, ii, 846) show that Rinmann's green is not a definite substance, but rather a series of solid solutions of the components zinc oxide and cobalt oxide, since its composition may vary considerably. The series of mixed crystals is isodimorphic, since zinc

oxide is hexagonal, and cobalt oxide generally regular, although in one case the latter oxide has probably been obtained in hexagonal crystals.

T. S. P.

**Chromic Oxide Jellies.** E. H. BUNCE and L. S. FINCH (*J. Physical Chem.*, 1913, 17, 769—779).—Experiments have been made to determine the conditions of formation of chromic oxide jellies. If a sufficient amount of sodium acetate is added to a solution of chromic sulphate or chloride, the subsequent addition of a suitable amount of alkali metal hydroxide or ammonia causes gelatinisation. The chromic oxide jelly is violet, if prepared by the addition of ammonia or of a slight excess of alkali metal hydroxide. If this is added in larger quantity, the jelly is green in colour. The concentrations of the chromic salt and sodium acetate may be varied within fairly wide limits, without interfering with the formation of the jelly.

If, after the addition of sodium acetate, the solution is heated, the time required for gelatinisation is found to diminish appreciably. Apart from this, prolonged heating of the solution has no effect on the subsequent gelatinisation, provided acetic acid is not driven off during the process. Chromic oxide jellies dissolve in hydrochloric acid, but are re-formed when the solution is neutralised, if sufficient sodium acetate is present. The addition of sodium or potassium chloride has no appreciable influence on the gelatinisation, but this is prevented by the freezing or stirring of the solutions.

Chromic oxide jellies can also be obtained by adding sodium or potassium hydroxide to a solution of chrome alum, but not by the addition of ammonia. The addition of sodium acetate to the chrome alum solution appears to be without influence on the result. Although jellies are obtained by the addition of potassium hydroxide to solutions of chromic acetate and chrome alum, this is not the case when the alkali is added to solutions of chromic nitrate, chloride, or sulphate.

The acetate method of preparing jellies gives no result in the case of salts of manganese, aluminium, copper, and cadmium.

H. M. D.

**Chromic Silicofluoride. Its Transformations. Fluopenta-aquo chromic Silicofluoride.** A. RECOURA (*Compt. rend.*, 1913, 157, 1525—1528. Compare A., 1913, ii, 603).—In explanation of the fact that the normal ferric silicofluoride is decomposed, as formed, giving the compound  $\text{Fe}_2\text{F}_6 \cdot 2\text{SiF}_4$ , the author expresses the view that ferric fluoride itself is really a complex to be represented by  $(\text{Fe}_2\text{F}_2)\text{F}_4$ , and thus the double compound prepared is a true silicofluoride,  $(\text{Fe}_2\text{F}_2)(\text{SiF}_4)_2$ . In support of this he shows that the latter compound reacts with potassium chloride to give potassium silicofluoride, and a compound,  $(\text{Fe}_2\text{F}_2)\text{Cl}_4$ , in which the fluorine is masked.

In the case of chromium, the silicofluoride,  $\text{Cr}_2\text{F}_6(\text{SiF}_4)_3$ , is obtained in solution, although it is not possible to isolate it, as the violet solution spontaneously and gradually turns bluish-green, and

from it a green solid can be isolated, to which the author assigns the constitution  $(\text{CrF}_5\text{H}_2\text{O})\text{SiF}_6$ , and compares it with the two silicofluorides,  $(\text{CrCl}_5\text{NH}_3)\text{SiF}_6$  and  $(\text{CrCl}_5\text{H}_2\text{O}_4\text{NH}_3)\text{SiF}_6$ , prepared by Jørgensen. The violet solution, immediately after its preparation, reacts normally with potassium chloride, giving potassium silicofluoride and chromic chloride, but on remaining, it reacts to give potassium silicofluoride and the compound  $(\text{Cr}_2\text{F}_2)\text{Cl}_4$ , from which the fluorine cannot be precipitated by addition of barium chloride. The compound  $(\text{CrF}_5\text{H}_2\text{O})\text{SiF}_6$  is perfectly stable when kept in a desiccator, even in a vacuum, but on exposure to air, it slowly loses silicon fluoride, ultimately yielding a green chromic fluoride,  $\text{Cr}_2\text{F}_6\cdot 7\text{H}_2\text{O}$ .

Aluminium silicofluoride gives analogous results.

W. G.

#### Metastability of Metals Prepared by an Electrolytic Method.

ERNST COHEN and W. D. HELDERMAN (*Chem. Weekblad*, 1914, 11, 83—84).—At  $18^\circ$ , grey tin is converted into the white modification. The white modification is also deposited by electrolysis of a solution of a tin salt at  $-20^\circ$ .

A. J. W.

**The Action of the Silent Electric Discharge on a Mixture of Hydrogen and Titanium Tetrachloride Vapour. II. A Polymorphic Titanium Trichloride.** F. BÖCK and L. MOSER (*Monatsh.*, 1913, 34, 1825—1849).—In a previous communication (A., 1913, ii, 9), a brown substance was described, which was considered to be a polymorphic form of ordinary violet titanium trichloride. In the present communication, the authors describe an improved apparatus for preparing and handling this substance.

The change from brown to violet trichloride is not reversible; the heating curve of the brown modification, the temperature being gradually raised above that at which transformation takes place, did not differ appreciably from that of the cooling curve of the violet modification thereby formed.

The heats of solution in water of various known mixtures of the brown and violet trichlorides with titanium tetrachloride were determined, as also the heat of solution of pure titanium tetrachloride. From the results, the following figures were obtained:  $(\text{TiCl}_4\text{,aq.})$ , 59030 cal.; (brown  $\text{TiCl}_3\text{,aq.})$ , 48150—48837 cal.; (violet  $\text{TiCl}_3\text{,aq.})$ , 44287—45800 cal. These figures are taken to prove that the brown and violet titanium trichlorides are monotropic modifications.

T. S. P.

**Compounds of Thorium with Boric Acid.** HANS BUCHTALA (*J. pr. Chem.*, 1913, [ii], 88, 771—785).—An account of the preparation of a number of thallous borates.

*Thallous tetraborate*,  $\text{Tl}_2\text{B}_4\text{O}_7$ , prepared by dissolving thallous carbonate (1 mol.) and boric acid (1—4 mols.) in water, crystallises with  $2\text{H}_2\text{O}$ . It is also obtained, together with the *hexaborate*,  $\text{Tl}_2\text{B}_6\text{O}_{10}\cdot 3\text{H}_2\text{O}$ , when the carbonate is fused with boric acid (6 mols.) and the product crystallised from water; if the fusion is carried out with a greater excess of boric acid (8 mols.), a mixture of the hexaborate and *decaborate*,  $\text{Tl}_2\text{B}_{10}\text{O}_{16}\cdot 8\text{H}_2\text{O}$ , is produced.

*Thallous octaborate*,  $\text{Ti}_2\text{B}_8\text{O}_{13}, 4\text{H}_2\text{O}$ , and *thallous dodecaborate*,  $\text{Ti}_2\text{B}_{12}\text{O}_{19}, 7\text{H}_2\text{O}$ , are prepared by dissolving thallous carbonate in an excess of aqueous boric acid (10 mols.); the last-named borate also crystallises with  $5\text{H}_2\text{O}$  in twinned, monoclinic crystals

( $a:b:c=1.556:1:1.920$ .  $\eta=94.20^\circ$ ).

*Thallous perborate* is obtained as a white powder by the addition of 30% hydrogen peroxide to an aqueous solution of any of the preceding borates. It shows the usual reactions of a per-salt, and decomposes explosively when rapidly heated. The amount of oxygen liberated by heating the perborate with water corresponds

with the formula  $\begin{array}{c} \text{TiO} \cdot \text{B} \cdot \text{O} \cdot \text{O} \\ | \\ \text{TiO} \cdot \text{B} \cdot \text{O} \cdot \text{O} \end{array} > \text{O}$ ; the aqueous solution, on evaporation, yields a red *thallous metaborate*, which becomes blackish-red on exposure to air, and crystallises from water in radially-arranged, colourless, wedge-shaped crystals of the composition  $\text{Ti}_2\text{B}_2\text{O}_4, \text{H}_2\text{O}$ . F. B.

## Mineralogical Chemistry.

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**Decomposition of Hauerite in the Air and its Action on Silver and Copper.** A. BEUTELL (*Centr. Min.*, 1913, 758—767).—Strüver, in 1901, noticed that crystals of hauerite ( $\text{MnS}_2$ ), in contact with silver or copper, produced a dark stain on the metal. The same action takes place without contact (up to a distance of 1 cm.); it is ascribed to the oxidation of the mineral, and the liberation of free sulphur. When the mineral is heated at 50—60° in a vacuum, the free sulphur is distilled off, and only after remaining again in the air for twenty-four hours is the activity regained.  
L. J. S.

**Brucite and Metabrucite.** OTTO WESTPHAL (*Diss., Leipzig*, 1913, 1—41).—Etch-figures on brucite, from Texas, Lancaster Co., Pennsylvania, prove the mineral to be ditrigonal-scalenohedral in symmetry. D 2.38, H  $2\frac{1}{2}$ . The axial ratio  $a:c$  varies from 1:1.5208 at 20°, to 1:1.5301 at 200°. The refractive indices for light of different wave-lengths were determined for the same range of temperature; at 20°, for sodium-light,  $\omega=1.5662$ ,  $\epsilon=1.5853$ . When heated, the mineral does not give off its water at a definite temperature, but there is a gradual loss of the bulk of the water between 380° and 480°; at 550°, about 1% is still held. The substance thus behaves as an adsorption compound, rather than as a crystalline hydrate. The completely dehydrated material ("metabrucite") still retains its crystalline structure, being optically uniaxial, but now negative ( $\omega_{Na}=1.644$ ,  $\epsilon_{Na}=1.634$ ). D 3.666, which is increased to 3.683 by intense ignition. Metabrucite re-



absorbs water from a moist atmosphere, but to a smaller degree than does amorphous magnesium oxide. Less water is reabsorbed after the material has been intensely ignited. L. J. S.

**Optical Constants of Calcite, etc.** ERWIN MARRBACH (*Diss., Leipzig*, 1913, 1—47).—The refractive indices of fluorite, halite, sylvite, calcite, aragonite, and boracite were determined for light of different colours over considerable ranges of temperature (up to 670°). The values for calcite from Egremont, Cumberland, vary slightly from those obtained by other authors for Iceland-spar, this difference being attributed to a slight difference in chemical composition. Analyses by Dreibrodt gave I for calcite from Egremont, II from Iceland:

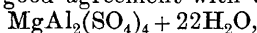
	CaO.	SrO.	MgO.	CO <sub>2</sub> .	Total.
I.	56.33	trace	0.13	44.33	100.79
II.	56.41	—	trace	44.25	100.66

Aragonite is transformed into calcite at 425°, and boracite becomes optically isotropic at 290°. L. J. S.

**Pickeringite from the Schurovski Glacier.** V. A. ZILBERMING (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 997—1000).—The sample of pickeringite described was obtained from the Schurovski glacier on the northern slopes of the Turkestan Mountains, and consists of thin crusts and stalactites containing many mechanical admixtures. Its composition is:

Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	NiO.	CoO.	K <sub>2</sub> O.	SO <sub>3</sub> .	Cl.	H <sub>2</sub> O.	Total.
11.91	0.74	trace	3.12	0.37	1.21	0.10	0.16	37.76	trace	44.74	100.11

These results are in good agreement with the formula



in which part of the MgO is replaced by other oxides of the form RO and by K<sub>2</sub>O. T. H. P.

**Pisanite from Tennessee.** FRANK ROBERTSON VAN HORN (*Amer. J. Sci.*, 1914, [iv]. 37, 40—47).—Pisanite is found in considerable amount, as encrusting botryoidal and stalactitic masses, on surfaces of pyrite, pyrrhotite, and chalcopyrite in the abandoned open workings at Isabella in the Ducktown district. The material is transparent, and blue or green in colour. Analyses by W. R. Veazey gave I for the blue and II for the green variety:

	SO <sub>3</sub> .	FeO.	CuO.	MgO.	H <sub>2</sub> O.	Total.
I.	27.87	17.18	8.50	0.47	46.47	100.49
II.	28.72	21.45	3.83	0.39	45.58	99.97

Both conform to the general formula  $\text{RSO}_4 \cdot 7\text{H}_2\text{O}$ , being intermediate between boothite ( $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ ) and melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ).

Analysis I corresponds with  $2\text{FeO}, \text{CuO}, 3\text{SO}_3, 21\text{H}_2\text{O}$ , and II with  $6\text{FeO}, \text{CuO}, 7\text{SO}_3, 49\text{H}_2\text{O}$ . A crystallographic description is given of the blue pisanite, and also of arsenopyrite crystals and large crystals of staurolite from the Ducktown district. L. J. S.

**Dimorphism of the Apatite Group.** WILLY EISSNER (*Diss., Leipzig*, 1913, 1—54).—Detailed measurements were made of the crystal angles of apatite, vanadinite, pyromorphite, and mimetite, and of the optical constants of apatite, over considerable ranges of temperature ( $-160^{\circ}$  to  $+650^{\circ}$ ). The curves plotting these results show, in the case of pyromorphite and mimetite, a considerable break, indicating that these substances are dimorphous. Artificially prepared vanadinite ( $3\text{Pb}_3\text{V}_2\text{O}_8, \text{PbCl}_2$ ), pyromorphite ( $3\text{Pb}_3\text{P}_2\text{O}_8, \text{PbCl}_2$ ), and mimetite ( $3\text{Pb}_3\text{As}_2\text{O}_8, \text{PbCl}_2$ ) fuse at  $976^{\circ}$ ,  $1103^{\circ}$ , and  $1079^{\circ}$  respectively, and show a transformation point at  $710^{\circ}$ ,  $670^{\circ}$ , and  $395^{\circ}$  respectively.

L. J. S.

**New Occurrence of Cuprodescloizite.** ROGER C. WELLS (*Amer. J. Sci.*, 1913, [iv], 36, 636—638).—The mineral is found in the Shattuck Arizona mine, at Bisbee, Arizona, in the form of stalactites and reniform masses. On fractured surfaces it shows a radiating structure and a dark brown colour; the streak is "dark olive-buff." The mineral is soluble in dilute nitric acid, and on analysis gave:

PbO.	CuO.	ZnO.	V <sub>2</sub> O <sub>5</sub> .	As <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	CrO <sub>3</sub> .	H <sub>2</sub> O.	Insol.	Total.
55.64	17.05	0.31	21.21	1.33	0.24	0.50	3.57	0.17	100.02

These results agree approximately with the descloizite formula with the zinc replaced by copper, namely,  $2\text{PbO}, 2\text{CuO}, \text{V}_2\text{O}_5, \text{H}_2\text{O}$ . The percentage of copper, which is higher than in any cuprodescloizite yet recorded, suggests psittacinite, but this mineral is possibly only an altered form of descloizite.

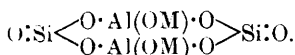
L. J. S.

**Silicic Acid Gels Obtained by the Decomposition of Silicates.** MARTIN THEILE (*Diss., Leipzig*, 1913, 1—39).—Heulandite and scolecite from Berufjord, Iceland, stilbite from the Færoe Islands, and natrolite from the Puy de Marman, Auvergne, were examined by Tschermak's method (A., 1906, ii, 771; A., 1908, ii, 490) for the determination of the composition of the silicic acid separated by the action of acid. It was found that the break in the drying curves varies in its position according to the temperature at which the drying takes place, and also with the nature of the drying agent. When the water of the gel is replaced by alcohol, chloroform, or carbon tetrachloride, the amounts that are taken up vary with the densities of these liquids. Artificially prepared ortho- and metasilicates of lead and of lithium in all cases yielded a silicic acid of the same composition (with a break in the drying curve at about 26%  $\text{H}_2\text{O}$ , and therefore all corresponding, according to Tschermak, with metasilicates). Fayalite ( $\text{Fe}_2\text{SiO}_4$ ) from a slag and artificial forsterite ( $\text{Mg}_2\text{SiO}_4$ ), on the other hand, gave widely differing results (38.31 and 22.47%  $\text{H}_2\text{O}$  respectively), although here with isomorphous substances the results should be the same if the method is to really indicate the constitution of the silicate.

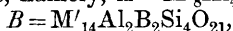
L. J. S.

**The Chemical Formula of Tourmaline.** V. I. VERNADSKI (*Zeitsch. Kryst. Min.*, 1913, 53, 273—288).—Penfield and Foote's general formula as modified by Schaller, namely,  $\text{H}_{20}\text{B}_2\text{Si}_4\text{O}_{21}$  (A., 1913,

ii, 68), is discussed in connexion with the author's theory of the alumosilicates (A., 1901, ii, 249). Since tourmaline is sometimes formed by the alteration of felspar, and on weathering yields kaolin or alkali-mica, it may be regarded as possessing a constitution analogous to these, and thus be an additive derivative of the kaolin ring,  $M'_2Al_2Si_2O_8$ :



Further, since boron is an essential constituent, it is necessary to assume a similar ring with boron in place of aluminium; and by joining the two rings the formula becomes  $M'_4Al_2B_2Si_4O_{16}$ . By the addition of various groups to this double ring three fundamental molecules are arrived at, namely,  $A = M'_8Al_4B_2Si_4O_{21}$ ,



and  $C = M'_2Al_6B_2Si_4O_{21}$ , each conforming to Schaller's formula; structural formulæ are written. The composition of all tourmalines is expressed by the mixing of these three components, which are referred to as *kalbaite*, *belbaite*, and *elbaite* respectively. Schaller's analysis of pale red tourmaline from Elba corresponds approximately with the molecule *C*, and tourmaline from De Kalb, New York, contains 97% of molecule *A*, with 3% of molecule *B*.

L. J. S.

[Zeolites from near Leitmeritz, Bohemia.] J. E. HIBSCH and F. SEEMANN (*Tsch. Min. Mitt.*, 1913, 32, 1—128).—Explanation of the geological map of the Bohemian Mittelgebirge, sheet ix, Leitmeritz and Triebtsch. Several analyses are given of the volcanic rocks. A brief account is given of the mineral species, principally zeolites, that are found in this district. Analyses are given of the following: all from the basaltic rock at Eulenberg (=Katzenburg), near Schüttenitz. Phillipsite, I colourless, II rose-red crystals. Sanidine (III–V) occurring as small, colourless crystals and drusy coatings on the phillipsite and on calcite; D 2·568. Thomsonite (VI and VII), D 2·388.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	48·73	19·89	—	5·45	—	7·36	2·31	16·26	100·00
II.	51·31	18·31	—	4·94	—	6·96	2·37	16·12	100·01
III.	63·64	19·46	—	0·16	—	15·00	1·84	0·45	100·55
IV.	65·11	18·72	—	0·38	0·31	12·87	1·26	0·50	99·15
V.	61·46	18·58	1·48	0·60	0·25	15·73	1·93	0·75	100·78
VI.	38·44	31·48	—	13·60	—	—	3·53	12·93	99·98
VII.	36·90	31·83	—	13·66	—	0·72	4·01	13·36	100·48

L. J. S.

Colour of Zircons and its Radioactive Origin. Hon. R. J. STRUTT (*Proc. Roy. Soc.*, 1914, [A], 89, 405—407).—Of the two brown varieties of zircon, the opaque kind occurs in plutonic rocks, whilst the transparent zircon is found only in basalts and other lavas. The transparent zircons are thermoluminescent, but colour and thermoluminescence are both destroyed by heating to about 300°. In view of this, the question arises as to how the basaltic mineral has regained its colour and its capacity to glow. Since zircon con-

tains hundreds of times as much radioactive matter as ordinary rock masses, it is suggested that the zircons found in lavas have had their colour and thermoluminescence restored by the slow action of the radium which they themselves contain.

The opaque brown zircons are not thermoluminescent, nor can they be made so by exposure to radium. They are not decolourised by moderate heating. In the belief that the transparent are formed from the opaque zircons by the action of molten basalt, an attempt has been made to imitate this experimentally. After twenty-four hours' immersion in molten basalt, it was found that the opaque brown zircon had become white, although not transparent. On exposure to radium, the zircons assumed the deeper red colour of hyacinths, and became, like them, thermoluminescent.

H. M. D.

**Chemical Investigation of Certain Minerals from Ceylon Gravel.** IV. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 1029—1041. Compare A., 1913, ii, 970).—The mineral here described is obtained from the Southern Province of Ceylon, and occurs as small pebbles which give transparent thin sections containing very small crystals of calcium fluoride and, more rarely, tetragonal prisms of titanite. Sections taken from near the surfaces of the pebbles include earthy, brownish-red, opaque particles, the number of which increases as the periphery is approached. The fluor spar crystals are distributed uniformly throughout the main bulk of the pebble, but, beginning with the zone containing the earthy particles, increase considerably in number towards the surface. In one direction the pebbles form thin cleavage plates exhibiting an intense vitreous lustre, and the fracture is imperfectly conchoidal, the streak white and the brittleness slight; the specific gravity is 3.49, and the hardness almost identical with that of orthoclase. Chemical analysis gives the results:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Cb <sub>2</sub> O <sub>5</sub> + Ta <sub>2</sub> O <sub>5</sub> .	ZrO <sub>2</sub> .	FeO.	MnO.	CaO.
31.97	2.48	4.03	30.63	4.50	4.43	9.57

MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	F.	Total, less O ≡ 2F.
0.04	0.32	7.50	2.24	2.36	99.08

These results give the formula:

$34\text{SiO}_2, 2\text{TiO}_2, \text{Cb}_2\text{O}_5, 16\text{ZrO}_2, 4\text{FeO}, 4\text{MnO}, 11\text{CaO}, 8\text{Na}_2\text{O}, 8\text{H}_2\text{O}, 8\text{F}$ , which may be expressed thus:  $4\text{Na}_2\text{O}(\text{ZrO}_2)_2 + 4\text{Na}_2\text{O}(\text{SiO}_2)_2 + \text{CaO}(\text{ZrO}_2)_2 + (\text{CaO})_3\text{Cb}_2\text{O}_5 + \text{CaO}(\text{TiO}_2)_2 + \text{CaO}(\text{SiO}_2)_2 + 4\text{CaF}_2 + 4\text{FeO}(\text{SiO}_2)_2 + 4\text{MnO}(\text{SiO}_2)_2 + 4\text{ZrO}_2(\text{SiO}_2)_2 + 8\text{H}_2\text{O}$ .

The properties of the mineral indicate its close resemblance to lävenite.

T. H. P.

**General Principles Underlying Metamorphic Processes.** JOHN JOHNSTON and PAUL NIGGLI (*J. Geol.*, 1913, 21, 481—516, 588—624).—The authors give an account of the more important general principles which may be usefully applied in the study of rock metamorphism. The influence of temperature, pressure, stress

(non-uniform pressure), and gross composition of the system when metamorphism occurs are considered in detail with reference to certain special cases of changes in condensed systems. H. M. D.

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## Analytical Chemistry.

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**A Modified Hempel Gas Pipette.** STANLEY R. BENEDICT (*Biochem. Bull.*, 1913, 3, 1).—The pipette is designed to avoid shaking, the gas being made to bubble through the apparatus. W. D. H.

**Filter from which a Precipitate may be Removed Quantitatively.** E. TRUTZER (*Chem. Zeit.*, 1914, 38, 55).—A tube, slightly widened out at its lower end, fits over the upper end of a second tube which is connected with a pump. A perforated plate carrying a layer of filtering material (asbestos) is placed in the upper tube, and rests on the edge of the lower tube. After the precipitate has been collected and washed, the lower tube and the perforated plate are removed, and the filtering material and precipitate are rinsed into any suitable vessel. W. P. S.

**Properties of Some Chlorohydrocarbons and their Uses in Chemical Analysis.** L. GOWING-SCOPES (*Analyst.*, 1914, 39, 4—20).—After recording the physical constants of the chloroethanes and chloroethylenes, the author describes the action of these substances on various metals and other inorganic substances. The solubility of 248 organic substances in the chlorohydrocarbons was determined, and the results are given in tabular form; these organic substances included hydrocarbons, ethers, alcohols, phenols, aldehydes, ketones and quinones, acid anhydrides, acids and esters, carbohydrates, glucosides, halogen derivatives, amides, nitro-compounds, purine derivatives, azo-compounds, gums and resins, colouring substances (aniline dyes), etc. The different solubilities of the colouring substances in the chlorohydrocarbons suggests a method of separating these substances, and a table is given indicating the kind of separations possible, but much further work is required in this direction. Trichloroethylene is suitable as a solvent for fat extractions (compare A., 1910, ii, 647), and the chloroethanes and dichloroethylene may be found useful in the analysis of caoutchouc. Various reactions of the chlorohydrocarbons are described. W. P. S.

**Winkler's Method for the Estimation of Oxygen in Water; the Effect of Nitrite and its Prevention.** FRANK E. HALE and THOMAS W. MELIA (*J. Ind. Eng. Chem.*, 1913, 5, 976—980).—The results obtained by this method are trustworthy and are not affected by the presence of nitrites in quantity less than 0.2 part per million.

With larger amounts of nitrites the results are too high owing to the reaction between the nitrous acid and hydriodic acid; the reaction is catalytic, the nitric oxide formed absorbing oxygen from the air and yielding nitrous acid, which in turn decomposes a further quantity of hydriodic acid. This effect may be prevented by carrying out the method in the usual way and introducing 2 c.c. of potassium acetate solution (1000 grams per litre) when the precipitate has dissolved in the added hydrochloric acid. The acetate solution should be added by means of a pipette reaching to the bottom of the bottle.

W. P. S.

**Estimation of Oxygen in Organic Compounds. II.** MAITLAND C. BOSWELL (*J. Amer. Chem. Soc.*, 1914, **36**, 127—132).—The method described in an earlier paper (A., 1913, ii, 334) gives satisfactory results with highly oxygenated compounds, but if the oxygen is less than 30—40%, the results are too high. A method has now been devised which can be applied to any organic compound, irrespective of its oxygen content. It consists in heating a weighed quantity of the substance in a quartz combustion tube in a current of nitrogen, causing the vapours to pass over a small quantity of heated copper oxide, of known oxidising value, distributed over a long layer of asbestos, weighing the water and carbon dioxide formed, and determining the oxidising value of the copper oxide which has not been reduced. The weight of oxygen,  $x$ , in the weighed quantity of substance is calculated by means of the equation,  $x = b + c + d - a$ , where  $a$  is the weight of the total oxygen available from the copper oxide in the tube,  $b$  the weight of oxygen available from the copper oxide remaining after the combustion,  $c$  the amount of oxygen in the water produced, and  $d$  the amount of oxygen in the carbon dioxide formed. The hydrogen content of the substance may be calculated from the weight of water produced.

This method gives results differing by 0.3% from the calculated values in the case of hydrogen, and by 0.3—1.0% in the case of oxygen.

E. G.

**Rapid Estimation of Sulphur in its Different States in Biological Liquids and in Particular in Urine.** R. GAUVIN and V. SKARZYNSKI (*Bull. Soc. chim.*, 1913, [iv], **13**, 1121—1127).—The authors have estimated the total sulphur, sulphur as sulphates, and sulphur as ethereal sulphates in urine as follows. For total sulphur the oxidation was performed by boiling with dilute hydrochloric acid and potassium chlorate for twenty minutes, the excess of oxidising agent being destroyed by addition of 1 c.c. of a 10% sugar solution. The solution was just neutralised, 2 c.c. of hydrochloric acid added, and the sulphates present precipitated by addition of a dilute solution of benzidine hydrochloride in excess according to Raschig's method. The sulphates and ethereal sulphates were precipitated together by the same reagent after hydrolysing the esters by boiling with dilute hydrochloric acid. Finally, the sulphates in the urine were estimated by direct precipitation with benzidine hydrochloride solution. In each case the benzidine sulphate pre-

precipitate was collected, well washed, and finally suspended in water and titrated at boiling point with  $N/10$ -sodium hydroxide, using phenolphthalein as indicator. W. G.

**Decomposition of Large Quantities of Organic Substance in Kjeldahl's Method.** ÉMILE CARPIAUX (*Bull. Soc. chim. Belg.*, 1913, 27, 333—334).—In order to avoid troublesome frothing when large quantities of organic substance are digested with sulphuric acid the following procedure is recommended. Thirty grams of the substance (for instance, straw or hay) are placed in a 500 c.c. flask and about 30 c.c. of sulphuric acid are added, the mixture is shaken, and set aside for about one hour. The spongy mass is then treated with a further quantity of sulphuric acid and heated until a clear, colourless solution is obtained. The greater part of the excess of sulphuric acid may be removed by adding small quantities of sugar to the boiling solution. W. P. S.

**Estimation of Ammonia in Urine.** STANLEY R. BENEDICT and EMIL ÖSTERBERG (*Biochem. Bull.*, 1913, 3, 41—44).—Steel recommends that in urines containing ammonio-magnesium phosphates, sodium hydroxide and sodium chloride should be employed to replace the sodium carbonate employed in Folin's method to liberate ammonia. In the present research, it is shown that all urines yield more ammonia when Steel's method is followed. The reason is that the addition of sodium carbonate to urine always causes the formation of ammonio-magnesium phosphate crystals, and this substance does not yield its ammonia quantitatively when decomposed by sodium carbonate. Folin's latest micro-chemical method of urea estimation is also criticised, for as Folin and Macallum themselves state, a trace of something which colours Nessler's reagent continues to come off, long after all the ammonia is removed. This unknown factor may lead to results 12% too high. W. D. H.

**Aeration Methods for the Estimation of Ammonium Nitrogen. III. The Ammonium Nitrogen in Beef.** JACOB SHULANSKY and WILLIAM J. GIES (*Biochem. Bull.*, 1913, 3, 45—53).—Steel's method gives better results than Folin's for the reason stated in the preceding abstract. The error may be specially great in the case of meat subjected to cold storage if the original Folin method is used. W. D. H.

**Estimation of Nitrogen by the Nitrometer.** C. M. JOYCE and HARRY LA TOURETTE (*J. Ind. Eng. Chem.*, 1913, 5, 1017—1018).—The nitrometer used by the authors consists of a gas generating bulb, fitted at the top with a two-way tap leading to a dissolving cup and an exit tube; the bottom of the bulb is connected with a levelling tube. The gas measuring apparatus consists of a graduated tube connected with a levelling tube through a T-piece leading to an equilibrium tube. Three drops of sulphuric acid are introduced into the latter at the time the volume of air in it is adjusted. The apparatus gives trustworthy results in the case of nitrate



nitrogen, but is not available for the estimation of nitrogen in celluloid or other substances containing carbon ring compounds. In the case of nitrocellulose, abnormally high results were obtained when the estimations were made at a temperature above  $28^{\circ}$ . This was due to the diminished solubility of nitric oxide in sulphuric acid, and to the partial decomposition of cellulose into carbon monoxide and carbon dioxide. The algebraic sum of these two corrections for temperatures from  $20^{\circ}$  to  $35^{\circ}$  is as follows:  $20^{\circ}$  to  $27.5^{\circ}$ ,  $+0.90$  c.c.;  $28^{\circ}$ ,  $+0.74$  c.c.;  $29^{\circ}$ ,  $+0.34$  c.c.;  $29.5^{\circ}$ ,  $+0.10$  c.c.;  $30^{\circ}$ ,  $-0.14$  c.c.;  $30.5^{\circ}$ ,  $-0.70$  c.c.;  $31^{\circ}$  to  $35^{\circ}$ ,  $-0.94$  c.c.

W. P. S.

**Comparative Investigation of Certain Reactions for the Detection of Nitrites in Potable Water.** M. BORNAND (*Chem. Zentr.*, 1913, **2**, 1823—1824; from *Mitt. Lebensmittelunters. Hyg.*, 1913, **4**, 285—289).—The following processes have been investigated: (1) the von Ilosva-Lunge method in which, on the one hand, sulph-anilic acid (0.5 gram) is dissolved in dilute acetic acid (150 c.c.), whilst, on the other hand, solid naphthylamine (0.2 gram) is boiled with water (20 c.c.), the colourless solution filtered from the bluish-violet residue, treated with dilute acetic acid (150 c.c.), and the two solutions mixed. The reagent (2 c.c.) is mixed with 50 c.c. of the water under investigation; after five to ten minutes, the presence of the slightest trace of nitrous acid is indicated by the red coloration of the liquid. (2) Rochaix's method (*Semaine Méd.*, 1909, **6**, 72), in which 20 c.c. of a 0.2 per cent. solution of neutral-red are treated with 10 c.c. of the water, and then with 1 to 3 c.c. of 20% sulphuric acid; the presence of nitrites (even 0.00005 gram  $\text{N}_2\text{O}_3$  in 1 litre) yields a violet to blue colour. (3) Barbet and Jandrier's method (A., 1897, ii, 234), according to which resorcinol (0.1 gram) is dissolved in the water (2 c.c.) and concentrated sulphuric acid (1 c.c.) added; the presence of nitrite (0.1 mg. per litre) causes a rose coloration at the junction of the liquids. (4) The method of Denigès (A., 1911, ii, 655), and (5) that of Chwilewsky (*Chem. Zentr.*, 1913, i, 1218).

According to the author's experience, all the above methods are well adapted for the detection of nitrous acid in potable waters with the exception of that of Denigès, which is unsuited for practical use in the laboratory, on account of the instability of the reagent. The first-described process is, however, preferred, as it can be readily used, not only in the laboratory, but also at the place of collection of the sample.

H. W.

**Gravimetric Estimation of Nitrites.** N. BUSVOLD (*Chem. Zeit.*, 1914, **38**, 28).—1.4—1.5 Grams of silver bromate are dissolved in 100 c.c. of water, 110 c.c. of 2*N*-acetic acid are added, and the whole heated to  $80^{\circ}$ ; 200 c.c. of the sodium nitrite solution (about 1 gram per litre) are added from a dropping funnel, and then 30 c.c. of dilute sulphuric acid (1:4) at  $85^{\circ}$ . The precipitate, consisting of silver bromide, is washed with boiling water, collected in a Gooch crucible, and dried at  $130^{\circ}$ . From the weight should be deducted

any silver chloride determined previously; 1 mol. of silver bromide = 3 mols. of nitrous acid. L. DE K.

**Phenoldisulphonic Acid Method for Estimating Nitrates in Soils.** C. B. LIPMAN and L. T. SHARP (*Bied. Zentr.*, 1913, 42, 721—726; from *Univ. California Publ. Agric. Sci.*, 1912, 1, 21—37).—In presence of sodium sulphate, considerable losses of nitrogen take place when the phenoldisulphonic acid method is employed; the losses are, however, less than when chlorides are present. Low results are also obtained with soil extracts which have been clarified by means of alum or animal charcoal; and small losses occur when a clay filter is employed. Calcium hydroxide (2% of the weight of soil) may be employed. The presence of sodium carbonate in soil extracts seems to be without appreciable effect. N. H. J. M.

**The Pemberton-Kilgore Method for the Estimation of Phosphoric Acid.** P. L. HIBBARD (*J. Ind. Eng. Chem.*, 1913, 5, 998—1009).—This method, which consists in precipitating the phosphoric acid with molybdic acid and titrating the yellow precipitate formed, has been submitted to a critical examination by the author, mainly with the object of eliminating certain sources of error in the process. The phosphate solution should contain about 0.02 gram of  $P_2O_5$  per 100 c.c., and this quantity requires 15 grams of ammonium nitrate and 30 c.c. of 5% molybdic acid solution containing 7% of free nitric acid, for precipitation. Chlorides in general cause low results, whilst the presence of sulphates causes the results to be too high. When the yellow precipitate is contaminated from any cause, it may be purified by re-precipitation. Ignition with magnesium oxide is recommended for the removal of organic substances from a phosphate, previous to the estimation of the phosphoric acid, and the use of silver phosphate is suggested for standardising the sodium hydroxide employed for the titration of the yellow precipitate. W. P. S.

**Preparation of Neutral Ammonium Citrate Solution.** PAUL RUDNICK and W. L. LATSHAW (*J. Ind. Eng. Chem.*, 1913, 5, 998).—Two separate ammonium citrate solutions, when examined according to the method described by Patten and Marti (A., 1913, ii, 790), showed ratios of ammonia to citric acid of 1:3.786 and 1:3.748 respectively. Comparative analyses of a sample of acid phosphate with these two solutions yielded identical figures, indicating that the variation of these solutions from the ratio given by Patten and Marti (1:3.765) was not sufficient to affect the results obtained. W. P. S.

**Rapid Method for the Estimation of Arsenic in Sulphuric and Hydrochloric Acids.** H. KOELSCH (*Chem. Zeit.*, 1914, 38, 5—6).—Twenty-five c.c. of sulphuric or 100 c.c. of hydrochloric acid are diluted in an Erlenmeyer flask with 200 c.c. of water, 5 c.c. of potassium iodide (50 grams per litre) are added, and the whole is

boiled until the liquid becomes yellow. Five c.c. of sodium sulphite solution (25 grams of crystals per litre) are added, and the boiling is continued for another five minutes. After neutralising the acid with alkali hydroxide solution (the total volume should then be 700 c.c.), a little sodium hydrogen carbonate is added, and the arsenious acid formed titrated, as usual, with standard iodine. Minute traces of nitric acid do not interfere with the process

L. DE K.

**Estimation of Arsenic and Antimony in Alloys and of Arsenic in Copper.** G. BRESSANIN (*Ann. Chim. anal.*, 1913, 18, 465—468).—The process is based on the fact that tin, in the higher state of oxidation and dissolved in sulphuric acid of D 1.53 (a little tartaric acid may be added to facilitate solution), is precipitated as stannic iodide on adding potassium iodide, whilst arsenic and antimony, in the quinquivalent state, liberate iodine, and are precipitated as the lower iodides, which may then be readily estimated iodometrically.

Arsenic in commercial copper is estimated by dissolving 0.8 gram in 5 c.c. of *aqua regia*, the solution is evaporated to dryness, and the residue dissolved in 250 c.c. of sulphuric acid (D 1.53). When cold, 25 c.c. of 30% potassium iodide are added; this precipitates both copper and arsenic as the lower iodides, which are collected on an asbestos filter, and washed with 30—40 c.c. of the above acid, to which have been added 5% potassium iodide solution. The arsenic tri-iodide is now dissolved off the filter by means of 100 c.c. of dilute sulphurous acid, and to the clear filtrate is added starch solution and sufficient iodine to impart a very faint blue colour. Excess of sodium hydrogen carbonate is then added, and the arsenic titrated with weak standard iodine.

L. DE K.

**Method for Estimating Extremely Small Quantities of Boron in Organic Substances.** GABRIEL BERTRAND and H. AGULHON (*Compt. rend.*, 1913, 157, 1433—1436).—A colorimetric method of estimating minute quantities of boron in dry matter of animal or vegetable origin. The method is based on the reaction of boric acid with turmeric under conditions already described (compare A., 1910, ii, 241, 345). The dry matter is rendered alkaline by the addition of a few drops of sodium hydroxide, and calcined at a red heat. The ash is triturated with phosphoric acid, transferred to a flask, and distilled with methyl alcohol, the distillate being collected in a capsule containing five drops of *N*-sodium hydroxide solution. This is then evaporated to dryness, four drops of *N*/10-hydrochloric acid added, and the whole transferred to a test-tube by means of distilled water, the volume being made up to 1.5 c.c. A strip of turmeric paper, 45 mm. long and 3 mm. wide, is inserted, allowing 15 mm. to project, and the amount of boron present is determined by the length of the coloration produced at the end of the paper after two hours at 35°, as compared with standard control solutions.

W. G.

**A Dennstedt Combustion Furnace with Internal Electric Heating.** C. MILCHSACK and W. A. ROTH (*Zeitsch. angew. Chem.*, 1914, **27**, 5—7).—The disadvantage of the ordinary Dennstedt furnace with electric heating is that the contents of the tube cannot be observed during the combustion. The authors describe an arrangement by means of which the tube can be electrically heated internally, and the process of combustion observed continuously. Good results were obtained with such substances as naphthalene, benzoic acid, toluene, and cinchonine. T. S. P.

**Volumetric Estimation of Small Amounts of Potassium.** LEOPOLD ZALESKI (*Landw. Versuchs.-Stat.*, 1913, **83**, 221—255).—Direct precipitation with de Koninck's reagent is considered more certain as well as simpler than Mitscherlich's method, especially when the following modifications are adopted. The reagent, which is added in drops, or a thin stream, and stirred in, is employed in considerable excess (0.5 to 1 c.c. of reagent per mg. of  $K_2O$ ). Filtration follows after twelve to twenty-four hours, and the potassium factor is simultaneously tested under the same conditions as the estimation. N. H. J. M.

**Estimation of Lead in the Defecated Liquids of Molasses.** H. PELLET (*Ann. Chim. anal.*, 1913, **18**, 475—476).—The lead (in absence of interfering substances) is precipitated as sulphite by passing a current of sulphur dioxide. The precipitate is collected on a counterpoised filter and dried. Multiplied by 0.721, the amount of lead is obtained. Sometimes the sulphite is somewhat coloured, but this does not appreciably affect the weight. L. DE K.

**Method for the Assay of Native Copper Sulphides, Pyrites, Copper Mattes, etc.** L. BERTIAUX (*Ann. Chim. anal.*, 1913, **18**, 468—478).—A process for the estimation of copper, silver, gold, arsenic, antimony, nickel and cobalt, iron, bismuth, lead, sulphur, and silica in the above materials, and practically the same as that published by Holland and Bertiaux (*Analyse des Metaux*, 2nd Ed.). L. DE K.

**Separation of Iron and Aluminium.** HERMANN BORCK (*Chem. Zeit.*, 1914, **38**, 7).—The old process of separating the two oxides by igniting in a mixed current of air and hydrogen chloride (when the alumina is left) is but rarely applied, as it is not very accurate. The author, however, finds that by using a boat made of quartz instead of one made of platinum or porcelain, the results are quite trustworthy. An illustration of a convenient apparatus is given. L. DE K.

**The Estimation of Chromium by Oxidation in Alkaline Solution.** F. BOURION and A. SÉNÉCHAL (*Compt. rend.*, 1913, **157**, 1528—1531).—The estimation of chromium, by oxidation in alkaline solution in the cold with hydrogen peroxide, removal of the excess of hydrogen peroxide by boiling, reduction of the

chromic acid with a known quantity of ferrous sulphate in the presence of sulphuric acid, and titration of the excess of ferrous sulphate with potassium permanganate, gives exact results in the presence of iron, but is vitiated by the presence of nickel, cobalt, and manganese. Sodium sulphate greatly facilitates the destruction of the large excess of hydrogen peroxide which is necessary, and this action is also catalysed by ferric oxide. W. G.

**Electro-analytical Studies.** [Arsenic. Bismuth.] BURT P. RICHARDSON (*Zeitsch. anorg. Chem.*, 1913, **84**, 277—317).—The experiments have been made with a gauze cathode and a rotating anode, using a cylindrical glass vessel with tap and outflow tube.

Arsenic is reduced during electrolysis from the quinquevalent to the tervalent condition. The deposition of copper free from arsenic is only possible when the arsenic is originally present in the quinquevalent form. To deposit 0.27 gram of copper from a solution containing 0.1 gram of arsenic, the total volume should be 70 c.c. and the temperature 50°, 0.6 c.c. of concentrated nitric acid being present. Using 2 amperes, deposition of pure copper is complete in twenty minutes.

Bismuth is best deposited at 50° from a solution containing tartaric acid (15 grams for 0.16 gram of bismuth), the voltage being reduced in stages from 1.9 to 1.5, and the total time thirty-five minutes. This is necessary in order to lessen the evolution of hydrogen. The deposited metal must be washed, a voltage of 1.7 being maintained, with 1% sodium hydroxide solution; otherwise there is a loss of bismuth by re-solution.

It is not practicable to separate bismuth electrolytically from antimony. Arsenic should be present in the quinquevalent form, at a temperature of 60°. Bismuth is separated from cadmium in a solution containing lactic acid at the ordinary temperature. The voltage is gradually lowered during the deposition. Some anomalies in the process are still unexplained. Bismuth, deposited in the ordinary way, is separated quantitatively from lead.

Measurements of the cathode potential during the deposition of several metals have also been made, and the results brought into relation with the formation of spongy deposits under certain conditions. The best cathode potential having been once determined, it is sufficient in practical determinations to measure the difference of potential between the electrodes.

Bismuth does not form complex ions with tartaric acid to any considerable extent. C. H. D.

**Determination of the Oxidisability of Mineral Waters.** N. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1697—1700).—The determination of the oxidisability (oxygen absorbed) of natural waters containing chlorides by means of permanganate in presence of sulphuric acid results in interaction of the hydrochloric acid set free and the permanganate, with liberation of chlorine. It is therefore necessary to diminish the total amount of permanganate used up by that destroyed by the chlorine. The addition of manganese sulphate, which retards the action of permanganate,

does not seem to ensure satisfactory results, there being no guarantee that the organic matter is completely oxidised or that the chlorides are not oxidised to some extent. A better method consists in absorbing the chlorine in potassium iodide solution. The iodine liberated may then be titrated with sodium thiosulphate, or the potassium iodide and iodine solution may be added to the excess of permanganate in the oxidation flask, and the whole of the iodine titrated with sodium thiosulphate. Diminution of the original volume of permanganate by that corresponding with the iodine liberated, gives the amount employed in oxidising the water.

In determining the oxygen absorbed by a saline water containing 0.5855 gram of sodium chloride and 0.0565 gram of potassium chloride per litre, the author prepared a control solution free from organic matter, but otherwise of the same composition as the saline water. To each of two flasks containing 100 c.c. of the water and the control solution were added, in equal amounts, sulphuric acid and a large excess of permanganate solution. The flasks were immersed in a bath of saturated salt solution, which was heated in twelve minutes to boiling, this being maintained for exactly ten minutes; at the end of this time the flasks were removed from the bath, left in the air for fifteen minutes, and then cooled under the tap. After addition of a known amount in excess of standard sodium oxalate solution, the contents of each flask were titrated with the permanganate solution. The difference between the amounts of the latter used up in the two flasks represents the organic matter of the water. The uncorrected value for the saline water is four to nine times as great as the value obtained after correction for the control solution.

T. H. P.

**Estimation of the Acidity or Alkalinity of Waters. A Study in Indicators.** JAMES MOIR (*J. Chem. Met. Mining Soc. S. Africa*, 1913, 14, 114—118. Compare A., 1907, ii, 389).—Attention is directed to the misleading conclusions which may be drawn as to the acidity of a mine water or the alkalinity of a town water, if the titrations are made with the wrong class of indicator. The true neutral point is difficult to fix, and no hard and fast rule can be laid down as to the indicator to be used, especially in the case of mine waters; for instance, methyl-orange indicates the point at which free acid has been neutralised, lacmoid that at which the free acid and iron and aluminium salts have been neutralised, and so on. A "neutral" solution, prepared by mixing recently-boiled *M*/10-solutions of disodium hydrogen phosphate and sodium dihydrogen phosphate in the proportion of 1 volume of the former to 3 volumes of the latter, may be used for determining the neutral colour of any indicator. The author tabulates some fifty-four colour substances in the approximate order of their "strength" as indicators.

W. P. S.

**Formation of Sediment in Bottled Mineral Waters. Estimation of Silica, Iron and Aluminium in Natural Mineral Waters.** L. DEDE (*Chem. Zeit.*, 1914, 38, 53—55).—The liability

of mineral waters to yield a quantity of sediment after being stored for some length of time in bottles appears to depend on the amounts of alumina and silica contained in the waters; the formation of the sediment is not due to the presence of iron salts, since many highly ferruginous waters do not give a deposit. Generally, the sediment consists chiefly of hydrated ferric oxide, alumina, silica, and calcium carbonate. It is probable that ferrous carbonate is first of all oxidised, and the resulting hydrated ferric oxide causes the precipitation of alumina, silica (also finely-divided clay held in suspension), and calcium carbonate. For the estimation of silica, etc., it is recommended that the water be neutralised with hydrochloric acid, evaporated to a small volume in a silver basin, then transformed to a platinum basin, and evaporated with an excess of hydrochloric acid to dryness. The residue should be heated to  $110^{\circ}$  for thirty minutes before the silica is collected. W. P. S.

**Estimation of the Lime Requirement of Soils.** J. A. BIZZELL and T. L. LYON (*J. Ind. Eng. Chem.*, 1913, 5, 1011—1012).—Albert (*Zeitsch. angew. Chem.*, 1888, 1, 533) has proposed a method in which the solution is distilled with barium hydroxide solution and ammonium chloride, the amount of ammonia found in the distillate being taken as a measure of the free barium hydroxide not required to saturate the soil (barium hydroxide is preferable to calcium hydroxide, since the compounds of the latter with the soil tend to decompose and react with the ammonium chloride). The absorption of the barium hydroxide by the soil is not, however, immediate, and certain soils when boiled with ammonium chloride yield considerable quantities of ammonia. The author, in order to avoid these sources of error, carries out the method as follows: Twenty-five grams of the air-dried soil are heated on a boiling water-bath for one hour with 50 c.c. of boiled water and 50 c.c. of  $N/10$ -barium hydroxide solution. One hundred and fifty c.c. of water and 5 grams of ammonium chloride are then added, and the mixture is distilled, the ammonia being titrated in the distillate. A further quantity of 25 grams of the soil is then distilled with 5 grams of ammonium chloride, omitting the barium hydroxide. The results obtained by the modified method agree with those found by the Vietch process. W. P. S.

**Identification of Ethyl Alcohol and Methyl Alcohol.** J. J. BLANKSMA (*Chem. Weekblad.*, 1914, 11, 26—29).—Ethyl alcohol and methyl alcohol can be identified by the action of their sodium derivatives on 1-chloro-2:4-dinitrobenzene, the identity of the 2:4-dinitrophenetole or 2:4-dinitroanisole formed respectively being given by the melting point. A. J. W.

**Determination of the Methoxyl Group.** R. J. MANNING and M. NIERENSTEIN (*Ber.*, 1913, 46, 3983—3984).—The authors find that the addition of acetic anhydride, as sometimes recommended for the Zeisel determination, introduces a source of error, for in the absence of any third substance the mixture of acetic anhydride

and hydriodic acid may give rise to the formation of appreciable quantities of silver iodide. The application of phenol is also untrustworthy for a similar reason.

D. F. T.

**New Method for the Estimation of Glycerol in Wine.** S. ROTHENFUSSER (*Zeitsch. Nahr. Genussm.*, 1913, 26, 535—544).—The method depends on the oxidation of the glycerol to oxalic acid by means of permanganate after other oxidisable substances (sugars) have been removed by treatment with ammoniacal lead acetate solution. In the case of wine containing not more than 1% of sugars, 50 c.c. of the sample are mixed with 30 c.c. of a 20% sodium carbonate solution, 5 grams of crystallised stannous chloride are added, the mixture is diluted to 250 c.c., and filtered; 200 c.c. of the filtrate are then treated with ammoniacal basic lead acetate solution (40 c.c. of basic lead acetate solution mixed with 20 c.c. of 10% ammonia), diluted with 10% ammonia to 300 c.c., filtered, and 200 c.c. of the filtrate are evaporated to 50 c.c., after the addition of 5 c.c. of 10% sodium phosphate solution and 6 grams of anhydrous sodium carbonate. The solution, without filtration, is now transferred to a flask, diluted to 100 c.c., cooled to 25°, and 10 grams of potassium carbonate and 2 grams of potassium permanganate are added. After forty-five minutes, the excess of permanganate is destroyed by the addition of hydrogen peroxide, the mixture is diluted to 250 c.c., filtered, and the oxalic acid is precipitated from 220 c.c. of the filtrate as calcium oxalate, the solution being first acidified with acetic acid. The calcium oxalate is then collected, and titrated with standardised permanganate solution.

With wines containing up to 6% of sugars, 50 c.c. of the sample are mixed with 15 c.c. of sodium carbonate solution and 2.5 grams of stannous chloride, diluted to 250 c.c., filtered, and 220 c.c. of the filtrate are diluted with 5% ammonia to 250 c.c. A mixture, consisting of equal volumes of basic lead acetate solution and 10% ammonia, is then added until a small portion of the solution, after filtration, gives a black precipitate with ammonium sulphide, and no longer reduces Fehling's solution; 20 c.c. of 10% ammonium carbonate solution are now added, the whole is diluted with 10% ammonia to 500 c.c., and filtered. To 250 c.c. of the filtrate are added, 5 c.c. of 10% sodium phosphate solution and 6 grams of anhydrous sodium carbonate, and the process is proceeded with as described. The method may also be applied to sweet wines.

W. P. S.

[**Estimation of Cholesterol.**] JOSEPH SAMUEL HEPBURN (*Chem. Zentr.*, 1913, ii, 2052—2053; from *J. Franklin Inst.*, 1913, 176, 405—452).—See this vol., i, 168.

**Rotatory Power of Lævulose and of Invert Sugar.** J. LABORDE (*Ann. Falsif.*, 1913, 6, 650—660).—Lævulose was found to have  $[\alpha]_D^{20} = 93.60^\circ$ , and invert sugar  $[\alpha]_D^{20} = 20.30^\circ$  (compare A., 1913, ii, 447); the method of preparing the lævulose or invert sugar



(heating with hydrochloric acid or by enzymic action) does not affect these constants. If, however, a solution containing lævulose has been heated with an acid, then cooled, and neutralised, the polarimetric reading must not be taken until after the solution has been kept at 20° for about one hour; when the reading is taken immediately after the solution has been cooled and neutralised, the result will differ by several degrees from the true value. This is due to the muta-rotation of the lævulose; this source of error may also be eliminated by taking the reading on the acid solution or after the addition of a slight excess of ammonia. Dextrose exhibits muta-rotation to a much less extent than does lævulose. The rotation of lævulose is also affected by temperature, since it increases as the temperature is lowered; for readings between 9° and 25° the correction is 0.32° (polarimetric) for each degree of temperature when the latter differs from 20°. Since lævulose is more readily destroyed than dextrose by caramelisation and by the action of yeasts, the presence of added dextrose ("glucose") in sweets, etc., is not indicated with certainty unless the excess of dextrose over the lævulose exceeds 9% (calculated on the quantity of the two sugars).

W. P. S.

#### Estimation of Carbohydrates, especially in Plant Extracts.

WILLIAM A. DAVIS and ARTHUR JOHN DAISH (*J. Agric. Sci.*, 1913, 5, 437—468).—The plant extract is evaporated under 700—740 mm. pressure, and made up to definite volume (500 c.c.), of which two portions of 20 c.c. are used for estimating dry matter, whilst the rest is precipitated with basic lead acetate, filtered, washed, and diluted to two litres. A portion of this (300 c.c.) is precipitated with solid sodium carbonate and diluted to 500 c.c. This solution is employed (1) for direct reduction and polarisation, and (2) for sucrose; 50 c.c. are inverted by invertase after being made faintly acid to methyl-orange by a few drops of sulphuric acid. Autolysed yeast (1—2 c.c.) and two or three drops of toluene are added to the solution, which is kept for twenty-four hours at 38—40°; it is then treated with 5—10 c.c. of alumina cream, filtered, washed, and diluted to 100 c.c. It is then polarised, and the reducing power estimated in 50 c.c. Another portion is inverted by 10% citric acid by adding 10% of the crystallised acid to the solution, slightly acidifying with sulphuric acid, and boiling for ten minutes. It is then cooled, neutralised to phenolphthalein with sodium hydroxide, and diluted to 100 c.c. This is polarised and the reducing power estimated. The values obtained by the two methods should agree closely.

Maltose is estimated in another 300 c.c. of the original solution, which is precipitated with hydrogen sulphide, filtered and washed until the filtrate is about 450 c.c. Air is then drawn through for one and a-half hours, and a little ferric hydroxide added to remove the last traces of hydrogen sulphide. The filtered solution is made up to 500 c.c., and portions of 50 c.c. fermented with *S. marxianus*, *S. anomalus*, and *S. exiguus* respectively, and two others with ordinary yeast. The difference between the average reducing power

of the first three and that of the last two solutions gives the reduction due to maltose.

When the reduction in the first solution (precipitated with sodium carbonate) due to pentose and maltose has been allowed for, the remaining direct reduction is due to dextrose and lævulose, the actual amounts of which are calculated from the reducing power combined with the corrected specific rotation.

As regards the gravimetric method, the purification of the asbestos by boiling with 20% sodium hydroxide should be continued for not less than half an hour.

The volumetric method of Ling is preferable to that of Bertrand, which is only roughly approximate.

The employment of basic lead acetate does not give rise to losses of sugar, the supposed loss being probably due to incomplete inversion in presence of sodium acetate.

Maltose cannot be completely hydrolysed by dilute hydrochloric acid, either at 70° or 100°, without destroying large amounts of lævulose or dextrose. The only available method consists in employing special maltose-free yeasts, such as the three referred to, a correction being introduced, for pentoses, etc., by a special fermentation with bakers' or brewers' yeast.

N. H. J. M.

**Fatty Acids and Detection of Arachidic Acid.** S. FACHINI and G. DORTA (*Chem. Zeit.*, 1914, 38, 18).—The authors have noticed that the potassium salts of the liquid (oleic) acids are readily soluble in solution of acetone, whilst those of the solid acids are insoluble therein. In order to detect arachidic acid in the acids isolated, as usual, from 10 grams of olive oil, these are dissolved in 90 c.c. of pure acetone at boiling heat, and 10 c.c. of *N*-potassium hydroxide are added. When quite cold, the crystals are collected on a filter using a suction apparatus, and washed with small portions of acetone. The fatty acids liberated by means of dilute acid are, if necessary, purified by means of light petroleum, and then tested as to their melting point and molecular weight.

Arachidic acid may be isolated and further identified by recrystallisation from 90% alcohol. If to the acetone solution is added an insufficient amount of potassium hydroxide, the precipitate will consist mainly of the arachidic compound, and the identification will then be easier.

L. DE K.

**Applied Microchemistry of Plants. VIII. Identification of Lichesteric Acid.** O. TUNMANN (*Chem. Zentr.*, 1913, ii, 2060—2061; from *Apoth. Zeit.*, 1913, 28, 892—893).—The identification of lichesteric acid in Iceland moss can be accomplished by sublimation of the finely-divided thallus, whereby rhombic crystals and granular aggregates are obtained, which are unchanged by ferric chloride, insoluble in water, soluble in alkalis, alcohol, and ether, slowly soluble in acetic acid. The microchemical preparation of the ammonium and sodium salts is particularly adapted to the detection of lichesteric acid. The latter appears to be previously formed in Iceland moss and to be localised in the under layer of the lichen.

H. W.

**A Colour Reaction of Glycine when Boiled with Chloral Hydrate.** EDWIN D. WATKINS (*Biochem. Bull.*, 1913, 3, 26—27).—Glycine, even in very dilute solutions, gives a red colour when boiled with chloral hydrate. Phenol, glycerol, resorcinol, acetone, ethyl alcohol, glyoxylic acid, orthophosphoric acid, and chloral, when boiled with glycine, yield no colour. Acetone boiled with barium hydroxide solution and then with glycine solution yields a green colour which changes to red in thirty minutes.

W. D. H.

**Detection and Estimation of Benzoic Acid in Milk and Cream.** E. HINKS (*Analyst*, 1913, 38, 555—557).—The presence of 0.01% or more of benzoic acid in milk or cream may be detected with certainty by means of the following method: 25 c.c. of the milk, or from 10 to 20 grams of the cream, are heated with an equal volume of concentrated hydrochloric acid until the curd has dissolved completely. The mixture is cooled, shaken with 25 c.c. of a mixture consisting of 2 volumes of light petroleum and 1 volume of ether, the ethereal solution is separated, and shaken after the addition of 1 drop of ammonia and 5 c.c. of water. The aqueous layer is now separated, heated on a water-bath for a few minutes to expel the excess of ammonia, and then tested with ferric chloride solution. On the addition of the ammonia, a precipitation of ammonium benzoate takes place, and this reaction, although less characteristic, is more sensitive than the ferric chloride test.

The quantity of benzoic acid present may be estimated by heating 25 c.c. of the milk with hydrochloric acid under a reflux apparatus, extracting the cooled solution three times with 20 c.c. of the mixture of light petroleum and ether, and shaking the separated ethereal portions with 10 c.c. of water and 1 drop of ammonia; this extraction is twice repeated. The mixed aqueous portions are then acidified with hydrochloric acid, extracted three times with the ethereal solvent, the extracts are evaporated at the ordinary temperature, and the residue is dried in a desiccator to constant weight. The benzoic acid is then volatilised at 100°, the loss in weight giving the amount of the acid.

W. P. S.

**The Identification of Carbamide and its Precipitation from Extremely Dilute Solutions.** R. FOSSE (*Compt. rend.*, 1913, 157, 948—951).—By means of its xanthhydrol derivative, it is possible to separate carbamide and identify it by analysis at a dilution of 5 parts in 100,000. It can be identified microscopically at a dilution of 1 in 100,000, and precipitated at a dilution of 1 in 1,000,000. At the first dilution the precipitation is best carried out by adding to 2 parts of the solution 7 parts of acetic acid and 1 part of a 10% alcoholic solution of xanthhydrol. In the second and third cases, acetic acid should be added until the final solution contains 10% of this acid. The precipitate recrystallised from alcohol forms radiating, microscopic filaments.

W. G.

**Volumetric Estimation of Carbamide.** ADOLF JOLLES (*Biochem. Zeitsch.*, 1913, 57, 414—419).—It is found that by the addition of

potassium ferricyanide to the hypobromite solution results nearer to those required by theory are obtained than when the former substance is omitted; 2.5 c.c. of the carbamide solution (diluted so as to contain 2.3% urea) are treated with 5 c.c. of 20% potassium ferricyanide solution, and then 20 c.c. of a solution produced by dissolving 150 grams of sodium hydroxide and 25 grams of bromine in 250 c.c. of water are added. The nitrogen evolved is collected in a nitrometer, a convenient form of which is described and figured in the text.

S. B. S.

**Estimation of Caffeine in Kola Preparations, particularly in Granulated Kola.** MAURICE FRANÇOIS (*Ann. Falsif.*, 1913, 6, 596—608).—The whole of the caffeine present in kola preparations, such as the extract, fluid extract, and granulated products, may be extracted by means of chloroform, provided that the preparation is mixed with magnesia, dried thoroughly, and then ground up with sand before the extraction is commenced. The caffeine thus obtained is free from ash, and does not contain more than 1% of impurities which are insoluble in hydrochloric acid. In the case of kola nuts themselves, the method yields low results owing to the fact that the magnesia does not penetrate the particles sufficiently to liberate the whole of the caffeine; in this respect the method requires further investigation.

W. P. S.

**New Test for the Cinchona Alkaloids.** G. N. WATSON (*Amer. J. Pharm.*, 1913, 85, 502).—A yellow precipitate is formed when a sulphuric acid solution of quinine, cinchonine, or cinchonidine is treated with a few drops of a saturated alcoholic solution of  $\alpha$ -naphthol to which a small quantity of sulphuric acid has been added; the precipitate is soluble in excess of the reagent, yielding a yellow solution. Other white alkaloids do not give the yellow coloration. The test will detect the presence of the cinchona alkaloids in mixtures of the same with atropine, morphine, cocaine, strychnine, caffeine, brucine, and codeine.

W. P. S.

**A Colorimetric Method for the Estimation of Histidine.** MORIZ WEISS and NIKOLAUS SOBOLEV (*Biochem. Zeitsch.*, 1913, 58, 119—129).—The Pauli diazo-reaction for histidine was employed. The reagents used were a solution of sulphanilic acid in hydrochloric acid, and a solution of sodium nitrite. A mixture of these was added to the solution under investigation, and then 10% sodium carbonate was added. The total volume of the mixture was kept constant, and the colour obtained was then compared with that got, under similar conditions, with a 1/10,000 histidine solution. The solution under investigation was then diluted, and the test repeated until a dilution equivalent to a histidine content of 1/10,000 was obtained. For accurate estimations, the control and test solutions could then be compared in a Duboscq colorimeter. Certain inhibitory substances are sometimes present, which appear to combine with the diazonium compound. In these cases larger quantities of the reagents must be employed, and a scheme is

suggested by means of which the influence of the inhibitory substances can be removed, by carrying out the reaction systematically in the presence of varying amounts of the reagents.

S. B. S.

**The Non-interference of "Ptomaines" with Certain Tests for Morphine.** JACOB ROSENBLOOM and S. ROY MILLS (*J. Biol. Chem.*, 1913, **16**, 327—330).—Bacterial products formed during aerobic and anaerobic putrefaction of human organs did not in any way give reactions simulating those due to the presence of morphine, and in no way interfered with the detection of morphine when this alkaloid was added. Each of the many reactions for morphine are dealt with.

W. D. H.

**The Reaction of Some Purine, Pyrimidine, and Hydantoin Derivatives with the Uric Acid and Phenol Reagents of Folin and Denis.** HOWARD B. LEWIS and BEN H. NICOLET (*J. Biol. Chem.*, 1913, **16**, 369—374).—Many derivatives of the groups mentioned give the reactions referred to; long lists of these are given in reference to these reactions. With the exception of thiocarbamide, no substance was observed to react typically with the phenol reagent which does not contain a phenol group or react with the uric acid reagent. With the exception of the thiopurines, none of the purines react positively. Funk and Macallum's suggestion that in the purines the substitution of the hydrogen atoms of the ring lessens or destroys the power to react with the uric acid reagent, does not hold for the hydantoin group.

W. D. H.

**Estimation of Gliadin in Flour and Gluten.** GEO. A. OLSON (*J. Ind. Eng. Chem.*, 1913, **5**, 917—922).—The simplest method for the estimation of gliadin in flour consists in estimating the nitrogen in the uncoagulable portion of the alcohol extract, and deducting the result from the total alcohol-soluble nitrogen. Alcohol solutions extract two groups of nitrogenous substances from flour; when the alcoholic solution is evaporated and water is added, gliadin separates whilst the other group of substances remains in solution. A 1% sodium chloride solution extracts a part of the gliadin contained in wheat flour. Solutions containing from 50% to 65% by vol. of alcohol extract equivalent amounts of gliadin from flour; when the alcoholic strength is above 65% the amount of coagulable nitrogen diminishes. For the estimation of gliadin the use of 50% alcohol is, therefore recommended. About 68% of the total alcohol-soluble nitrogen is coagulable, whilst the soluble portion may be precipitated completely by means of phosphotungstic acid.

W. P. S.

## General and Physical Chemistry.

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**Index of Refraction of Binary Mixtures.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 691—696).—The author replies to the criticisms of Schweser (A., 1913, ii, 453, 537).  
T. H. P.

**Ultra-violet Emission Bands of the Mono-, Di-, and Tri-atomic Oxygen Molecule.** J. STARK (*Ann. Physik*, 1914, [iv], 43, 319—336).—Experiments are described the object of which was to ascertain the ultra-violet spectra emitted by oxygen molecules containing one, two, and three atoms. The observations were made with a special form of end-on discharge tube having a quartz plate at right angles to the capillary.

It has been previously shown (Goldstein, A., 1903, ii, 723) that ozone is formed in the discharge through oxygen at low pressures, and it is to be expected that the emission spectra of both  $O_2$  and  $O_3$  will be observable in these circumstances. By reference to the absorption spectra of oxygen and ozone it is possible to assign certain bands in the emission spectrum to  $O_2$  and others to  $O_3$ . In this way it has been found that the triatomic molecule gives rise to a large number of bands which stretch from the green of the visible spectra up to  $\lambda$  210  $\mu\mu$ . These bands are shaded off towards the long-waved end of the spectrum and can be resolved into lines. The diatomic oxygen molecule emits bands which extend from  $\lambda$  200 to beyond  $\lambda$  185  $\mu\mu$ . These bands correspond exactly with the fluorescence bands of oxygen.

The so-called "ultra-violet water vapour bands" in the region  $\lambda$  340 to  $\lambda$  230  $\mu\mu$  have been shown by Steubing (A., 1910, ii, 913) to be due to oxygen, and evidence is now brought forward in support of the view that these are emitted by monatomic oxygen. These bands make their appearance in pure oxygen when the energy of the electrical discharge is sufficiently high. They appear in greater intensity if oxygen compounds are present, which on dissociation give rise to oxygen atoms and other molecules which are stable at low temperatures. Such compounds are water and carbon dioxide, which on dissociation yield atomic oxygen and the stable molecules  $H_2$  and CO respectively.  
H. M. D.

**Line Spectrum of Nitrogen in a Geissler Tube.** C. PORLEZZA (*Gazzetta*, 1913, 43, ii, 699—708).—This paper gives the results of measurements of the wave-lengths of the lines of this spectrum, many of which have hitherto been ascertained only approximately. A table is given showing also the wave-lengths determined by others, both in a Geissler tube and at atmospheric pressure.

R. V. S.

**Precise Study of the Second Group of Bands of Nitrogen in the Magnetic Field. Recognition of the Nature of the Displacements.** H. DESLANDRES and L. D'AZAMBUJA (*Compt. rend.*, 1914, 158, 153—159).—A study of the second group of bands in the spectrum of nitrogen produced in a field of 35,000 gauss, the observation being photographic. The results show that the law that the rays of an even arithmetic series are all displaced in the same sense or are all divided in the same manner with dissymmetries of the same type, the displacements, variations, and ratios of the brightness of the components being variable only from one ray to another, holds good for this group, and is probably general. They also verify Deslandres' previous views on displacements in band spectra. In this group the displacements occur with division and polarisation, and result in slightly modified ordinary Zeeman divisions. Further, these divisions show only a feeble difference between components which can correspond with mobile electric charges, positive or negative, and of a mass greater than that of the electron. W. G.

**Wave-length Normals of the Third Order from the Arc Spectrum of Iron between  $\lambda 4282$  and  $\lambda 4903$ .** L. JANICKI (*Zeitsch. wiss. Photochem.*, 1914, 13, 173—185).—Accurate measurements of wave-lengths of lines in the arc spectrum of iron have been made with the aid of a large concave grating. A table is given in which the lines suitable for use as standards of the third order are grouped together. It has been found that more accurate measurements can be obtained by using the middle portion of a long arc than by observations on a relatively short arc. Lines which are comparatively indistinct in the short arc, become quite sharp when a long arc is utilised as the source of light. It is probable that the observed differences are due to differences in the density of the vapour. In the neighbourhood of the cathode, the temperature is much higher than in the more remote regions, and the density of the vapour is consequently much larger. With a short arc, the cathode influence extends more or less over the whole region occupied by the arc. H. M. D.

**Absorption Spectra of Some Salts of Uranium.** ARRIGO MAZZUCHELLI and UGO PERRET (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 445—451. Compare Mazzucchelli and Greco d'Alceo, A., 1913, ii, 167).—Further experiments show that although, as formerly stated, the addition of carbamide to dilute solutions of uranyl nitrate does not alter the absorption spectrum, yet in concentrated solutions (30% of carbamide to 40% solution of uranyl nitrate) a change is produced which is not due merely to the basic properties of carbamide, because ammonia, although more basic, produces less alteration.

When potassium hydroxide, ammonia, pyridine, or aniline is added to a solution ( $M/10$ ) of uranyl malate, the absorption spectrum is altered, but the new spectrum is almost the same in all four cases, so that potassium hydroxide and the amines appear

to act only in virtue of their basic properties, and not in the direction of forming specific complexes. The addition of free acid to a solution of uranyl malate does not render the absorption bands sharper, but, on the contrary, more diffuse.

The spectra of the following compounds, both before and after the addition of a base, are described: uranyl tartrate, citrate, lactate, and quinate.

The reaction between uranyl sulphate and potassium malate or tartrate can be followed spectroscopically to some extent, but the method does not lend itself to accurate determinations.

The spectra are described of a number of organic salts of quadrivalent uranium, including the malate, tartrate, quinate, citrate, lactate, glycollate, and oxalate, as well as potassium uranotetroxalate and potassium uranomalonate.

R. V. S.

**The Phototropy of Inorganic Systems.** JOSÉ RODRIGUEZ MOURELO (*Compt. rend.*, 1914, 158, 122—125).—Several samples of calcium sulphite examined were phototropic as well as phosphorescent, whilst others exhibited only one of the two phenomena. The effective rays are the violet rays for both phosphorescence and phototropism. There is a limit temperature above which both these properties disappear. In all cases where the calcium sulphide or other similar sulphides were phototropic, it was found that they contained traces of manganese, to the presence of which the author considers that this phenomenon is due.

W. G.

**Polymerisation of  $\beta$ -Methylantracene (Correction).** FRITZ WEIGERT and OTTO KRÜGER (*Zeitsch. physikal. Chem.*, 1914, 86, 383. Compare this vol., ii, 11).—It is shown that the specific photochemical action  $\phi_{th} = 1.22 \times 10^{-5}$  mols. per cal. is one-half the value given in the previous paper (*loc. cit.*).

J. F. S.

**Dependence of the Relative Ionisation in Various Gases by  $\beta$ -Rays on their Velocity and its Bearing on the Ionisation Produced by  $\gamma$ -Rays.** R. D. KLEEMAN (*Proc. Camb. Phil. Soc.* 1914, 17, 314—320. Compare A., 1910, ii, 474).—Further experiments on the relative ionisations produced in hydrogen, air, and methyl iodide by  $\beta$ -rays indicate that the relative ionisation is independent of the velocity of the  $\beta$ -ray. The  $\beta$ -rays from radium were admitted into an ionisation chamber through an aluminium window, 0.16 mm. in thickness. By means of a magnetic field, the beam of rays could be hardened to any desired extent by deflecting the more slowly moving rays. The application of the field was found to have practically no influence on the relative ionisation values for the three gases under examination.

According to previous experiments on the ionisation produced by  $\gamma$ -rays of varying hardness (A., 1909, ii, 636), it appears that the ionisation in methyl iodide relative to that in air increases greatly with the softness of the rays. Since this cannot be due to differences in the nature of the  $\beta$ -rays which are given off by the walls of the vessel, it is probable that the observed change in relative



ionisation is due to the secondary  $\gamma$ -rays given off by the walls. One part of the ionisation due to these rays varies as the square of the pressure of the gas, and the other part directly as the pressure. The latter ionisation effect increases with increase in the softness of the rays. H. M. D.

**Secondary  $\gamma$ -Radiation.** D. C. H. FLORENCE (*Phil. Mag.*, 1914, [vi], 27, 225—244).—The origin of the scattered  $\gamma$ -rays which emerge at all angles when a beam of primary  $\gamma$ -radiation is passed through matter is discussed, and the conclusion is arrived at that they are primary  $\gamma$ -rays which have lost energy and have become altered in type. They are not in any way characteristic of the material by which they are produced. Their penetrating power is less the greater the angle they make with the direction of the original primary beam, and they are completely heterogeneous. With heavy elements as radiators, there is a small amount of a soft radiation returned from the incidence side of the radiator which may possibly be a characteristic radiation. The quality and distribution of the scattered  $\gamma$ -radiation under a variety of conditions have been examined. F. S.

**Analysis of the  $\gamma$ -Rays from the Uranium Products.** H. RICHARDSON (*Phil. Mag.*, 1914, [vi], 27, 252—256).—The  $\gamma$ -radiation from uranium- $X$ , separated from 3 kilos. of uranyl nitrate, has been examined. The absorption curve in aluminium showed the presence of a radiation amounting to about 40% of the total, completely absorbed by 2 mm. of aluminium, for which  $\mu$  was 24 (cm.)<sup>-1</sup>. The determination for greater thicknesses was difficult owing to the smallness of the effects, but the results confirmed those of Soddy and Russell, with the uranium- $X$  from 50 kilos. of uranyl nitrate, in showing, in addition to the very penetrating  $\gamma$ -rays for which  $\mu$  is 0.140 (cm.)<sup>-1</sup>, an intermediate type for which  $\mu$  is 0.70 (cm.)<sup>-1</sup>. It is assumed as most probable that the most penetrating type of  $\gamma$ -rays arises from uranium- $X_2$ , and the two less penetrating types from uranium- $X_1$ . The softest radiation, for which  $\mu$  is 24, is probably a characteristic radiation of the  $L$ -series, and this absorption coefficient for an element of atomic weight 234, in relation to those of the other radiations of the same type given by the other radio-elements, supports the view that actinium is a branch product of uranium- $X$  and has an atomic weight 230. F. S.

**The Number of Ions Produced by the  $\gamma$ -Rays of Radium.** A. S. EVE (*Phil. Mag.*, 1914, [vi], 27, 394—396).—A recent redetermination of  $K$ , the constant of the equation  $q = KQ/r^2 e^{\mu r}$ , where  $q$  ions are produced per c.c. of air at  $N.T.P.$  by  $Q$  grams of radium at distance  $r$  cm., and  $\mu$  is the absorption coefficient of the  $\gamma$ -rays in air, gave the value  $4 \times 10^9$  in good agreement with earlier results. The total number of ions  $N$ , produced per gram of radium by the  $\gamma$ -rays, calculated from  $N = 4\pi KQ/\mu$ , is  $8.4 \times 10^{14}$ . This is considerably less than a value for  $N$ ,  $13 \times 10^{14}$ , obtained by Moseley and Robinson, but the discrepancy may be due to the latter value including the softer  $\gamma$ -rays of radium- $B$ , not included in the former

result. For the purpose of calculation of the atmospheric ionisation due to radium and its equilibrium products in the earth, the former value should be used. Whereas, for calculations of the heating effects of the  $\gamma$ -rays of radium, it is necessary to include also the effects of the softer rays, and the calculation becomes a difficult one.

F. S.

**Positive Ions from Hot Metals.** O. W. RICHARDSON (*Proc. Roy. Soc.*, 1914, A, 89, 507—524. Compare A., 1913, ii, 903, and previous papers).—The apparatus employed in previous experiments has been improved in a number of details, and a new series of observations has been carried out with platinum, iron, manganin, and potassium sulphate.

In the case of all three metallic substances the values obtained for the electric atomic weight are in general very close to 40, which is the value found for the ions emitted by potassium sulphate. The wide distribution of potassium and its highly-developed capacity for ionising, lead the author to the conclusion that the above value for the electric atomic weight is really due to the emission of potassium ions resulting from adventitious impurities in the heated metals. The experimental data are entirely opposed to the view that the positive ions consist of charged atoms or molecules of one or more of the common gases, such as carbon monoxide, carbon dioxide, hydrogen, oxygen, or nitrogen. Argon is the only common gas for which the electric atomic weight is in close agreement with the experimental value, but in view of the strong evidence in favour of potassium, it is difficult to suppose that any appreciable part of the emission effect is due to argon. It might also be supposed that the carriers are calcium atoms with a single positive charge, but the ionising tendency of calcium is too small to account for the observed facts.

From experiments with platinum in which the metal was heated for a long period of time, it would seem possible to exhaust the metal of the impurities which give rise to the potassium ion. After such prolonged thermal treatment, the electric atomic weight was found to fall from 40 to about 23 (sodium ion), afterwards rising quickly to about 60. This is supposed to correspond with the emission of singly-charged iron atoms.

H. M. D.

**Tables of Exponential Functions Relating to the Radium Emanation.** LÉON KOLOWRAT (*Le Radium*, 1913, 10, 389—392).—This consists of a reprint of the tables relating to the disappearance and accumulation of radium emanation with the value for the disintegration constant  $\lambda = 0.00751$  (hour)<sup>-1</sup>. The first table gives the fraction of radium emanation remaining at hourly intervals from 0 to 52 hours, at two-hour intervals from 54 to 72 hours, at three-hour intervals for the fourth and fifth day, and so on for thirty days. The second table gives the amount of emanation accumulating in a radium solution for the same intervals, in terms of the hourly rate of production as the unit, or of the equilibrium amount,  $1/\lambda$ , as 133.156.

F. S.

**Dependence of the Photoelectricity of Metals on the [Surrounding] Gas with Special Reference to the Cause of the Strong Photoelectricity of Potassium.** G. WIEDMANN and W. HALLWACHS (*Ber. Deut. physikal. Ges.*, 1914, 16, 107—120).—The question as to whether the photoelectric behaviour of metals is dependent on the presence of gas in the surface layer has been examined with reference to the observation that electrons are emitted during chemical reactions (compare Haber and Just, A., 1909, ii, 853). As a result of the recent work of Ullmann and of Paech (this vol., ii, 89), there can be little doubt that the photoelectric emission of metals is to a large extent dependent on the nature of the surrounding gaseous medium. On the assumption that the gas might prove to be essential for the development of the photoelectric effect, experiments have been made with potassium cells. By means of a special form of apparatus in which the potassium could be subjected to a succession of distillations during which the highest possible degree of exhaustion was maintained, it has been found that potassium is ultimately obtained in a condition in which it is photoelectrically inactive. This result indicates conclusively that the presence of gas in the surface layer of the metal is necessary for the development of its photoelectric properties.  
H. M. D.

**Influence of Temperature and of the Occlusion of Gases on the Photoelectric Behaviour of Metals, Metallic Oxides, and Metallic Sulphides.** ADOLF HALLERMANN (*Zeitsch. wiss. Photochem.*, 1914, 13, 186—207).—From experiments on the photoelectric properties of platinum, gold, palladium, and of the oxides of copper, calcium, barium, zinc, cerium, thorium, and uranium at various temperatures up to about 600°, it has been found that the photoelectric activity is in all cases independent of the temperature. Fatigue effects are not observed at higher temperatures, and this fact is considered to be in favour of the view that such effects are connected with the adsorption of gases by the electrodes.

The current potential curves, which are obtained by plotting the photoelectric current against the potential applied to the electrodes, are found to be of exactly the same form for the oxides as for the metals, and the nature of these curves is the same at high as at low temperatures. Rise of temperature reduces, however, the sparking potential.

From experiments made with cupric and silver sulphide, which exhibit transition points at 105° and 170° respectively, it has been found that the polymorphic change is without influence on the photoelectric activity of the sulphides.

When a metal has been employed as anode in the glow discharge, its photoelectric sensitiveness is found to be diminished, whilst the opposite effect is observed when the metal has been used as cathode. The influence of the electrical treatment diminishes with rise of temperature, and it is no longer observable at temperatures above 400°. The nature of the gas in the discharge tube does not appear to have any influence on the change in the photoelectric

behaviour of the metal. According to Skinner (A., 1905, ii, 797), gases are evolved when the metal functions as cathode, and absorbed when it acts as anode; this would seem to show that the occlusion of gases diminishes the photoelectric activity.

H. M. D.

**Dielectric Constant of Hydrogen at High Pressures.** A. OCCHIALINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 482—484. Compare following abstract).—Measurements of the dielectric constant of hydrogen at pressures between 94 and 196 atmospheres lead to the formula  $(K-1)/(K+2)d=90154(10^{-9})$ . Extrapolation gives the value 1.0002705 for the dielectric constant of hydrogen at ordinary pressure.

R. V. S.

**Dielectric Constant of Nitrogen at High Pressures.** E. BODAREU (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 480—482).—Determinations of the density ( $d$ ) and dielectric constant ( $K$ ) of nitrogen at pressures ranging from 87 to 226 atmospheres lead to the formula  $(K-1) \cdot 10^7/(K+2)d=1954$ . By extrapolation the value 1.000587 is obtained for the dielectric constant of nitrogen at the ordinary pressure.

R. V. S.

**Experiments with Liquid Helium. The Electrical Resistance, etc.** VIII. **The Sudden Disappearance of the Ordinary Resistance of Tin and the Super-conductive State of Lead.** H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 673—688. Compare A., 1913, ii, 748, 822).—The electrical resistance of tin and lead wires has been investigated at helium temperatures. In the case of tin, the resistance practically disappears when the temperature is lowered to  $3.8^\circ K$ , the ratio of the resistance at this temperature to that at  $273^\circ K$  being less than  $10^{-7}$ . In addition to the sudden disappearance of the resistance, it has been found, as in the case of mercury (*loc. cit.*), that for each temperature below the vanishing point, there is a "threshold value" of the current density below which the current passes without any perceptible fall of potential. For current densities higher than this, the passage of the current is accompanied by potential phenomena which increase rapidly as the excess of the current above the "threshold value" increases.

Pure lead also passes into the super-conducting state at helium temperatures. The temperature at which the resistance disappears has not yet been determined, but from observations made at helium and hydrogen temperatures, it lies between  $4.3^\circ K$  and  $14^\circ K$ .

Further observations have reference to the potential phenomena in the super-conducting condition, and from these conclusions are drawn relative to the maximum value of the residual resistance in the super-conducting state. For tin the ratio of the resistance at  $1.8^\circ K$  to that at  $273^\circ K$  is less than  $6 \times 10^{-10}$ , whilst the corresponding ratio for lead is less than  $0.5 \times 10^{-10}$ . For mercury at  $2.45^\circ K$ , this ratio was found to be less than  $2 \times 10^{-10}$ .

H. M. D.

**Couples with Flames Charged with Chlorine.** G. MOREAU (*Compt. rend.*, 1914, **158**, 260—262).—The *E.M.F.* of the couple Pt|flame|flame|Pt coated with an alkaline earth oxide (compare this vol., ii 22), and of the similar couple where one flame is charged with the vapour of some salt (compare this vol., ii, 22), is increased by 0.55 volt on the introduction of chlorine or bromine into the flame in contact with the pure platinum. The same results are obtained by the introduction of chloroform or carbon tetrachloride. This is explained by the fact that the radiation from the platinum electrode is annulled by the active substance, and the *E.M.F.* is increased by an amount equal to the *E.M.F.* of a couple

Pt cold|pure flame|Pt hot.

The results give a value of  $4.4 \times 10^7$  cm./sec. for the mean velocity of emission of corpuscles from the platinum (compare *loc. cit.*).

W. G.

**Study of the Hydrogen Electrode, of the Calomel Electrode, and of Contact Potential.** C. N. MYERS and S. F. ACREE (*Amer. Chem. J.*, 1913, **50**, 396—411).—In earlier papers (Loomis and Acree, A., 1912, ii, 124, 125; Desha and Acree, A., 1912, ii, 125), an account has been given of a study of the hydrogen electrode and its application to the determination of hydrogen ion concentrations in organic reactions.

In continuation of this investigation, efforts have been made to render the hydrogen electrode more accurate for the purpose, and to make the calomel cell more nearly standard. The present paper gives a preliminary account of the work.

A record is given of a 0.1N KCl—HgCl—Hg battery, showing the changes taking place from the time that the battery was first prepared. The cells required thirty-six to forty-eight hours to settle down, and then their relation remained approximately constant for over a year. The total change in a battery amounted to 0.000085 volt in a year, but the individual cells did not vary to so great an extent. A comparison of two freshly-prepared calomel batteries shows that they were in good agreement after a year. The relation between a freshly-prepared battery and one of a year's standing is also given; in the first three months, the difference of potential between them was about 0.000045 volt. Hydrogen electrodes, after standing dry throughout the summer, showed considerable disagreement, and some difficulty was experienced before they gave satisfactory agreement. A typical comparison is given of the hydrogen electrode, 0.1N HCl—Pt—H<sub>2</sub>, and a fresh calomel electrode, and the methods of applying the correction are shown. The corrected average value agrees closely with those obtained with two fresh calomel batteries. The results are recorded of experiments in which Bjerrum's "sandfüllung" was used between the calomel and hydrogen electrodes, and also of a typical contact potential experiment with one Hg—HgCl—0.1N HCl battery against a fresh calomel battery.

The results of the work show a constancy in the values of the

various systems mentioned, which is explained by their having been completely saturated with hydrogen before being joined.

E. G.

**Application of the Theory of Allotropy to Electromotive Equilibria.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 699—710).—The author's theory of allotropy (A., 1910, ii, 195, 400) is applied to the electrolytic dissolution and deposition of metals which consist of mixtures of allotropic modifications.

The theory indicates that electrolytic deposition will in many cases give the metastable form. If the reversible changes take place with very small velocity, it is shown further that the surface of the metal will become more noble during the process of electrolytic dissolution. The periodic oscillations in the potential difference at the surface of contact between a metal and solution can be accounted for from the same point of view. The fact that the contact of a metal with the solution of one of its salts exerts an accelerating influence on the setting up of the equilibrium between the allotropic forms is also consistent with the theory.

The remarkable chemical reactivity of metals obtained by reduction at low temperatures is supposed to be due to the wide divergence between the actual condition and the equilibrium condition. Pyrophoric forms may possibly be explained in this way, the metals in this condition containing an abnormally large proportion of simple molecules.

H. M. D.

**Nickel-plating on Aluminium.** J. CANAC and E. TASSILLY (*Compt. rend.*, 1914, **158**, 119—121).—Aluminium is readily plated with a durable coating of nickel by the following procedure. The metal to be plated is first plunged in a bath of boiling potassium hydroxide solution, and then scrubbed with milk of lime. This is followed by steeping in a 0.2% solution of potassium cyanide for several minutes, after which it is transferred to a bath made up of 500 grams of hydrochloric acid and 1 gram of iron in 500 c.c. of water. Between each bath it is well washed with water, and after the last washing it is plated electrolytically in a solution of nickel chloride. The deposit so obtained is very adhesive and durable, as the metal can be folded or hammered without it cracking. The metal can be heated to the melting point of aluminium without the nickel separating, and is not attacked by dilute alkali, glacial acetic acid, or concentrated sodium chloride solution, cold or hot. From the point of view of the conduction of electrical energy, the coefficient of dilatation of the metal is lowered by plating. The Kelvin effect is nil. The success of the plating apparently depends on the use of the ferruginous bath.

W. G.

**Measurements in the Electromagnetic Spectrum of Water with Feebly Damped Vibrations of 65 to 20 cm. Wavelength.** A. R. COLLEY (*Ann. Physik*, 1914, [iv], **43**, 309—318).—A reply to Rukop's criticism (compare A., 1913, ii, 1018) of the author's measurements. Further observations relating to the nature of the electromagnetic spectrum confirm the results obtained in the previous experiments.

H. M. D.

**Uses of the Concentrated Filament Tungsten Lamp in the Laboratory.** F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1914, **36**, 454—455).—A stereopticon type of tungsten lamp, rated at 100 watts for 110 volts, and giving about 60 c.p., is recommended for use in microscopic work and for the polarimetry of highly coloured or turbid liquids. No bright-line images of portions of the filament are formed in the field of the instrument, and the intensity is very much greater than that obtainable with the frosted-bulb lamp.

T. S. P.

**Temperature of Non-homogeneous Flames.** HEDWIG KOHN (*Physikal. Zeitsch.*, 1914, **15**, 98—105).—If a Nernst filament is placed in close proximity to a flame containing the vapour of a metallic salt, so that the rays emitted by the filament pass through the heated salt vapour on their way to the slit of a spectrometer, it is found that the lines emitted by the vapour appear bright or dark according to the intensity of the continuous spectrum which is emitted by the filament. The temperature at which transition occurs from one condition to the other has been termed the inversion temperature, and measurements of this temperature have been made by Kurlbaum and Schulze (*A.*, 1906, ii, 726) for a number of metallic salts. Similar experiments have been carried out by the author, who finds that the inversion temperature for a Bunsen flame containing the chlorides of lithium, sodium, potassium, thallium, and rubidium depends on the nature of the salt introduced into the flame. In the case of the lithium line  $\lambda = 670 \mu\mu$ , it was found that the inversion temperature increases when sodium, potassium, or rubidium chloride is simultaneously introduced with the lithium chloride into the flame. These results are in general agreement with the observations made by Kurlbaum and Schulze.

The theoretical discussion of the observed changes in the inversion temperature indicates that these can be satisfactorily explained on the assumption of pure temperature radiation if the inhomogeneity of the flame is taken into consideration.

H. M. D.

**The Critical Condition.** PAUL HEIN (*Zeitsch. physikal. Chem.*, 1914, **86**, 385—426).—The phenomena occurring at the critical temperature have been examined in the case of carbon tetrachloride, sulphur dioxide, and carbon dioxide. In the case of the two last-named substances, experiments have been carried out in which air has not been entirely removed, and in which the gas was not contaminated by more than 1 part of air in 40,000 of the gas. The substances under examination were placed in narrow, cylindrical tubes, together with a number of "density pellets," and sealed up. The temperature was then slowly changed from a few degrees below the critical temperature to a few degrees above, and observations made on the density and the formation of fog in the tube. It is shown that the presence of impurities in the substances examined affect the phenomena occurring near the critical temperature in a marked degree. Density differences are observable with pure substances above the critical temperature, but these vanished

in the case of carbon dioxide at a temperature  $0.46^{\circ}$  above the temperature at which the meniscus disappeared, and they were only of the smallest character. On the other hand, with carbon dioxide containing air, density differences amounting to 13% were observable at a temperature  $3.2^{\circ}$  above the temperature at which the meniscus disappeared. The author is of the opinion that his results are in accord with the two-phase theory at the critical temperature rather than with the one-phase theory. J. F. S.

**Determination of the Transformation Points of Sodium and Potassium Sulphates, Molybdates and Tungstates.** H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1914, 85, 49—64).—In place of cooling curves, heating curves have been adopted. The transformation point may be overstepped in this way, but by cooling until reconversion is complete, and again heating, the true point may be found, and recognised by the fact that it is independent of the rate of heating. The temperature is reproducible within  $\pm 1^{\circ}$ . The following transformation and melting points have been determined with this degree of accuracy:

	Trans- formation I.	Trans- formation II.	Trans- formation III.	M. p.
$\text{Na}_2\text{SO}_4$ .....	$241^{\circ}$	—	—	$884^{\circ}$
$\text{Na}_2\text{MoO}_4$ .....	445	$592^{\circ}$	$640^{\circ}$	687
$\text{Na}_2\text{WO}_4$ .....	587	—	—	694
$\text{K}_2\text{SO}_4$ .....	—	582	—	1067
$\text{K}_2\text{MoO}_4$ .....	327	454	479	919
$\text{K}_2\text{WO}_4$ .....	388	—	—	921

C. H. D.

**Matter in the Superfused State.** R. NASINI and U. BRESCIANI (*Mem. R. Accad. Lincei*, 1913, [v], 9, 735—750).—The authors have repeated and extended their investigations on sulphur (compare A., 1913, ii, 555), solidifying at  $114^{\circ}$ , and have confirmed the conclusions previously deduced.

Study of the superfusion phenomena of triphenylmethane, m. p.  $90.4^{\circ}$ , solidifying point  $87.8^{\circ}$ , and of trimethylcarbinol, solidifying point  $23.4^{\circ}$ , reveals no appreciable abnormality in either the ordinary or the differential cooling curves, so that these substances do not exhibit the "Moreschini effect."

Experiments on sodium thiosulphate indicate unexplained discordance between Bruner's data for the specific heat (A., 1895, ii, 482) and those afforded by the cooling curves.

Superfused thymol contains no nucleus capable of inducing crystallisation. Ultramicroscopic observations on acetic acid and anethole reveal no change occurring when the superfused liquids pass through the melting point. Even in the superfused state these liquids must therefore be regarded as optically empty, and if crystalline nuclei are formed, these must be of less than ultramicroscopic magnitude. T. H. P.

**The Temperature of Solid Carbon Dioxide Cooling Baths.** A. THIEL and E. CASPAR (*Zeitsch. physikal. Chem.*, 1914, 86, 257—293).—The temperatures of mixtures of carbon dioxide snow with ether,



alcohol, and acetone have been determined by means of a vapour-pressure thermometer. The method of measurement consisted in immersing a bulb containing pure carbon dioxide snow in the freezing mixture and measuring the vapour pressure of carbon dioxide in the bulb by means of a manometer, and from the known temperature-coefficient of the vapour pressure (57.0 mm. Hg per degree) calculating the amount by which the temperatures of the various baths differed from that of pure solid carbon dioxide. Theoretically, the temperatures ought in all cases to be the same as that of carbon dioxide snow itself, but experimentally they were found all to be a little higher; in the case of the ether mixture the temperature was about 0.09° higher. It is shown that the lower temperatures found for acetone mixtures are to be explained by the heat of solution of carbon dioxide, and that they do not represent the true equilibrium temperature. The vapour pressure of the ether in the ether mixture is so small that it cannot influence the temperature to a measurable amount. The reason for the slightly higher temperature is found in the fact that, in addition to the atmospheric pressure, the hydrostatic pressure of the liquid column has to be overcome. Calculations made show that the pressure of this column of liquid corresponds exactly with the experimentally found temperature differences. The phase-rule diagram ( $\theta c$ ) is worked out and described for the binary system carbon dioxide-ether, and the three-phase points characterised. J. F. S.

**Freezing Points of Organic Substances.** JEAN TIMMERMANS (*Bull. Soc. Chim. Belg.*, 1913, **27**, 334—342. Compare A., 1911, ii, 854).—The reduced melting point is defined as the ratio of the melting-point temperature to the critical temperature, both being expressed on the absolute scale. These reduced melting points have been compared for a large number of substances, but the results afford no evidence of the existence of general relations connecting the reduced temperature with the composition and constitution. The values range from 0.20 for helium and 0.235 for propane to 0.714 for carbon dioxide and 0.929 for phosphonium chloride.

H. M. D.

**Properties of Iodine as a Cryoscopic Solvent.** I. F. OLIVARI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 697—702).—The marked solvent power of iodine towards many organic solvents and various salts has been noted in the author's previous investigations (A., 1909, ii, 37, 39, 128, 226).

Determinations of the velocity of crystallisation of iodine give results which are of considerable magnitude near the melting point, and increase rapidly with the degree of superfusion. The crystallisation of iodine hence responds to the requirements of good thermometric readings, and this is confirmed by direct cryoscopic measurements. Dilute solutions of stannic, antimony, arsenic, and mercuric iodides give the mean value 213 for the molecular depression of the freezing point. Beckmann (A., 1909, ii, 642) gave 204 and Timmermans (A., 1906, ii, 429) 253.5.

The uncertainty of the value, 11.7 Cal., obtained by Favre and Silbermann for the latent heat of fusion of iodine, renders it impossible to calculate the cryoscopic constant by means of van't Hoff's formula. From Dewar's indirect data (P., 1899, 15, 241) Beckmann calculated the value 14.87 Cal., which gives 201.4 for the cryoscopic constant.

Cryoscopic investigation of solutions of iodoform, *p*-dibromobenzene, azobenzene, naphthalene, diphenyl, *p*-dinitrobenzene, benzoic anhydride, phenanthraquinone, and  $\beta$ -iodopropionic and benzoic acids, in fused iodine, confirm the earlier indications, that: (1) the molecular weights are normal in very dilute solution, but increase more or less rapidly with the concentration, even with compounds which exhibit no appreciable tendency to polymerise, and (2) this increase becomes more marked in passing from hydrocarbons to hydroxyl derivatives.

For solvents of high specific gravity, such as iodine, the weight-concentrations commonly adopted in osmotic calculations are much smaller than the volume-concentrations, which, according to van't Hoff's theory, should be used. Assuming, as a rough approximation, that solutions in iodine have *D* about 4, weight-concentrations of 1, 2, 3, etc., would correspond with volume-concentrations of 4, 8, 12, etc. For hydrocarbons and halogenated derivatives, the abnormalities disappear if volume-concentrations are used in the calculations, but for  $\beta$ -iodopropionic and benzoic acids they persist in diminished degree; intermediate behaviour is shown by benzoic anhydride and phenanthraquinone, which therefore exhibit a slight tendency to polymerise.

T. H. P.

**Cyanamide as a Cryoscopic Solvent.** U. PRATOLONGO (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 716—720).—The latent heat of fusion of cyanamide, m. p. 42.9°, is 49.8 ± 0.7 cals., and the value of the cryoscopic constant, calculated by means of van't Hoff's relation, 39.8. Direct determination of the cryoscopic constant with the following solutes gives the numbers: water, 28.4—26.1; ethyl alcohol, 28.1—26.6; formamide, 30.7—30.2; carbamide, 29.7—29.1; dicyanamide, 32.1—32.8. Thus, as in the case with solvents of analogous constitution, the calculated and experimental values of the cryoscopic constant for cyanamide differ appreciably. Further, this solvent shows marked associating properties, which are most clearly manifested with hydroxylic solutes.

T. H. P.

**Description of the "Cryoscope," and Several Freezing-point Determinations of a Single Sample of Fresh Milk with Varying Degrees of Supercooling.** M. C. DEKHUYZEN (*Chem. Weekblad*, 1914, 11, 126—131).—A modified form of Beckmann apparatus, designed to facilitate accurate measurement and rapid working. The cooling bath is large, and consists of two concentric glass cylinders, the inner one 17 × 27 cm., and the outer 23 × 30.5 cm. The copper cover is replaced by a thick plate of ebonite. The freezing tube is round at the closed end, and is surrounded by a two-walled Dewar vacuum tube. The part project-

ing above the ebonite cover is protected by a wooden air chamber to prevent change of temperature. Rapid cooling is promoted by immersing in the cooler a wide test-tube containing mercury cooled to a suitable temperature. The results of a series of experiments on a sample of milk are given.

A. J. W.

**New Formula for Determining the Latent Heat of Evaporation of Different Compounds.** (Mlle.) ALEXANDRA RODZEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, **39**, *Phys. Part*, 355—361).—All the ordinary empirical formulæ for calculating the latent heat of evaporation are inapplicable for high temperatures, and especially for temperatures approaching the critical point. This is also the case with the thermodynamical formula,  $\rho = AT(\sigma - s).dp/dT$ , where  $\rho$  is the latent heat of evaporation,  $A = 1/425$ ,  $\sigma$  is the specific volume of the saturated vapour,  $s$  the specific volume of the liquid, and  $p$  the vapour pressure at the absolute temperature  $T$ ; little is known of the values of  $\sigma$  and  $s$  at high temperatures.

The author shows that the above formula may be converted into the form  $\rho = NT^2(\pi - p)/m\pi p.dp/dT$ ,  $N$  representing a coefficient,  $\pi$  the critical pressure, and  $m$  the molecular weight. The coefficient  $N$  is derived as follows. The value of  $(\sigma - s)$  depends on  $p$  and  $T$ , the simplest assumption being that  $\sigma - s = kT(\pi - p)/p$ , from which follows  $k = (\sigma - s)p/T(\pi - p)$ ; with water and carbon disulphide,  $k$  is found to be independent of the temperature. It is further shown that, for a number of compounds of different chemical characters, the value of the product  $k.A.m.\pi$  is practically constant and equal to  $1.95 \times 10^3$  ( $1.90 - 2.03 \times 10^3$ ), and this product represents the coefficient  $N$  of the author's equation. The latter gives values for the latent heat of evaporation of water at various temperatures from  $0^\circ$  to  $200^\circ$  in good agreement with the experimental numbers obtained by different investigators.

T. H. P.

**Ebullioscopic Constants.** ERNST BECKMANN and OTTO LIESCHE (*Zeitsch. physikal. Chem.*, 1914, **86**, 337—348).—A simple deduction of the following five formulæ for calculation of the ebullioscopic constant is given: (1)  $k = M/100.p.(dt/dp)$ ; (2)  $k = mG\Delta/100g$ ; (3)  $k = RT^2/w$ ; (4)  $k = 0.0096MT$ ; and (5)  $k = 0.0011089T^2/a^2$ , in which  $k$  represents the constant,  $m$  the molecular weight of the dissolved substance,  $M$  that of the solvent,  $g$  the weight of the dissolved substance and  $G$  that of the solvent,  $p$  the vapour pressure of the solvent,  $dp$  the lowering of the vapour pressure,  $dt$  the boiling-point elevation due to  $dp$ ,  $\Delta$  the elevation of the boiling point when 1 gram molecule of a substance is dissolved in 100 grams of solvent,  $w$  the heat of vaporisation per gram of the solvent, and  $a^2$  the specific cohesion of the solvent at the boiling point. The second expression is also worked out for the case where the dissolved substance is volatile, and then has the form  $m = 100kg/\Delta G(1 - \alpha)$ , where  $\alpha$  is the ratio of the concentrations of the solvent and dissolved substance in the vapour and liquid phases (that is,  $n'N/nN'$ ). The trustworthiness of the five formulæ is discussed, and the uncertainty in the case of (4) and (5) has led to the deduction of the

formula (6),  $k = 0.004343MT(1-T/6)/\log \pi/p$ . This is based on work of Cederbergs (A., 1911, ii, 854), and is not limited like (4) and (5), which are based, respectively, on Trouton's rule and Walden's formula. This last formula is tested by means of data taken from the literature, and found to be trustworthy. J. F. S.

**The Experimental Handling of Small Quantities of Volatile Substances.** ALFRED STOCK (*Ber.*, 1914, 47, 154—156).—The author describes the advantages of the apparatus he has used extensively in his investigations of the boron hydrides and carbon sulphidotelluride and sulphidoselenide. The apparatus is so designed that fractional distillations can be carried out at low temperatures, during which it is completely closed, so that no substance is lost; a high vacuum is maintained in the apparatus during the operations.

The fractionation is carried out by using different freezing mixtures, by which temperatures varying from  $-20^{\circ}$  to  $-190^{\circ}$  are obtained, for cooling the various tubes in which condensation is to take place. The purity of each fraction is ascertained by determining its vapour tension at some particular temperature, a manometer forming part of the apparatus for this reason. T. S. P.

**Heats of Combustion of Octanes. Errata.** T. W. RICHARDS and R. H. JESSE (*J. Amer. Chem. Soc.*, 1914, 36, 248).—A list of corrections to the authors' previous paper (A., 1910, ii, 269).  
T. S. P.

**Higher Valencies in Oxygenated Organic Compounds.**  
**III. Basic Properties of Oxygen in Alcohols of the Aromatic Series.** V. V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1904—1911).—The author has measured the heat effects accompanying the formation of complexes of the three types,  $\text{Pr}\cdot\text{OMgI}\cdot\text{R}\cdot\text{OH}$ ,  $\text{Pr}\cdot\text{OMgI}\cdot 2\text{R}\cdot\text{OH}$ , and  $\text{Pr}\cdot\text{OMgI}\cdot 3\text{R}\cdot\text{OH}$ , for phenylcarbinol, diphenylcarbinol, triphenylcarbinol, phenylmethylcarbinol,  $\gamma$ -phenylpropyl alcohol, and cinnamyl alcohol (compare A., 1913, ii, 924, 925).

The results show that the aromatic nucleus has a very marked influence on the manifestation of higher valency by hydroxylic oxygen. Thus, the amounts of heat developed in the formation of the complex,  $\text{Pr}\cdot\text{OMgI}\cdot 3\text{R}\cdot\text{OH}$ , are 23.42 Cal., 17.94 Cal., and 0 for phenyl-, diphenyl-, and triphenyl-carbinol respectively; for methyl-, dimethyl-, and trimethyl-carbinol, the corresponding numbers are 29.63, 22.50, and 13.58.

The effect of replacement of methyl groups by phenyl is shown by the values 22.50, 18.68, and 17.94 Cal. for dimethyl-, phenylmethyl-, and diphenyl-carbinol respectively.

The influence of the distance of the phenyl group from the hydroxylic oxygen on the higher atomicity of the latter is illustrated by the values 14.18, 23.42, and 27.07 Cal. for phenol, phenylcarbinol, and  $\gamma$ -phenylpropyl alcohol respectively.

That unsaturation of the carbon chain is almost without influence

is seen from the practical identity of the values obtained for  $\gamma$ -phenylpropyl (27.07 Cal.) and cinnamyl alcohols (27.87 Cal.).

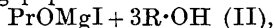
T. H. P.

**Higher Valencies in Oxygenated Organic Compounds.**  
**IV. Basic Properties of Oxygen in Alcohols of the Terpene Series.** V. V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1912—1917).—Measurements similar to those already described (see preceding abstract, and A., 1913, ii, 924, 925) have been made with menthol, terpineol, *d*-borneol, and *isoborneol*. Each of these alcohols forms complexes of the types  $\text{PrOMgI}\cdot\text{R}\cdot\text{OH}$  and  $\text{PrOMgI}_2\text{R}\cdot\text{OH}$ , but in no case is a tri-alcoholic complex formed, owing either to weakening of the higher valency in these alcohols or to steric influences.

The number of Calories developed by the addition of the first and second molecules of the alcohol to  $\text{PrOMgI}$  are: 7.44 and 2.30 for menthol; 5.76 and 2.14 for terpineol; 7.78 and 4.29 for *d*-borneol; 7.46 and 4.17 for *isoborneol*. The approximation of the values for menthol, borneol, and *isoborneol* is in correspondence with the characters of these alcohols, which are all secondary, and all possess substituents in the 2- and 5-positions to the hydroxyl. The lower values for terpineol are in accord with its tertiary structure, which in the aliphatic series is generally accompanied by a lower heat effect, and with the presence of the hydroxyl in the side-chain.

T. H. P.

**Higher Valencies in Oxygenated Organic Compounds.**  
**V. Relation between Principal and Supplementary Valencies in Alcohols.** V. V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1917—1925).—The author has measured, for a considerable number of aliphatic alcohols, phenols, aromatic alcohols, and alcohols of the terpene series, the heat effect of the reaction,  $\text{R}\cdot\text{OH} + \text{MgPrI} = \text{ROMgI} + \text{C}_3\text{H}_8$  (I), in benzene solution. The numbers thus obtained, which correspond with the functioning of the principal valencies of the oxygen, are then compared with those given in the preceding papers for the reaction,



in which the supplementary valencies of the oxygen function.

In general, it is found that if a change from one alcohol to another is accompanied by increase of the heat effect of reaction (I), the heat effect of reaction (II) exhibits a decrease.

T. H. P.

**Acoustic Method for the Measurement of the Density of Gases and Liquids.** A. KALÁHNE (*Ber. Deut. physikal. Ges.*, 1914, 16, 81—92).—The frequency of an acoustic vibrator varies to some extent with the density of the surrounding medium, and this variation is made the basis of a method of determining the density of gases or liquids. In order to obtain effects sufficiently large for this purpose, it is essential that the mass of the vibrating system should be small and the surface relatively large.

The apparatus designed and employed by the author for density

measurements consists of a seamless aluminium tube, which is clamped at the nodal points, and is made to vibrate transversely by striking it with a small hammer. The change in frequency when the tube is made to vibrate in air, and afterwards in the gas under investigation, can be ascertained by counting the beats which are produced when a suitable tuning-fork is made to vibrate simultaneously. This change is found to be proportional to the difference in the densities, but is otherwise unaffected by the nature of the gas.

The acoustic pycnometer is recommended for the measurement of the densities of compressed gases, and modified types of the instrument are described which have been designed for technical purposes.

H. M. D.

**Density of Some Metals in the Liquid State.** PAUL PASCAL and A. JOUNIAUX (*Compt. rend.*, 1914, 158, 414—416).—The authors have determined the density in the liquid state of some six metals, at their melting points and at various temperatures up to 1300°, by weighing a flask of quartz suspended in the molten metal. Formulæ are given for each metal, by means of which it is possible to calculate their specific volumes at any temperature inside a given range. In the case of tin, the curve of specific volumes possesses a point of inflexion at 620°, corresponding with a very rapid increase of dilatation at high temperatures, and suggests a possibility of dynamic allotropy.

W. G.

**Theory of Molecular Volumes.** GERVAISE LE BAS (*Phil. Mag.*, 1914, [vi], 27, 344—356).—An examination of the relations between the molecular volumes of substances at their boiling points has shown the necessity of changing many of the values previously assigned to the elements as representing their atomic volumes. The values deduced by the author are as follows: carbon, 14·8; hydrogen, 3·7; oxygen-hydroxyl, ester and phenolic 7·4, ethereal 11·0, in combination with sulphur, nitrogen, or phosphorus, 8·3; sulphur, bivalent, 22·1 and 25·6, quadrivalent and sexavalent, 25·6; phosphorus, trivalent and quinquivalent, 27·1; nitrogen, trivalent and quinquivalent, 15·6, in primary amines, 8·6, in secondary and tertiary amines, 10·0—11·5. It is said that double and triple linkings have very little influence on the volume of carbon compounds at their boiling points, but that benzene ring formation is accompanied by a contraction represented by -14·3.

When a comparison is made between the volumes of phosphorus trichloride and pentachloride, and of phosphorus tribromide and pentabromide, it is found that the combination of the two halogen atoms is accompanied by a contraction of about 8 units, and it is suggested that this may be due to ring formation.

The existence of periodic relations between the atomic volumes of the elements is discussed in reference to the available data. If the volumes are plotted against the atomic weights, four curves are obtained which pass through the points corresponding with elements

of the same fundamental valency. The univalent elements fall on the lowest, and the quadrivalent elements on the highest, curve.

H. M. D.

**Contraction on Mixing Abnormal Liquids.** E. V. BIRON and (Mlle.) O. M. MORGULEVA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1985—2002).—The object of the work described in this and the following papers was to explain the form of the curves showing the contraction occurring on mixing, on the one hand, associating liquids, and, on the other, liquids which enter into chemical combination one with the other.

The liquids here considered are aniline and nitrobenzene; the latter is usually regarded as non-associating, but the magnitude of its dielectric constant and other properties tend to indicate that it is not quite normal. Besides mixtures of aniline and nitrobenzene, mixtures of each with a typical normal liquid, benzene, were investigated. The following symbols are used:  $x$  is the molecular content of the component named first,  $S$  the specific gravity of the mixture,  $V$  its actual molecular volume, and  $\Sigma V$  that calculated from the law of mixtures,  $D$  the contraction accompanying mixing  $= \Sigma V - V$ , and  $M_1$ ,  $M_2$  the molecular weights of the liquids.

For aniline and nitrobenzene a few mixtures were examined by Dutoit (Thesis, "Effets theramiques produits par les mélanges des liquides organiques," 1897), but his results are insufficient to show whether the variable character found for the coefficient  $K$  of the relation holding for normal liquids, namely,  $D = Kx(1-x)$  (I), is accidental or characteristic of these liquids. More complete measurements by the authors show that for 30—70 mol. % of aniline the contraction is expressed approximately by the above formula; the other mixtures show abnormal contraction. This behaviour the author regards as due to dissociation of the associated aniline (or nitrobenzene) molecules by dilution with the other constituent of the mixture; association being slight in amount, the aniline (or nitrobenzene) soon reaches concentrations such that its condition is that of a normal liquid, that is, composed of simple molecules. A similar explanation has been advanced by Schroeder to account for the variation of the specific heat of alcohol dissolved in normal liquids. If such explanation is correct, a solution of aniline or nitrobenzene in a normal liquid should give contraction curves which obey the law for normal liquids in the region where the molecules of the abnormal liquid are completely dissociated, and which depart from the simple law when the aniline or nitrobenzene is in considerable excess.

With aniline and benzene, the simple law is obeyed by solutions containing about 30—65 mol. % of aniline, the maximum contraction corresponding with 50 mol. %.

With benzene and nitrobenzene, the maximum contraction is shown by the solution containing about 65 mol. % of benzene, so that formula (I) cannot hold. Solutions containing excess of benzene obey the law,  $D = K^1x^2(1-x)$  (II), but for those containing excess of nitrobenzene the curve assumes a complex course.

Mixtures of aniline and *o*-toluidine obey the law for normal liquids.

Doroshevski's data (A., 1911, ii, 468) have been employed for calculating the contractions for various binary mixtures of monohydric alcohols. With methyl and ethyl alcohols, all mixtures exhibit expansions, but these are so small as to lie almost within the limits of error; the same is the case with ethyl and propyl alcohols. With methyl and propyl, and with ethyl and *isobutyl* alcohols, appreciable expansions occur, and these obey the law for normal liquids. With methyl and *isobutyl* alcohols, however, the curve follows a course completely analogous to the benzene-nitrobenzene curve.

It will be seen from these results that mixtures of typical associating liquids, such as alcohols, may represent solutions of different degrees of complexity, some forming isofluidic mixtures, others obeying, and others again not obeying, the law of contraction for mixtures of normal liquids. The one or the other degree of complexity is conditioned by the positions of the components in the homologous series.

T. H. P.

**Contraction on Mixing Liquids which Unite to Form Chemical Compounds.** E. V. BIRON, N. I. NIKITIN and S. G. JAKOBSON (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 2002—2013. Compare preceding abstract).—At 35° aniline and phenol, which form the stable crystalline compound  $\text{NH}_2\text{Ph}\cdot\text{PhOH}$ , undergo considerable contraction on mixing, the maximum contraction corresponding with 50 mol. % of aniline, and the coefficient  $K$  of the expression  $D = Kx(1-x)$  (I) (see preceding abstract) gradually diminishing as the concentration of the aniline increases. This diminution in the value of  $K$  occurs also with mixtures of other liquids with aniline, and is evidently a secondary phenomenon, probably connected with change in the degree of association of the relatively strongly associated component. Indeed, for all the liquids used in the present investigation, the temperature-coefficient of the surface energy is less than the normal value, 2·12.

Aniline and *m*-cresol, and aniline and *p*-cresol, at 20° exhibit behaviour exactly analogous to that of aniline and phenol. With *o*-toluidine and phenol, at 35°,  $K$  is practically constant for the range 30—60 mol. % of the amine, but has lower values outside these limits.

Each of the above four pairs of liquids forms one compound,  $\text{R}\cdot\text{OH}\cdot\text{R}'\text{NH}_2$ , and each shows very marked contraction, varying from 0·35% to 0·7% of the volume for the 50 mol. % mixture. It may be assumed that the contraction depends on two factors, one determined by a physico-mechanical and the other by a chemical modification of the molecules. If such factors are characterised by the constants  $K_1$  and  $K_2$ , then  $D = K_1x(1-x) + K_2x(1-x) = (K_1 + K_2)x(1-x)$ , so that  $\bar{K} = K_1 + K_2$ , and the mixtures should obey the law for normal liquids.

Phenol and acetone form the compound  $\text{CH}_3\cdot\text{COMe}\cdot 2\text{PhOH}$ , containing 66·67 mol. % of phenol. From the law of mass action,



it follows that the contraction formula takes the form

$$D = K_1 x^2(1-x) + K_2 x(1-x).$$

If the contraction is conditioned almost exclusively by the chemical factor, this equation will become  $D = K_1 x^2(1-x)$ , and the maximal contraction will correspond with 66.67 mol. % of phenol. But if the physico-mechanical factor plays the chief part, the equation takes the form  $D = K_2 x(1-x)$ . If neither factor is negligible, the curve will exhibit an intermediate form, and in this case  $K$  will not be constant, but will vary linearly with  $x$ , that is,  $K = K_1 x + K_2$ . At 35°, the maximal contraction of 1.8% corresponds more nearly with 50 than with 66.67 mol. % of phenol, so that the physico-mechanical factor exerts a predominating influence. The values  $K_1 = -1.77$  and  $K_2 = +6.44$  give calculated values in close agreement with the observed contractions.

A series of measurements on mixtures of phenol and acetone was also made at 15.6°. It is not possible to supercool phenol to this temperature, so that the molecular volumes of phenol, and mixtures containing it in excess, could not be ascertained. The character and magnitude of the contraction may, however, be determined in the following manner:  $D = V_1 x + V_2(1-x) - V$ , where  $V$  is the volume of a gram-mol. of the solution, and  $V_1$  and  $V_2$  the molecular volumes of the components. If the contraction obeys equation (I), so that  $D = Kx(1-x)$ , substitution gives

$$V = V_1 x + V_2(1-x) - Kx(1-x),$$

or if  $[V - V_2(1-x)]/x$  be termed  $\Phi$ ,  $\Phi = V_1 - K(1-x)$ , which is a linear function of  $x$ , but if  $D = K_1 x^2(1-x)$ , then

$$\Phi = V_1 - K_1 x(1-x),$$

which represents a curve of the second order with respect to  $x$ , and gives a maximum or minimum for  $x=0.5$ . Calculation from the results obtained at 15.6° shows that the values of  $\Phi$  increase gradually with  $x$ , the method of least squares applied to the expression  $\Phi = V_1 - K(1-x)$  giving  $V_1 = 87.577$  and  $K = 5.44$ . The values of  $\Phi$  obtained with the help of these constants do not agree well with the experimental values, the greatest divergence corresponding with a 50 mol. % solution. The use of the more complex expression,  $\Phi = V_1 - K_1 x(1-x) - K_2(1-x)$ , gives slightly improved agreement, but the experimental data are evidently of insufficient accuracy for such complicated calculations. The results obtained show, however, that both at 35° and at 15.6° the contraction of mixtures of phenol and acetone is conditioned principally by the physico-mechanical factor.

T. H. P.

**Minimum Temperatures for Annealing.** HANRIOT and LAHURE (*Compt. rend.*, 1914, 158, 262—264).—The hardness of a metal after annealing varies with the temperature and duration of the annealing, and in the case of silver and zinc, the two metals studied, the annealing effect was found to be marked at comparatively low temperatures, providing sufficient time was allowed.

W. G.

**Ascending and Descending Hammer Hardening.** HANRIOT and LAHURE (*Compt. rend.*, 1914, 158, 404—406).—A comparison of

the physical properties of plates of the same metal having the same hardness, but prepared on the one hand by annealing the plates from maximum hardness, and on the other by hardening the metal from complete annealing. The results obtained for physical measurements differ considerably in the two series, those for the plates obtained by annealing varying the more regularly with varying hardness. These plates have greater breaking strains, elongate further, and harden more readily under the same effort than the corresponding plates obtained by hardening. The former also anneal more rapidly at the same temperature than the latter.

W. G.

**Viscosity of Undercooled Water as Measured in a New Viscometer.** GEORGE F. WHITE and RALPH H. TWINING (*Amer. Chem. J.*, 1913, 50, 380—389).—A method is described for determining the viscosity of liquids which obviates many of the known sources of error, and is applicable to the exceptionally viscous, undercooled liquids. The accuracy of the method has been tested by measurements of the viscosity of undercooled water, and the results obtained agree closely with those recorded by previous observers. For details of the method and a description of the apparatus, which is a modified form of that devised by Bingham and White (A., 1912, ii, 1144), the original should be consulted.

E. G.

**Viscosity of Liquids under High Pressures.** O. FAUST (*Zeitsch. physikal. Chem.*, 1914, 86, 479—495).—A method of measurement of viscosity at high pressures is described and employed for the measurement of the viscosity of ether at 0°, 20°, and 34°; ethyl alcohol at 0°, 20°, 40°, and 54°; and carbon disulphide at 0, 20°, and 40°. The determinations were carried out at pressures up to 3000 kilograms per sq. cm. It is shown that in the region of small volumes, in which, according to Tammann (A., 1912, ii, 538), the molecular attraction is constant, the viscosity is approximately a linear function of the volume. All three liquids exhibit a viscosity which increases with the pressure in a manner which is almost linear up to a pressure of 1500 kilograms per sq. cm. Above this pressure all three substances have viscosities which increase more rapidly with pressure, that of ethyl alcohol increasing the most and that of carbon disulphide the least.

J. F. S.

**Relationship between the Viscosity, Density, and Temperature of Salt Solutions.** W. J. WALKER (*Phil. Mag.*, 1914, [vi], 27, 288—297).—Measurements have been made of the viscosity and density of aqueous solutions of sodium and calcium chloride at temperatures between 0° and 100°. For sodium chloride solutions at 17°, the connexion between the viscosity ( $\mu$ ) and the density ( $\rho$ ) is given by the equation

$$\mu = 0.042265 + 0.04428(\rho - 1) + 0.03228(\rho - 1)^2.$$

If  $\log(\rho - 1)$  is plotted against  $\log(1 - \mu'/\mu)$ , where  $\mu'$  is the viscosity of pure water at the same temperature, it is found that

straight lines are obtained for both the sodium and calcium chloride solutions. The relation between viscosity and density may therefore be expressed by the equation  $(\rho - 1)^n = A(1 - \mu'/\mu)$ , where  $n$  and  $A$  depend on the nature of the dissolved salt and also on the temperature. In the case of sodium chloride,  $n$  is given by the equation  $n = 1.4 - 0.004T$ , and for calcium chloride by the equation  $n = 0.95 - 0.002T$ , where  $T$  is the temperature on the Centigrade scale. The corresponding variations of  $A$  with temperature are given by  $\log A = -0.6790 + 0.00374T$  for sodium chloride, and  $\log A = -0.3580 + 0.0005T$  for calcium chloride. H. M. D.

**The Sorption of Hydrogen by Wood Charcoal at the Temperature of Liquid Air.** JAMES B. FIRTH (*Zeitsch. physikal. Chem.*, 1914, **86**, 294—308).—The author has examined the sorption of hydrogen by cocoanut charcoal by means of pressure determinations effected at measured times after the introduction of the gas to the charcoal. The charcoal prepared from the shell of the cocoanut absorbs more hydrogen than that made from the nut itself when equal volumes of the two charcoals are compared, but if equal weights are compared, the amount of gas absorbed is similar in both cases. The sorption of hydrogen by charcoal is made up of two processes: (1) an adsorption, that is, a condensation of gas on the surface, which is complete in a very few minutes, and (2) an absorption, that is, the formation of a solid solution, which takes place slowly, and only reaches an equilibrium after several hours. One gram of charcoal dissolves 15 c.c. of hydrogen, after the gas has stood in contact with the charcoal for twelve hours at atmospheric pressure and at the temperature of liquid air. This volume, although constant for a given specimen of charcoal, varies when other specimens are employed. It is shown that all forms of wood charcoal contain both a crystalline and an amorphous variety of carbon, the former of which has little absorptive power; the absorptive power of a given specimen of charcoal depends mainly, therefore, on the percentage content of amorphous carbon.

J. F. S.

**Sorption of Hydrogen by Palladium.** FRANZ HALLA (*Zeitsch. physikal. Chem.*, 1914, **86**, 496—505. Compare Holt, Edgar, and Firth, A., 1913, ii, 330; Andrew and Holt, A., 1913, ii, 839).—The work of the above-mentioned authors is discussed. It is shown that the palladium characterised by Graham as inactive is not in reality inactive, but apparently so owing to a film of occluded oxygen on its surface. It is also shown that the occlusion of hydrogen by active palladium is not affected by the contact of inactive palladium with the active variety. The author's absorption curves are shown to be in agreement with those of the above-mentioned authors.

J. F. S.

**Theory of Dyeing.** WILDER D. BANCROFT (*J. Physical Chem.*, 1914, **18**, 1—25).—The nature of the process involved in the dyeing of wool, silk, and cotton fibres is discussed in reference to the

experimental data recorded in the literature. The author arrives at the conclusion that dyeing is generally due to adsorption, although definite compounds may be formed in certain special cases.

On the assumption that all the constituents of the dye-bath are adsorbed to a greater or less extent, it has been found possible to give a satisfactory interpretation to many facts recorded by previous observers.

Since the hydrogen and hydroxyl ions are readily adsorbed, it follows that the acid or alkaline nature of the dye-bath will have an important influence on the adsorption of the dye. The adsorption of hydrogen as ion will tend to increase the adsorption of an acid radicle, whilst the adsorption of hydroxyl as ion will tend to increase the adsorption of a basic radicle. In accordance with this, it is found that an acid dye is taken up most readily in an acid solution, that a readily adsorbed anion decreases the adsorption of an acid dye, and that a readily adsorbed cation increases the amount of an acid dye taken up from solution. Since the sulphate ion is adsorbed more readily than the chloride ion, it follows that the addition of sulphates to the dye-bath will have a greater effect in diminishing the adsorption of an acid dye than the addition of chlorides. This is quite in accordance with practical experience.

H. M. D.

[Tension of Metal Ammonias.] FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1914, **86**, 506—507).—Polemical. An answer to Biltz (this vol., ii, 34; compare also Ephraim, A., 1913, ii, 677; Biltz, *ibid.*, ii, 404.)  
J. F. S.

**The Thickness and Structure of the Capillary Layer.** G. BAKKER (*Zeitsch. physikal. Chem.*, 1914, **86**, 129—176).—A theoretical paper in which the capillary layer of liquids is studied with respect to its thickness, energy relationships, and tension. The general results arrived at are investigated by means of experimental data in the case of a large number of substances. It is shown that the cohesion of a liquid cannot be explained by either the Boltzmann or the van der Waals forces. The author adopts the Laplace force as that acting between the molecules, and finds that the radius of the sphere of influence of this force is between six and seven times the molecular diameter. According to van der Waals, the dimension of the radius of the sphere of influence is given by  $2H/K$ , where  $H$  is the surface tension and  $K$  the molecular pressure. Kelvin gave the thickness of the capillary layer as  $H/K$ , this being the lower limit; the author deduces as the thickness of the capillary layer  $\zeta = 14H/K$ , and calculates the value of  $\zeta$  for water as 1—2 millimicrons. The expression

$$\zeta = 4.066 \times 10^{-9} e^{-1.05(1 - T/T_K)} \times H(\phi_1 - \phi_2)^2$$

is also found for water, in which  $\phi_1$  represents the density of the liquid, and  $\phi_2$  that of the vapour. As far as the determination of the values of  $H$ ,  $\phi_1$  and  $\phi_2$  have been made, it is shown that for water the value of  $\zeta$  is independent of the temperature, and between  $0^\circ$  and  $140^\circ$  has a value of 1.6 millimicrons, and by extrapolation

it is shown to have the same value at  $200^{\circ}$ . In the case of ether, the value of  $\zeta$  is shown by two different methods to be 2.6 and 2.1 millimicrons respectively. If the ratio of the energy change from liquid to capillary layer, and from capillary layer to vapour, is represented by  $q$ , then  $q = (\epsilon_2 - \epsilon) / (\epsilon - \epsilon_1)$ , and a general expression for the thickness of the capillary layer is obtained which has the form

$$\zeta = (1 + q) / (\phi_1 - q\phi_2) \times 2(H - T \cdot dH/dt) / r_i,$$

in which  $r_i$  is the internal heat of vaporisation. At lower temperatures, where  $\phi_2$ , the density of the vapour, can be neglected,  $q = \{7(1 + T/T_K) / (1 - T/H \cdot dH/dt)\} - 1$ . This formula gives a value for water at  $46^{\circ}$  of  $q = 5.2$ , and for mercury at  $0^{\circ}$   $q = 5.3$ . If the temperature-coefficient of the surface tension is represented by  $\gamma$ , and the coefficient of expansion of the liquid by  $k$ , then  $\gamma/k = 3.6-3.7$  for all liquids except water and amyl alcohol. If  $\alpha$  is the coefficient of the Laplace expression for the molecular pressure, then  $\zeta = 14H / \alpha(\phi_1 - \phi_2)^2$ , and if  $\alpha$  is given the value

$$\alpha = \text{constant} \times \nu^{(1 - T/T_K)},$$

where  $\nu$  is a constant, then  $\gamma = 2k + \nu/T_K$ , and it is shown that for many substances this formula evaluated has the form

$$\gamma = 2k + 1.15/T^K.$$

J. F. S.

**Osmotic Pressure and Moist Air.** WILDER D. BANCROFT (*J. Physical Chem.*, 1914, 18, 67-69).—An extract is given from a paper (Ferguson, this Journ., 1854, 6, 122) describing the absorption of water vapour by molasses contained in wooden casks which had been stored for a considerable period in a damp cellar.

H. M. D.

**The Molecular Condition of Some Substances in Solution.** NILRATAN DHAR (*Zeitsch. anorg. Chem.*, 1913, 85, 206-213).—The molecular condition of some substances dissolved in water is calculated by van't Hoff's formula from the known solubilities at different temperatures. The results obtained with carbon dioxide, sulphur dioxide, hydrogen sulphide, chlorine, bromine, ammonia, mercuric cyanide, cadmium iodide, thallium chloride, arsenious oxide, boric, acetic, and oxalic acids, and barium and calcium hydroxides, are in qualitative agreement with those obtained by other methods. The heat of solution thus calculated for mercuric chloride is too low.

C. H. D.

**Crystallisation and Solution in Aqueous Solution. II.** MAX LE BLANC (*Zeitsch. physikal. Chem.*, 1914, 86, 334-336. Compare *ibid.*, 1911, 77, 614).—The author has repeated a series of experiments on the velocity of crystallisation and solution of crystals of potassium dichromate in a saturated solution of the same salt. The method adopted differs from that in the earlier experiments (*loc. cit.*) in the fact that instead of exposing the whole crystal to the solution, only one face was exposed; this was carried

out by embedding the crystal in paraffin wax and leaving the brachypinacoid only free to the solution. Using the formula  $dx/dt = KO(C - c)$ , in which  $O$  is the uncovered surface, values of  $K$  are obtained which show that the process of solution is a pure diffusion phenomenon, whilst that of the growth of the crystal is not. These results are in accord with the earlier work, but they emphasise more clearly the difference in the nature of the two processes.

J. F. S.

**Analysis of Crystals by the X-Ray Spectrometer.** W. LAWRENCE BRAGG (*Proc. Roy. Soc.*, 1914, *A*, **89**, 468—489. Compare *ibid.*, 1913, *A*, **88**, 428).—The structure of a number of crystalline substances has been determined from observations on the reflection of X-rays with the aid of the X-ray spectrometer.

If monochromatic radiation, such as is emitted by an X-ray bulb with an anti-cathode of palladium, falls on a series of equally spaced planes, each of which can reflect only a small fraction of that radiation, reflection is practically inappreciable except when the relation  $n\lambda = 2d \sin \theta$  holds good. In this equation,  $\lambda$  is the wave-length of the incident radiation,  $\theta$  the glancing angle of reflexion,  $d$  the distance between the successive planes, and  $n$  a whole number. Reflection of the incident radiation is therefore observed at a series of angles,  $\theta_1, \theta_2, \theta_3$ , etc., the sines of which are in arithmetical progression.

In order to obtain the requisite data for the deduction of the structure of a particular crystal, the faces (100), (110), and (111) are examined in detail one by one. From the known value of  $\lambda = 0.576 \times 10^{-8}$  cm., and the observed angles of reflection,  $\theta_1, \theta_2$ , etc.,  $d$  may be obtained from the above equation.

The "normal" spectra reflected from a simple series of identical planes have intensities which diminish according to the series 1, 0.2, 0.07, 0.03, 0.01. If one of these spectra is missing or is abnormally strong, the reason is to be found in the existence of reflecting planes which occur in groups, each group containing several planes of different nature. By combining together the results obtained from the examination of the different faces, a number of equations are obtained, from which it is possible to obtain a solution of the structure of any crystal.

In this way the author has obtained the structure of zinc blende, fluorspar, calcite, and iron pyrites. As was anticipated from its close structural relationship with calcite, sodium nitrate gives spectra in every way analogous to calcite. Rhodochrosite ( $\text{MnCO}_3$ ), chalybite ( $\text{FeCO}_3$ ), and dolomite, have also been examined, and on the basis of their X-ray spectra found to be structurally identical.

It has been previously found from observations on potassium chloride that atoms of approximately the same weight have the same diffracting power. A similar relation holds good when the diffracting power of a single atom ( $\text{Ca} = 40$ ) is compared with that of two atoms of half the atomic weight ( $\text{F} = 19$ ). According to these relations, the diffracting power of an atom is proportional to its atomic weight. This general relationship has been found to be

of considerable assistance in the deduction of the structural relations.

H. M. D.

**A Sudden Change in the Form of Liquid Crystals, Caused by a Molecular Transformation.** O. LEHMANN (*Compt. rend.*, 1914, **158**, 389—393).—An account of the changes, observed under a microscope, in liquid crystals of ammonium oleate and of protagon at their transformation temperatures. The different forms of the crystals are described, and the way in which they change into one another.

W. G.

**The Results of Colloid Investigation.** THE. SVEDBERG (*Ber.*, 1914, **47**, 12—38).—A lecture before the German Chemical Society, giving a review of the present knowledge of colloids.

D. F. T.

**Colloidal Solutions. III. Influence of Colloids on the Dissociation of Electrolytes.** E. PATERNO and M. CINGOLANI (*Gazzetta*, 1914, **44**, i, 36—50; *Kolloid-Zeitsch.*, 1914, **14**, 74—81. Compare Paternò and Salimei, A., 1913, ii, 849).—From numerous series of experiments (chiefly cryoscopic, but in some cases by determination of the electrical conductivity) the authors find that solutions of electrolytes (potassium chloride, sulphate, and phosphate) do not alter in m. p. on addition of considerable quantities of colloids (gum arabic, dextrin), so that the latter do not appear to exert any influence on the electrolytic dissociation of salts. Experiments of the same kind with some other substances exhibit slight anomalies, for which specific explanations can be found.

R. V. S.

**Influence of Capillary Active Substances on Suspensoid Hydrosols.** H. R. KRUYT and C. F. VAN DUIN (*Koll. Chem. Beihefte*, 1914, **5**, 269—298).—The coagulation of arsenious sulphide hydrosol by electrolytes has been found to be influenced by the addition of organic substances, and experiments have been made to determine the change in the limiting concentration of the electrolyte, which is attributable to the added non-electrolyte. The organic substances examined were ethyl, propyl, isobutyl and isoamyl alcohols, and phenol, and from the observations made with them it appears that the limiting concentration of the electrolyte is diminished in the case of uni- and ter-valent inorganic cations, and increased for bi- and quadri-valent cations.

From the experiments with barium chloride, it is found that the increase in the coagulating concentration runs parallel with the absorbability of the organic substances by charcoal. In the case of univalent cations, the effect of phenol on the coagulating concentration is greater than that of isoamyl alcohol, whilst the reverse holds true for tervalent cations. The effect of the two substances is the same towards quadrivalent cations.

The added non-electrolytes have no appreciable effect on the ultramicroscopic appearance of the colloidal particles, on the viscosity of the suspension, or on the movement of the particles in an electrical field.

Some observations on the influence of phenol and *isoamyl* alcohol on the coagulation of a ferric hydroxide sol show that the limiting concentration of the electrolyte is diminished both in the case of uni- and bi-valent anions. From experiments with colloidal gold, it was found that the concentration of the electrolyte which produces a change in the colour of the gold solution is increased by ethyl ether and *isoamyl* alcohol in the case of uni- and ter-valent cations, and diminished when the coagulating ions are bivalent.

In connexion with the above experiments, some measurements have been made on the adsorption of phenol from solutions of potassium chloride. It is found that adsorbed phenol is not sensibly displaced by the electrolyte. On the other hand, both potassium and chlorine ions are displaced to a considerable extent by phenol.

The results are discussed from the point of view of the adsorption theory of Freundlich, and also in reference to the view that the dielectric constant of the dispersive medium is an essential factor in the determination of the stability of the colloidal particles. In neither case is it possible to obtain an entirely satisfactory explanation of the observed results.

H. M. D.

**The Precipitation of Colloids by Salts.** K. SPIRO (*Biochem. Zeitsch.*, 1914, **59**, 337—338).—A reply to a criticism of Pechstein (this vol., ii, 38).

S. B. S.

**Swelling of Gelatin in Aqueous Solutions.** RUDOLF EHRENBURG (*Biochem. Zeitsch.*, 1913, **53**, 356—390).—Experiments have been made on the swelling of gelatin jellies containing 10 or 20% of gelatin in aqueous solutions of acids, bases, and salts. The influence of salts on the swelling action of acids has also been investigated, and comparative observations made on the behaviour of pure aqueous jellies, and jellies containing various salts or dextrose. It has not been found possible to give any satisfactory explanation of the results obtained, but it seems quite certain that the facts are inconsistent with any simple osmotic interpretation.

From the results obtained with approximately isosmotic solutions (freezing point  $0.5^{\circ}$ ), it appears that at these concentrations the order in which the salts arrange themselves is not the same as that in which they are arranged according to the swelling powers of more concentrated solutions. The reduction in the swelling power of acids on the addition of small quantities of salts leads, however, to the same series, and in this case the order of the salts remains unchanged when the concentration is increased.

H. M. D.

**Experiments on Emulsions.** F. R. NEWMAN (*J. Physical Chem.*, 1914, **18**, 34—54).—The author has investigated the nature of the emulsions which are formed by benzene and water, and has determined the conditions under which different types of emulsions can be obtained.

When benzene and water are emulsified by shaking in presence of small quantities of sodium oleate, water always forms the external phase. Emulsions can be obtained containing up to



0.5% of benzene by volume, and also from about 80 to 90% of benzene. In the preparation of the latter series it was found necessary to add the benzene gradually. When the quantity of sodium oleate per c.c. of water is decreased from 0.05 to 0.02 gram, the maximum volume percentage of benzene in the emulsions decreases from 99 to 98.

When magnesium oleate is used as emulsifying agent, emulsions are obtained in which benzene is the external phase. These emulsions are much more stable if a little sodium oleate is also present. By varying the proportions of magnesium oleate and sodium oleate, it is possible to prepare emulsions of water in benzene or of benzene in water. Emulsions of the former type, which were obtained with the author's shaking apparatus, contained from 75 to 96% of water, but it is considered that these limits are of no particular significance, and would be changed by more perfect emulsification.

Whether one liquid is emulsified in a second, or the second in the first, depends on the nature of the emulsifying agent. A hydrophile colloid will tend to cause water to become the external phase, whilst a hydrophobe colloid will have the opposite effect. An active emulsifier must be capable of forming a coherent film round the external phase.

For determining which of two liquids is the external phase in an emulsion, the so-called drop method is recommended. A small drop of the emulsion is placed on a glass plate, and a drop of water placed on the drop of emulsion, and the two stirred together by means of a glass rod. If the emulsified globules spread in the water, water is the external phase, whereas if no spreading is observed, water is present in the emulsion as internal phase.

Some observations are also recorded with respect to the emulsions formed by carbon disulphide, olive oil, and linseed oil with water. In mixed paints, water is the internal, and oil the external, phase, and it has been found that rosin acts as the emulsifying agent.

H. M. D.

**Equation of Condition, Equilibrium Diagram, and Association Hypothesis.** LÉON SCHAMES (*Ber. Deut. physikal. Ges.*, 1914, **16**, 121—122).—A correction of certain statements made in a previous paper (A., 1913, ii, 1036).

H. M. D.

**Equilibria in Ternary Systems. XI.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 597—609. Compare this vol., ii, 41, 113).—A discussion of the nature of the equilibria in ternary systems for the case that a binary compound occurs as one of the solid phases.

H. M. D.

**Chemical Equilibria in Gaseous Systems. II.** UGO GRASSI (*Nuovo Cim.*, 1913, [vi], **6**, ii, 164—172. Compare A., 1913, ii, 395).—The author deduces formulæ which permit of the confirmation of Nernst's formulæ regarding the chemical equilibria in gaseous systems by experiments similar to those described in the earlier

paper (*loc. cit.*), and his results with acetone, methyl ethyl ketone, diethyl ketone, and dipropyl ketone confirm these formulæ in the interval of temperature in which the reactions were studied (137—182°).  
R. V. S.

**The Equilibrium between Lead Chloride and Potassium Chloride in Aqueous Solution.** (Mme.) DEMASSIEUX (*Compt. rend.*, 1914, **158**, 183—184. Compare Lorenz and Rückstühl, A., 1906, ii, 853).—A study of the equilibrium between lead chloride and potassium chloride in aqueous solution at 14°, 50°, and 100°. The curves obtained, with the results at each temperature, are similar in character, and show three transition points, namely,  $\text{PbCl}_2$  to  $2\text{PbCl}_2, \text{KCl}$ ;  $2\text{PbCl}_2, \text{KCl}$  to  $\text{PbCl}_2, \text{KCl}, \frac{1}{3}\text{H}_2\text{O}$ ; and  $\text{PbCl}_2, \text{KCl}, \frac{1}{3}\text{H}_2\text{O}$  to  $\text{KCl}$ .  
W. G.

**Theory of Binary Mixtures and Concentrated Solutions. The Mixture Benzene-Carbon Tetrachloride.** ALFRED SCHULZE (*Zeitsch. physikal. Chem.*, 1914, **86**, 309—333. Compare Dolezalek and Schulze, A., 1913, ii, 482).—The vapour pressures of mixtures of benzene and carbon tetrachloride have been determined at temperatures from 10° to 65°. Measurements are also given of the specific heats of the various mixtures, and of the refractive power for light of long wave-length. The object of the work is to examine the Dolezalek vapour-pressure hypothesis in the case of a binary mixture which contains an associated component. The hypothesis has previously (*loc. cit.*) been applied to the case of a mixture (ether-chloroform), the components of which combine to some extent. A theory is put forward on the basis of the law of mass action and the Dolezalek hypothesis, which enables the molecular constitution of a binary mixture to be deduced from the vapour-pressure measurements. It is shown that on mixing unsaturated benzene vapour with unsaturated carbon tetrachloride vapour, a dilation occurs, which points to the association of one of the constituents in the vapour phase; this is shown to be the carbon tetrachloride, which at 90°, and under a pressure of one atmosphere, is associated to form double molecules to the extent of 0.3% in the vapour phase. The vapour-pressure curves of the benzene-carbon tetrachloride mixtures are concave to the composition axis, and they can all be obtained by calculations based on the Dolezalek hypothesis. The divergence of the curves from the straight-line curve, which would be obtained if the simple mixture law held, decreases as the temperature rises, a fact which is in accordance with the hypothesis. The specific heats of the mixtures are smaller than those calculated by the mixture law, but if the degree of association is taken account of in the calculations, the experimental values agree well with the calculated values. The same relationships are found for the refractive power for light of long wave-lengths, and quite generally it is shown that the whole physico-chemical behaviour of the mixture can be characterised from a single determination of the mass-action constant obtained from the vapour pressure of a single mixture.  
J. F. S.

**Binary Mixtures. The Mixtures Benzene-Ethylene Dichloride and Benzene-Stannic Chloride.** ALFRED SCHULZE and HEINRICH HOCK (*Zeitsch. physikal. Chem.*, 1914, **86**, 445—457 Compare Dolezalek and Schulze, A., 1913, ii, 482; Schulze, preceding abstract).—The vapour pressure of mixtures of benzene and ethylene dichloride have been determined at 8·75°, 25°, 85°, and 95°, and from the results it is shown that the vapour-pressure curve is a straight line, which is in accord with the Dolezalek theory (*loc. cit.*), since both substances are non-associated. In the same way, the molecular heat at 50° and 35° of mixtures also lies on a straight-line curve, but at 20° a slight divergence from the straight line is observed for mixtures containing a large amount of ethylene dichloride. This indicates that at lower temperatures ethylene dichloride is somewhat associated. The mixture benzene-stannic chloride was also investigated. The vapour-pressure curve is concave to the composition axis. On mixing the two liquids there is with decreasing temperature a considerable dilation and a negative heat change. It is shown that at 100° stannic chloride consists of double molecules to the extent of 80%, and that at 30° it is completely associated, and contains, in addition to double molecules, also more complex molecules. Knowing that stannic chloride is an associated liquid, its behaviour when mixed with benzene is strictly in accord with the Dolezalek theory of binary mixtures. J. F. S.

**Deflagrations in a Steady State in Conducting Media.** L. CRUSSARD (*Compt. rend.*, 1914, **158**, 125—128. Compare Jouguet, *ibid.*, 1913, **156**, 872).—The author shows that it is possible to write directly a first integral of the equation of conductivity, the consideration of which notably simplifies all researches on combustion. W. G.

**Influence of Temperature on the Velocities of Transformation of Physico-chemical Systems.** R. MARCELIN (*Compt. rend.*, 1914, **158**, 407—409. Compare this vol., ii, 115).—A mathematical discussion of a method for evaluating, by the application of the Boltzmann-Gibbs law of distribution, the critical energy,  $E$ , necessary to transform a molecule from the mean state into the active state, this being a measure of the energy necessary to convert a system into an unstable state, such that it will react to give a new system. A formula is given showing the variation with respect to temperature, and the author has shown that his results are in agreement with the experimental data for evaporation and sublimation in a vacuum, the former in the case of nitrobenzene, and the latter in the case of naphthalene and iodine. W. G.

**Expression of the Velocities of Transformation of Physico-chemical Systems as a Function of the Affinity.** R. MARCELIN (*Compt. rend.*, 1914, **158**, 116—118. Compare this vol., ii, 115).—A deduction from the Boltzmann-Gibbs rule, of the formula already given, expressing the relationship between the velocity of transformation of physico-chemical systems and their affinities. W. G.

**Limits of Inflammability and Specific Retardation of Ignition.** L. CRUSSARD (*Compt. rend.*, 1914, 158, 340—343).—A theoretical discussion of the conditions governing the specific retardation of ignition and retardation of the temperature of ignition of gaseous mixtures. W. G.

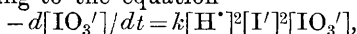
**A Case of Decrease in Reaction Velocity with Rise in Temperature.** A. SKRABAL and S. R. WEBERITSCH (*Ber.*, 1914, 47, 117—119).—Skrabal (*Chem. Zeit.*, 1913, 37, 1169) has shown that the temperature quotient,  $k_{t+10}/k_t$ , of a reaction must undergo a change if the substances taking part in the time reaction are transformed into complexes. The relation between the temperature quotient,  $\tau$ , of the original reaction, and the quotient  $\tau'$  of that between the complexes, is given by the relation

$$\tau'/\tau = e^{10(nQ_1 + pQ_2 + rQ_3 + \dots)/RT(T+10)},$$

where the  $Q$ 's represent the heat effects of the reactions forming the complexes, and the sum  $(n + p + r + \dots)$  represents the order of the reaction.

From this equation it follows that a decrease in reaction velocity with rise in temperature may be realised, if one starts with a reaction of high order and possessing a small temperature quotient, and causes at least one of the reacting substances to be transformed into a complex, with absorption of heat. The form of the above equation shows that such cases will be rare.

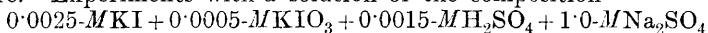
The authors have realised such a case with the reaction between iodate and iodide, which Dushman (A., 1904, ii, 718) has shown to proceed according to the equation



and to have the small temperature quotient 1.3. If sodium sulphate is added in sufficient quantity to a solution made acid with sulphuric acid, the hydrious are transformed into the complex  $\text{HSO}_4'$ -ions, according to the reaction  $\text{H}' + \text{SO}_4'' = \text{HSO}_4'$ , which takes place with the absorption of 5000 cal. The velocity of reaction is then represented by the equation

$$-d[\text{IO}_3']/dt = k'[\text{I}']^2[\text{IO}_3'][\text{HSO}_4']^2/[\text{SO}_4'']^2,$$

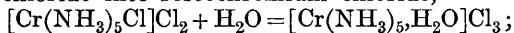
and the calculated temperature quotient is 0.73, which indicates that the reaction velocity should decrease with rise in temperature. Experiments with a solution of the composition



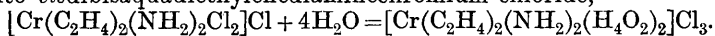
showed that the reaction proceeded more slowly at 80° than at 17.5°, and that the temperature quotient was 0.83. T. S. P.

**Measurement of Velocity of Reaction by means of Colloidal Precipitation.** H. FREUNDLICH and H. PAPE (*Zeitsch. physikal. Chem.*, 1914, 86, 458—478).—The coagulation of arsenic sulphide sols, containing about 3 grams per litre, is investigated for the following binary mixtures of electrolytes: potassium nitrate and sodium nitrate; potassium nitrate and strychnine nitrate; potassium nitrate and barium nitrate; potassium nitrate and cerous nitrate; and barium nitrate and cerous nitrate. The precipitation value was determined for a large number of different mixtures for each pair of electrolytes,

and the values obtained exhibited regularities which are strictly in accord with the absorption theory of colloid precipitation. The presence of even a small quantity of a cation of high valency or of one which is easily absorbed in a solution of a cation of lower valency, or one which is not easily absorbed, causes the concentration required for complete precipitation of the colloid to be very much reduced. With the help of the data collected in the foregoing experiments, the velocity of two reactions, in which there is a change in the valency of the cation, was determined. The reactions studied were: (1) the change of chloropurpureochromium chloride into roseochromium chloride,



(2) the change of *cis*dichlorodiethylenediaminechromium chloride into *cis*disisaquadiethylenediaminechromium chloride,



Both reactions are shown to proceed according to the scheme for unimolecular reactions. In the first case, the reaction velocity was measured at 25°, 30·3°, and 35°, and the temperature-coefficient is found to be 3·3 per 10° between 25° and 35°, and the reaction is in accord with the formula of Arrhenius,

$$\log_e k = -A/T + B.$$

The second reaction was investigated at 0° and 25°, and the temperature-coefficient calculated to 3·1 per 10° between 25° and 35°.

J. F. S.

**Completely Unstable Forms [of Substances].** A. H. RICHARD MÜLLER (*Zeitsch. physikal. Chem.*, 1914, **86**, 177—242).—Totally unstable substances are characterised by the fact that their thermodynamic potential (that is, the  $\zeta$  surface) lies above the corresponding surface of the stable form at all temperatures and pressures. The author has measured the velocity of crystallisation and the velocity of transformation, the volume changes, surface tension, heat of crystallisation, and heat of transformation of both the stable and unstable forms of 4-bromo-1:2-dinitrobenzene, phthalide, acetamide, monochloroacetic acid, sodium thiosulphate,  $\alpha\beta$ -dibromopropionic acid, ethyl  $\beta$ -aminocrotonate, erythritol, glycollic acid, nitro-*p*-acetotoluide, *m*-chloronitrobenzene, *m*-bromonitrobenzene, *m*-dinitrobenzene, 4-chloro-1:2-dinitrobenzene, *p*-nitrotoluene, *p*-bromotoluene, *p*-iodotoluene, acetanilide, benzamide, ethylcarbamide, and thymol. It is shown that the volume change ( $\Delta v$ ) on melting, and the heat of fusion,  $r_p$ , can be the same in the case of both the stable and unstable forms or widely different. If  $T$  and  $T'$  are the melting points of the stable and unstable varieties, the relationships  $T > T'$ ,  $r_p > r_p'$ , and  $\Delta v > \Delta v'$  hold, and consequently it is extremely unlikely the two forms can be in equilibrium at any point, and the unstable forms are therefore to be regarded as totally unstable forms. That these substances never can be in equilibrium with the stable forms is confirmed from the direction of the curves, which are calculated from the expression  $dT/dp = T\Delta v/r_p$ . From the molecular surface tension temperature-coefficient it is shown that, with the exception

of ethyl aminocrotonate and benzophenone, the whole of these substances are strongly associated. It is shown that in many of the cases examined, the velocity of crystallisation is abnormally dependent on the amount of supercooling, in the sense that in regions where the velocity of crystallisation should be independent of temperature, it increases with further supercooling. This abnormality is found only in those substances which are shown from the temperature-coefficient of the molecular surface tension to be associated. The maximum velocity of crystallisation of the stable form is shown to be greater than that of the unstable form in nine cases, and smaller in eighteen cases. A comparison of the maximum velocity of transformation of a substance with the maximum velocities of crystallisation of the stable and unstable forms shows that the velocity of transformation is not always the greatest, as might have been expected. It is shown that in many cases the velocity of transformation is nearer the velocity of crystallisation of the stable form than that of the unstable form.

J. F. S.

**Action of Hydrochloric Acid on Alcohol.** SULO KILPI (*Zeitsch. physikal. Chem.*, 1914, **86**, 427—444).—Equations have been deduced for calculating the velocity of the reaction between alcohol and hydrochloric acid in the presence of water. Three cases are treated in the equations: (1) that undissociated hydrogen chloride molecules alone take part in the change; (2) that chlorine ions only take part in the reaction; and (3) that both hydrogen chloride molecules and chlorine ions react. The action of hydrogen chloride on a 46·2% alcohol-water mixture has been observed at 97°, 102°, and 110°. The concentration of the hydrogen chloride was 0·25*N*, 0·5*N*, and 1·0*N* in the various cases. A further series of experiments were carried out, in which the influence of ammonium chloride on the reaction was investigated. In the calculations made from the experimental data, it is assumed that any action of the chlorine ions can be neglected. It is shown that the influence of temperature on the reaction between alcohol and hydrogen chloride is greater than that in the case of the reverse reaction, ethyl chloride and water. The relationship between the temperature and the velocity of reaction is in accord with the Arrhenius equation.

J. F. S.

**Velocity of Reaction between Mercuric Acetate and Aniline.** G. ROSSI (*Gazzetta*, 1913, **43**, ii, 665—669).—The author's measurements verify the law of chemical equilibria for this reaction, the value of the reaction constant being 0·000841 at 25°.

R. V. S.

**Velocity of Reaction in Catalytic Hydrogenations in the Presence of Platinum Black.** G. VAVON (*Compt. rend.*, 1914, **158**, 409—412. Compare A., 1911, i, 657; 1912, i, 628).—From a study of the rate of hydrogenation of limonene first into carvomenthene, and finally into menthane, by means of platinum black,

the amount of the catalyst employed being varied, the author shows that the curve of the velocities of hydrogenation of substances, capable of taking on several molecules of hydrogen, presents varied forms, according to the quantity and quality of the catalyst. By prior heating of the catalyst to temperatures between  $300^{\circ}$  and  $500^{\circ}$ , the second stage in the hydrogenation was hardly apparent, although on the introduction of more limonene this was still reduced to carvomenthene. By heating platinum black to suitable temperatures, it is possible to diminish its activity, and thus render it incapable of effecting difficult hydrogenations, although it is still capable of catalysing easy hydrogenations.

W. G.

**The Combustion of Oxalic Acid in Contact with Blood Charcoal and the Retardation of this Reaction by Indifferent Narcotics.** OTTO WARBURG (*Pflüger's Archiv*, 1914, 155, 547—560).

—The author shows that at  $38^{\circ}$  oxalic acid is oxidised to carbon dioxide and water at the surface of blood charcoal; the temperature quotient of the reaction for  $10^{\circ}$  is 2.1.

Investigation of the action of the indifferent substances methyl-, ethyl-, propyl-, and phenyl-urethane shows that they diminish the velocity of oxidation, the order of their effect being the same as that already observed by the author in his experiments with red blood corpuscles (A., 1911, ii, 49). The influence of increase in concentration of the narcotic is, however, not so great as in the case of the blood corpuscles.

T. S. P.

**Application of Spectroscopy to the Study of Chemical Equilibria. The Systems Formed by Oxalic Acid and Uranyl Salts.** VICTOR HENRI and MARC LANDAU (*Compt. rend.*, 1914, 158, 181—183).

—The quantitative measurement of the absorption spectra in the ultra-violet can be used to study chemical equilibria and velocities of reaction in the case of substances which possess absorption spectra different from those of the initial substances. This method has been applied to mixtures of oxalic acid and uranyl salts in aqueous solution. The mixture oxalic acid + uranyl salt produces a greater absorption of the ultra-violet rays than the sum of the absorption of the two constituents, this being a further proof of the general law that chemical lability causes an increase in absorptive power for ultra-violet rays. The increase of absorption produced by oxalic acid is greatest with uranyl sulphate and nitrate, and least for the chloride and acetate.

Uranyl acetate and oxalate absorb ultra-violet rays much more strongly than the chloride, nitrate, and sulphate. There is a direct relation between the photocatalytic power of uranyl salts and the increase in absorption produced by these salts on oxalic acid.

W. G.

**Study of Diazotisation by the Spectroscopic Method.** E. TASSILLY (*Compt. rend.*, 1914, 158, 335—338).—The author has applied the spectroscopic method for studying the progress of

diazotisation of aniline (compare this vol., ii, 42) to the diazotisation of a number of other bases, and has found in each case the time necessary for complete diazotisation. W. G.

**Velocity of Reaction in Phototropic Transformations.** M. PADOA and TERESA MINGANTI (*Atti R. Accad. Lincei*, 1913, [v] 22, ii, 500—505. Compare Padoa and Tabellini, A., 1912, ii, 879).—The preparation of solutions of the two forms of the phototropic substance salicylidene- $\beta$ -naphthylamine (Senier, Shephard and Clarke, T., 1912, 101, 1950) has enabled the authors to prepare mixtures containing known proportions of the two modifications in this case. By matching the colours of these mixtures with suitable dyes, standard tints are obtained, by means of which the phototropic change can be followed quantitatively. The value for the reaction constant obtained (which is the product of the true reaction constant and the intensity of the light) is constant on the assumption that the reaction is unimolecular. The temperature-coefficient is 1.47. Similar experiments on the decolorisation of the substance indicate that this reaction is bimolecular, and the temperature-coefficient has the value 2.0. From these results it appears that phototropic change in the solid state is due to a polymerisation.

The observations made in the case of benzaldehydephenylhydrazone are similar. The colouring reaction is unimolecular, and its temperature-coefficient is 1.065—1.068. The decolorising action is bimolecular, and in this case the temperature-coefficient is 1.7. R. V. S.

**Temperature-coefficients of Phototropic Transformations.** II. M. PADOA and B. FORESTI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 576—579. Compare preceding abstract).—From the results of their previous work on this subject, the authors deduce the law that the ratio of the intensities of light required to maintain in a phototropic substance the same coloration at two temperatures differing by  $10^{\circ}$  is equal to the ratio between the temperature-coefficient of the colouring reaction and that of the inverse reaction. Experiments with salicylidene- $\beta$ -naphthylamine and benzaldehydephenylhydrazone yield results in accordance with this law.

R. V. S.

**Heterogeneous Catalysis in Rigid Systems.** ROBERT MARC (*Zeitsch. anorg. Chem.*, 1914, 85, 65—74).—The view that the lowering of the velocity of crystallisation by the presence of impurities is due to adsorption (Freundlich, A., 1910, ii, 1045) is preferable to the view that the effect is merely one of lowering of melting point (Tammann, A., 1912, ii, 1147), as the latter would require an abnormally high temperature-coefficient of the velocity. The idea of adsorption must also be applicable to the crystallisation of glasses, and to the polymorphic transformation of solids. The acceleration of the change  $\text{Se}_8 \rightarrow \text{Se}_4$  by the presence of silver selenide (A., 1906, ii, 742) is probably a case of heterogeneous



catalysis in a rigid system. The two modifications of selenium probably form a compound,  $\text{Se}_{AB}$  (A., 1906, ii, 280), which would be adsorbed by metallic selenides (compare this vol., ii, 196).

C. H. D.

**Experiments on Abel's Theory that Incombustible Dusts Act Catalytically in Igniting Weak Mixtures of Methane and Air.** HAROLD B. DIXON and H. M. LOWE (*Mem. Manchester Phil. Soc.*, 1913, 57, No. 15, 1—10).—A critical discussion of the available evidence is first given, and then new experiments are described. Two series of experiments were made: (1) the direct combustion of weak mixtures of coal-gas and air with and without non-combustible dust (calcined magnesias), in order to see whether any difference in the propagation of the flame could be noticed; (2) the heating of a length of platinum wire in weak mixtures by an electric current, to show that by this means a non-explosive mixture could not be made to explode, as Abel supposed, but rather that an explosive mixture thus treated would become non-explosive owing to the combustion on platinum wire.

Great care was taken in mixing thoroughly the gases, this being the weak point of Abel's experiments. It was found that the presence of a non-combustible substance does not cause the ignition of a weak gas mixture which is not ignited by a flame or spark, and that if any local combustion takes place on the dust, causing self-heating, such an action causes the remainder of the gas to be less, and not more, explosive.

T. S. P.

**The Structure of the Atom.** W. PEDDIE (*Phil. Mag.*, 1914, [vi], 27, 257—268).—A theoretical paper in which the question of atomic structure is discussed in reference to recent work on radiation. Although the phenomena of radiation have led to the postulation of a unit of energy which is regarded as an actual physical entity, it may be doubted whether the emission or absorption of energy in multiples of definite quantities is not really due to structural peculiarities of the emitting or absorbing mechanism. Bohr's deduction of formulæ for line spectra (A., 1913, ii, 689, 943) is referred to in particular, and it is shown that atomic structures are possible, for which it does not appear to be necessary to throw over the ordinary dynamical laws in order to explain the properties of the atom.

H. M. D.

**Constitution and Structure of the Elements.** HAWKSWORTH COLLINS (*Chem. News*, 1914, 109, 26—28. Compare A., 1913, ii, 1045).—If the nearest whole numbers to the atomic weights of the elements in the second horizontal row of the Periodic Table are taken, they may be written as 23,  $23+1$ ,  $23+1+3$ ,  $23+1+3+1$ ,  $23+1+3+1+3$ , etc. The number of parts into which the atomic weight (nearest whole number) is thus divided corresponds with the maximum valency of the element. Assuming that one valency emanates from a mass of 23(Na), one from a mass of 1(H), and two from a mass of 4( $=1+3=\text{He}$ ), the author deduces that sodium

is the basis of all these elements, the expulsion of helium from any element giving the element with next but one lower atomic weight.

Other elements of higher atomic weight are then considered in pairs, consisting of elements which are especially associated in chemistry or mineralogy or both. The differences between the atomic weights of the pairs are found to be approximate multiples of 23; for example,  $112.40(\text{Cd}) - 65.37(\text{Zn}) = 2 + 23.515$ , and hence it is deduced that  $\text{Cd} = \text{Na}_2\text{Zn}$ . Eight pairs of elements have a difference of 90, which corresponds with the atomic weight of zirconium; this element is assumed to contain three atoms of sodium in its constitution. From such results the author states the principle: "sodium takes a prominent part in the formation of all elements of greater atomic weight than itself." T. S. P.

**The Electron Conception of Valence. V. Polar and Non-polar Valence.** K. GEORGE FALK and J. M. NELSON (*J. Amer. Chem. Soc.*, 1914, **36**, 209—214).—Polemical against the views of Bray and Branch (*A.*, 1913, ii, 945), the authors maintaining that valence is of a polar nature in all cases. T. S. P.

**Stratified Systems.** RAPHAEL ED. LIESEGANG (*Kolloid. Zeitsch.*, 1914, **14**, 31—34).—The formation of stratified systems may be modified, not only by external rhythmic disturbances, but also by internal disturbances of a similar rhythmic type. The question as to whether it is possible to distinguish between the effects produced by external and internal rhythm is discussed, and the author arrives at the conclusion that this is not possible in the case of natural objects, or even of laboratory preparations which have not been under observation during the period of their evolution. H. M. D.

**Some Exercises in Physical Chemistry.** ANTONIO BACCARINI (*Nuovo Cim.*, 1913, [vi], **6**, ii, 286—290).—A scheme of work based on the reaction studied by Fraenkel (*A.*, 1907, ii, 746). R. S. V.

**Contributions to the History of Science (Period of Priestley—Lavoisier—Dalton) Based on Autograph Documents.** KURT LOEWENFELD (*Mem. Manchester Phil. Soc.*, 1913, **57**, No. 19, 1—50).—Historical, dealing (1) with Dalton and his contemporaries, William Henry, William Charles Henry, and letters by Berzelius, Schönbein, and Volta; (2) with Priestley and Lavoisier. T. S. P.

**A New Steam Generator.** J. ALAN MURRAY (*Chem. News*, 1914, **109**, 29—30).—The apparatus consists of a copper cylinder 5 inches high by 4 inches in diameter, and fitted with an airtight lid; the bottom is externally concave. A copper tube, half an inch in diameter, which passes through the bottom and projects to within about  $1\frac{1}{2}$  inches from the top, is coiled in two folds in the hollow outside the bottom. A space of about one-eighth of an

inch is left between the two folds of the coil, and also between the upper fold and the bottom of the cylinder, to allow the proper spread of the flame used for heating. Water is maintained at a constant level by the usual arrangement.

Steam is generated very quickly, and is superheated in the coil.

T. S. P.

**An Apparatus for Extraction with Hot Solvents.** H. THAR (*Biochem. Zeitsch.*, 1914, 58, 503—505).—The apparatus is on the principle of that of Soxhlet. The condenser has a wide prolongation, which is ground at the lower end to fit the flask in which the solvent is heated. In this is suspended the cylinder with the syphon, which contains the material to be extracted. The apparatus is figured in the text.

S. B. S.

**A New Gas Generator for the Permanent Generation of Large Quantities of Gases.** BRODTMANN and RODEWALD (*Chem. Zeit.*, 1914, 38, 187).—The apparatus consists essentially of an outer vessel containing the acid and an inner bell-jar fitted with a two-holed rubber bung. Through the one hole passes an outlet tube fitted with a stop-cock, and through the other central hole a glass rod supporting a special cage, open at both ends, containing the material to be acted on by the acid, which can be raised and lowered at will.

The outer vessel is constricted at the bottom, thus supporting the inner bell-jar, and then expands to form a foot, into which is fitted a stoppered tube for running off the waste acid. T. S. P.

**A Modified Kipp Apparatus.** LAU (*Chem. Zeit.*, 1914, 38, 147).—The middle globe is not fused to the lower half-globe, but drawn out funnel-shaped, and then ground into the neck of the lowest portion. The prolongation of the upper globe opens towards the bottom of the funnel, the lower end of the prolongation being drawn out and turned upwards. The side tube of the lowest globe is placed on the upper part, and fitted with a two-holed bung, through which pass a syphon tube and a T-tube. The manipulation of the apparatus is described, many advantages being claimed for it.

T. S. P.

**Arrangement for Emptying Kipp's Apparatus.** GEORG LOCKEMANN (*Chem. Zeit.*, 1914, 38, 222).—The side-tube of the middle bulb is fitted with a two-holed rubber bung; through one hole passes the usual gas tap, and through the other another tube fitted with a stop-cock. Connected with the latter tube by means of a piece of indiarubber tubing is a glass tube, which passes down into the bottom part of the kipp. By opening the stop-cock, the pressure of the gas in the apparatus forces the acid out through the tube.

T. S. P.

## Inorganic Chemistry.

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**Plumboxan Process for the Separation of Air into Oxygen and Nitrogen.** GEORG KASSNER (*Arch. Pharm.*, 1913, 251, 596—609).—The author describes his plumboxan process for the separation of the oxygen from the nitrogen in air. Plumboxan,  $\text{Na}_2\text{PbO}_3 \cdot \text{Na}_2\text{MnO}_4$ , is an emerald-green compound or solid solution of sodium metaplumbate and sodium manganate. This is contained in a combustion tube, which is placed in a slightly sloping position in a furnace, and heated at  $430\text{--}450^\circ$ . The ends of the tube are bent at obtuse angles, and are connected at the one end to supplies of steam and air (freed from carbon dioxide), and at the other end to the gasometers, water-pump, and a vacuum vessel. By passing steam over the plumboxan, oxygen is obtained; subsequently air is passed through the tube, whereby the plumboxan is regenerated, the issuing gas being practically pure nitrogen during the first stages of the regeneration. The oxygen obtained by the action of the steam on the plumboxan is also practically pure provided the combustion tube has been put, after the passage of the air and before the passage of the steam, into communication with the vacuum vessel, in order to remove the last traces of nitrogen from the pores of the plumboxan.

The plumboxan process has an advantage over the barium oxide process in that the absorption of the oxygen by the plumboxan and its regeneration by steam are two distinct and, at temperatures above  $400^\circ$ , irreversible reactions. According to the author's explanation, the liberation of the oxygen is not due to a mere thermal dissociation, but is a catalytic process in which the water in combination with the sodium metaplumbate in the plumboxan acts as the catalyst.

Several experimentally ascertained facts, taken in conjunction with the results of the author's previous researches on the behaviour of calcium ortho- and meta-plumbates, serve to indicate the course of the whole reaction. In the first place, free sodium hydroxide is not produced by the action of steam on plumboxan (as is the case in the Tessié du Motay process). Secondly, sodium plumbite is present, not in plumboxan itself, but only after it has been treated with steam. The following equations indicate the reactions which are supposed to occur: (1)  $2\text{Na}_2\text{MnO}_4 + 2\text{H}_2\text{O} = \text{O}_2 + 2\text{MnO}_2 + 4\text{NaOH}$ ; (2)  $2\text{NaOH} + \text{Na}_2\text{PbO}_3 = \text{H}_2\text{O} + \text{Na}_4\text{PbO}_4$ ; (3)  $\text{Na}_2\text{PbO}_3 + \text{H}_2\text{O} = \text{Pb}(\text{ONa})_2(\text{OH})_2$ ; (4)  $2\text{Pb}(\text{ONa})_2(\text{OH})_2 + 2\text{Na}_2\text{MnO}_4 = 2\text{H}_2\text{O} + 2\text{PbO}_2(\text{ONa})_2 + 2\text{Na}_2\text{MnO}_3$ ; (5)  $\text{PbO}_2(\text{ONa})_2 = \text{O}_2 + \text{Na}_2\text{PbO}_2$ ; (6)  $\text{Na}_2\text{PbO}_2 + \text{Na}_2\text{MnO}_4 = \text{Na}_2\text{PbO}_3 + \text{Na}_2\text{MnO}_3$ .

C. S.

**Ebullioscopy of Sulphur.** ERNST BECKMANN and OTTO LIESCHE (*Zeitsch. anorg. Chem.*, 1914, 85, 31—43).—The boiling vessel is of borosilicate glass with electrical heating (A., 1908, ii, 663), the

jacket being also of borosilicate glass, containing sulphur vapour, heated by a tin bath. The temperature is measured by means of a platinum resistance thermometer.

The ebullioscopic constant of sulphur is calculated to be 157.6 from determinations of the boiling point under different pressures. This is on the assumption that liquid sulphur at the boiling point contains 33% of  $S_8$  molecules, an assumption which is justified by recent determinations (Smith and Holmes, A., 1906, ii, 157; Kruyt, A., 1913, ii, 132). The heat of evaporation per gram is 64.8 cal. The following numbers of atoms in the molecule are found by ebullioscopic measurements at atmospheric pressure: Se, 2.42; Te, 1.32; As, 1.0; Sb, 1.17. C. H. D.

**Preparation of Sulphuric Acid Free from Oxygen Compounds of Nitrogen.** ACH. GRÉGOIRE (*Bull. Soc. chim. Belg.*, 1914, 28, 32—33).—The acid to be purified is diluted with its own volume of distilled water, and then boiled vigorously in a Kjeldahl flask until concentrated once more. If oxygen compounds of nitrogen still remain, the process is repeated. T. S. P.

**The Nature of the Catalysis of the Transformation of Selenium by Silver Selenide.** EDWIN BERGER (*Zeitsch. anorg. Chem.*, 1913, 85, 75—117. Compare Marc, this vol., ii, 191).—The true melting point of selenium is not readily determined, owing to the viscosity and the low velocity of crystallisation. Heating curves indicate that selenium rich in  $Se_8$  has a higher melting point than that rich in  $Se_4$ , but that equilibrium is reached during melting. Silver selenide does not appreciably lower the melting point of selenium. The sudden change of the electrical conductivity on melting allows of a more accurate determination, the result being  $220.2^\circ \pm 0.5^\circ$ .

Silver selenide in quantities of 0.1% is recognisable under the microscope in amorphous selenium. It is also insoluble in crystalline selenium, and the devitrification is not directly proportional to the silver content.

The electrical conductivity of selenium pastilles containing the maximum quantity of  $Se_8$  increases slowly with time at  $25^\circ$ . In presence of silver selenide the increase is more rapid, the effect being approximately proportional to the silver content up to 4%  $Ag_2Se$ . The catalysis thus occurs in a heterogeneous rigid system. A comparison of the electrical conductivity of selenium quenched from different temperatures favours the hypothesis of a compound,  $Se_{AB}$ , which forms solid solutions with both components.

The electrolytic potential of selenium in a solution of sodium selenide (0.3%) is  $-0.05$  volt, and is independent of the previous treatment of the selenium. C. H. D.

**Active Nitrogen.** III. ERICH TIEDE and EMIL DOMCKE (*Ber.*, 1914, 47, 420—425).—In continuation of their previous work (this vol., ii, 122), the authors have devised an apparatus by means

of which oxygen may be removed completely from nitrogen by heating with copper. With such nitrogen the Strutt phenomena are not observed; it is necessary, however, in removing the oxygen by this method not to heat the copper to a temperature above the dissociation temperature of copper oxide, otherwise the glow is always formed.

Using the pure nitrogen thus obtained, the authors have repeated Strutt's experiments with iodine, sulphur, sodium, and thallium chloride, and in no case obtained the phenomena he describes; the addition of the least trace of oxygen gives rise to the various phenomena.

T. S. P.

**The Nitrites.** MARCEL OSWALD (*Ann. Chim.*, 1914, [ix], 1, 32—112).—The only practical method for the preparation of pure nitrites of the alkali and alkaline-earth metals is by double decomposition of silver nitrite with the chlorides of these metals (compare A., 1913, ii, 135). Two new nitrites have been isolated, namely, *calcium nitrite*,  $\text{Ca}(\text{NO}_2)_2 \cdot 4\text{H}_2\text{O}$ , and *lithium nitrite*,  $\text{LiNO}_2 \cdot \text{H}_2\text{O}$ .

In the action of heat on sodium nitrite, in addition to the ordinary reactions, the following take place:  $\text{NaNO}_2 + \text{NO}_2 \rightarrow \text{NaNO}_3 + \text{NO}$ ;  $2\text{NaNO}_2 + \text{NO}_2 \rightarrow 2\text{NaNO}_3 + \text{N}$  (compare the action of heat on silver nitrite, A., 1911, ii, 281). The discovery of these reactions has enabled the author to explain the actions occurring in the action of nitrogen peroxide on lime and on the alkali and alkaline-earth carbonates, and in the decomposition of the complex nitrites of cobalt, nickel, and silver. When nitrogen peroxide acts on calcium oxide there is always a loss of free nitrogen, no matter what the conditions of temperature, in accordance with the equation  $2\text{CaO} + 5\text{NO}_2 \rightarrow 2\text{Ca}(\text{NO}_3)_2 + 0.5\text{N}_2$ , a fact which is of industrial importance.

The hydrated nitrites can be dehydrated in a vacuum over phosphoric oxide without undergoing decomposition; in concentrated aqueous solutions lithium nitrite and the alkaline-earth nitrites undergo hydrolysis at  $100^\circ$ .

The solid nitrites or their saturated solutions are not oxidised by oxygen at atmospheric pressure, neither are the dry salts acted on by nitric oxide, so long as decomposition of the salt itself does not occur. Oxidation of solutions of the nitrites only occurs in the presence of acids, and is then due to oxidation of the decomposition products (nitric oxide) of nitrous acid.

The solubility curves of the various nitrites have been determined (compare A., 1913, ii, 701, for that of sodium nitrite), and also the mutual solubilities of silver nitrite and the nitrites of potassium, sodium, lithium, barium, strontium, and calcium. The following *double* salts were the only ones formed:  $\text{Na}_3\text{Ag}_2(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$ ,  $\text{K}_2\text{Ag}_2(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$ , and  $\text{BaAg}_2(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$ . The physical properties of the various salts and solutions, and the action of heat on the various salts, were also studied in detail. The nitrites readily give supersaturated solutions, and barium and strontium nitrites,  $\text{Ba}(\text{Sr})(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ , were shown to be isomorphous by the method of inoculation.

T. S. P.

**The Melting Point of Arsenic.** R. GOUBAU (*Compt. rend.*, 1914, **158**, 121—122).—A determination of the melting point of arsenic, the metal being heated in a quartz flask immersed in sand, and the temperature measured by an electric thermometer. Arsenic melts at  $817^{\circ}$ , and if the heating is continued there is a violent explosion at  $900^{\circ}$ . The vapour pressure of arsenic is very high long before the melting point is reached. W. G.

**Melting Point of Arsenic.** PIERRE JOLIBOIS (*Compt. rend.*, 1914, **158**, 184—185. Compare A., 1911, ii, 720).—A claim for priority over Goubau (preceding abstract).

**Colloidal Carbon Obtained by a Chemical Method.** L. SABBATANI (*Kolloid. Zeitsch.*, 1914, **14**, 29—31).—A method for the preparation of a colloidal solution of carbon is described in which 2 grams of finely-powdered sucrose are slowly added to 20 c.c. of well-stirred sulphuric acid. After the dark-coloured solution has been kept for twenty-four hours at room temperature, it is poured slowly into 80 c.c. of distilled water, the mixture being shaken continuously during the process. The liquid is then filtered and dialysed until free from sulphuric acid. The solution prepared in this way is very stable, and the ultra-microscopic particles which it contains are found to be negatively charged both in acid and alkaline solution.

A form of gelatinous carbon has also been obtained. The solution prepared by dissolving 2 grams of sucrose in 20 c.c. of sulphuric acid is kept at room temperature for three or four days, and then poured into a shallow dish, which, together with a vessel containing water, is placed under a glass globe. Water vapour is absorbed by the sulphuric acid solution, and at the end of about a week it is found that the solution has been transformed into a gelatinous mass. This is transferred to a vessel containing distilled water, which is renewed from time to time until the sulphuric acid has been completely removed. During this process, the gelatinous mass retains its original form, but when removed from the water and dried in the air, it contracts very considerably. The dry powder swells to a slight extent in contact with water, and with alkalis, traces of carbon dissolve forming a colloidal solution. H. M. D.

**The Electrolytic Reduction of Carbon Dioxide and Carbon Monoxide in Solution under Pressure.** FRANZ FISCHER and OSKAR PRZIZA (*Ber.*, 1914, **47**, 256—260).—With the same apparatus as that used in the electrolytic reduction of dissolved oxygen (A., 1913, ii, 285), the authors find that with the very high current densities of 10—15 amperes per sq. dcm., carbon dioxide may be reduced quantitatively to formic acid (compare Coehn and Jahn, A., 1904, ii, 614; Ehrenfeld, A., 1906, ii, 83). High concentrations cannot be obtained owing to the migration of the anion of formic acid in the anolyte.

Carbon monoxide, under similar conditions, except that low current densities must be used, gives a poor yield of methyl alcohol.

For the above experiments, galvanised and afterwards amalgamated copper foil was used as cathode. Lead, purified according to Tafel's method, was also used, it being necessary then to use a lead anode and not one of platinum. The electrolyte used was an almost saturated solution of potassium sulphate; solutions of sodium and lithium sulphates gave similar results. T. S. P.

**Carbon Sulphidotelluride, CSt<sub>e</sub>.** ALFRED STOCK and PAUL PRAETORIUS (*Ber.*, 1914, **47**, 131—144).—When an arc is maintained under carbon disulphide between a graphite cathode and an anode of graphite and tellurium containing 10 parts or more of graphite to 100 parts of tellurium, the anode is disintegrated and reddish-brown solutions are obtained in which black particles of tellurium and graphite are suspended. The solution contains non-volatile decomposition products of carbon disulphide and the compounds C<sub>3</sub>S<sub>2</sub> (compare A., 1913, ii, 46) and CSt<sub>e</sub>, which are volatile with carbon disulphide vapours. The separation of these two compounds is a very difficult matter, owing to the extreme ease with which the carbon sulphidotelluride decomposes; it was accomplished by the authors by a combination of the following two methods: (1) The repeated fractional extraction of the solution with carbon disulphide vapours in a special apparatus, the distillate becoming poorer and poorer in carbon subsulphide, C<sub>3</sub>S<sub>2</sub>. (2) Transformation of the carbon subsulphide into a non-volatile compound and subsequent distillation of the solution; the non-volatile compound was thiomalononaphthylamide, produced by interaction of the subsulphide and  $\beta$ -naphthylamine (compare A., 1913, ii, 46).

The dilute solution of carbon sulphidotelluride thus obtained, after drying with phosphoric oxide, was concentrated on the water-bath to a strength of 5—10%, using a Hahn fractionating column (A., 1910, ii, 583). The isolation of the pure product could then only be carried out in a weak light, and when the temperature was maintained below  $-30^{\circ}$  continuously. This was accomplished by means of a special apparatus (this vol., ii, 171), when *carbon sulphidotelluride*, CSt<sub>e</sub>, was obtained as yellowish-red crystals, melting at  $-54^{\circ}$  to a brilliant red liquid of high refractive power, which becomes blood-red at room temperature, then black, and decomposes completely after a short time. The substance has a slightly penetrating, garlic odour; if it is smelled for a short time the breath retains a strong odour of garlic for a considerable time. Cryoscopic and ebullioscopic measurements in benzene and carbon disulphide respectively gave molecular weights varying from 176 to 181, theory 172.  $D_{-50^{\circ}}$  2.9 and vapour pressure at  $10^{\circ}$ , about 2 mm.

Carbon sulphidotelluride, either pure or in solution, decomposes very rapidly on attaining room temperature; it is very sensitive towards light, decomposition taking place even at  $-50^{\circ}$ . The solution in carbon disulphide gives a precipitate of tellurium tetrabromide with bromine; mercury extracts all the compound from solutions.

By the refined methods used in this investigation, no evidence



could be obtained of the existence of a carbon telluride,  $\text{CTe}_2$ ; the phenomena observed in a previous communication (Stock and Blumenthal, A., 1911, ii, 722) were due to the decomposition of carbon sulphidotelluride.

T. S. P.

**Carbon Sulphidoselenide.** ALFRED STOCK and ERNST WILLFROTH (*Ber.*, 1914, 47, 144—154).—Carbon sulphidoselenide,  $\text{CSSe}$ , was obtained in carbon disulphide solution by a method similar to that used in the preparation of carbon sulphidotelluride (compare previous abstract), the anode containing 17.5 parts of graphite to 100 parts of selenium. It was much more readily isolated from solution than the sulphidotelluride, owing to its greater stability.

At room temperatures, carbon sulphidoselenide forms an intense yellow liquid, stable in the air, and possessing a pungent odour of onions. It does not take fire when brought in contact with a flame, although the vapours of the boiling liquid burn with a beautiful blue flame. It has m. p.  $-85^\circ$ , b. p.  $84^\circ$ ,  $\mu_D^{20}$  1.7349, vapour pressure at  $10^\circ$ , 45 mm.,  $D^{20}$  1.979. It is decomposed by light, by heating, and on long keeping at room temperature, but is very much more stable than carbon sulphidotelluride. The decomposition products do not contain any substance corresponding with a compound of the formula  $\text{CSe}_2$ , nor has it been possible to prepare such a compound.

That carbon sulphidoselenide is analogous to carbon disulphide was shown by the fact that with an alcoholic solution of sodium ethoxide, sodium monoselenoxanthate,  $\text{SeC(SNa)(OEt)}$ , is produced. A solution of this very deliquescent, yellow, crystalline substance gives characteristic precipitates with solutions of the salts of the heavy metals, behaving very similarly to sodium xanthate.

Selenium vapours when passed over charcoal heated at  $1000^\circ$  in a vacuum do not give rise to the formation of any compound of carbon and selenium. Under similar conditions, sulphur gives carbon disulphide.

T. S. P.

**Action of Hydrogen Peroxide on the Silicic Acid Gel.** A. KOMAROVSKY (*Chem. Zeit.*, 1914, 38, 121—122).—The evaporation on the water-bath of a silicic acid gel with a slight excess of 30% hydrogen peroxide gives a vitreous, amorphous residue, which can be triturated to a white powder. It liberates chlorine from hydrochloric acid, iodine from potassium iodide, decolorises permanganate, and liberates ozone with concentrated sulphuric acid. It gradually and continuously evolves ozonised oxygen; analysis of the freshly-prepared substance gives a formula corresponding with either  $\text{H}_2\text{SiO}_4 \cdot 1.5\text{H}_2\text{O}$  or  $\text{H}_2\text{SiO}_3 \cdot \text{H}_2\text{O}_2 \cdot 0.5\text{H}_2\text{O}$ , that is, either a persilicic acid or a perhydrogel of silicic acid.

A similar compound is obtained when hydrogen peroxide is added to the hydrosol of silicic acid. It is not possible yet to say whether it is a peracid or a perhydrogel.

T. S. P.

**Persilicates.** EDUARD JORDIS (*Chem. Zeit.*, 1914, 38, 221—222). The author confirms many of the results of Komarovsky

(preceding abstract) with respect to the possibility of the existence of persilicates. He has also found that when sufficiently concentrated solutions of sodium silicate are left exposed to the air for several months, and then hydrochloric acid added, chlorine is evolved. T. S. P.

**Attempts to Observe the Production of Neon or Helium by Electric Discharge.** HON. R. J. STRUTT (*Proc. Roy. Soc.*, 1914, A, **89**, 499—506).—The experiments described were begun in the hope of confirming the work of Collie and Patterson (T., 1913, **103**, 419; P., 1913, **29**, 217), according to which helium and neon are to be found in tubes containing hydrogen which have been subjected to the action of an electrical discharge. The author's results are negative.

Special attention was devoted to the possibility of atmospheric contamination, for it has been found that the neon in less than 1/100 c.c. of air can be readily detected by the spectroscopic test. The capillary discharge tube employed in the detection of the neon was made from the finest thermometer tubing, and the discharge from an induction coil was passed through the tube by means of wires twisted round the outside of the tube. From a series of experiments in which varying small quantities of air were admitted into the apparatus and in which, after the oxygen had been absorbed by cooled charcoal, the residual gas was transferred to the capillary discharge tube, it would seem that the neon in 1/1000 c.c. of air is nearer the true limit of sensitiveness of the spectroscopic test.

In order to avoid the possibility of air contamination of this order of magnitude, a method was adopted by which the hydrogen could be removed in the discharge tube itself, and the test for neon applied without pumping the gas out of the apparatus or manipulating it over a pneumatic trough in any way. This result was attained by the attachment of a small tube to the apparatus which contained a small quantity of potassium permanganate. When the current had been passed through the hydrogen in the discharge tube for a sufficient length of time, a little oxygen was admitted and the discharge passed intermittently for a few seconds at a time. The water vapour formed was rapidly condensed in a cooled tube in close proximity to the discharge tube. The residual gas was then subjected to the action of well-cooled charcoal, and then transferred by means of freshly-distilled mercury into the capillary detection tube. The conditions of the discharge through the hydrogen were suitably varied in different experiments, but in no case, in which air contamination could be said to be rigidly excluded, was any evidence of either neon or helium obtained. The author is confident that the negative results are not due to any defect of the technique in looking for neon.

In two of the experiments which are described, potassium chloride and iodide respectively were introduced into the discharge tube and subjected to bombardment by the cathode rays. Although evidence of helium would have been expected in these circumstances

according to Thomson's results (A., 1913, ii, 820), its absence may possibly be due to deficient sensitiveness of the spectroscopic as compared with the positive ray method of analysis. H. M. D.

**Metastability of the Metals in Consequence of Allotropy and its Significance for Chemistry, Physics, and Technics.** ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 632—634. Compare A., 1913, ii, 779; this vol., ii, 52).—In view of the fact that a number of metals have been shown to consist of mixtures of two allotropic modifications, and the probability that many others will be found to be similarly constituted, it is pointed out that the physical constants of metals have in general no definite significance, since these constants refer to mixtures of undefined composition. It will be necessary to redetermine all the physical constants and study the physico-chemical properties by making use of the pure allotropic forms. H. M. D.

**New Crystalline Silicates of Potassium and Sodium, Their Preparation and General Properties.** GEORGE W. MOREY (*J. Amer. Chem. Soc.*, 1914, 36, 215—230. Compare Niggli, A., 1913, ii, 1036).—Known quantities of water and finely-pulverised glasses were heated to high temperatures, up to 500°, in a gold crucible contained in a specially constructed bomb, and the products obtained were investigated. The glasses were made by fusing mixtures of quartz and alkali carbonate in different proportions; the same components were also introduced into the bomb in other forms: the alkali as chloride, carbonate, hydroxide, and as silicate glass; the silica as quartz and as an amorphous precipitate; these variations, however, had no influence on the resultant product.

Four new crystalline *alkali silicates* have been prepared, namely,  $K_2Si_2O_5$ ,  $KHSi_2O_5$ ,  $Na_2Si_2O_5$ , and  $Na_2SiO_3$ . The first three are derivatives of disilicic acid, and form ortho-rhombic crystals, which differ markedly in their behaviour towards water.  $K_2Si_2O_5$  is quickly attacked by water,  $Na_2Si_2O_5$  less readily, whilst  $KHSi_2O_5$  may be left in contact with water, even for some hours at 100°, without appreciable decomposition. The fourth compound is anhydrous sodium metasilicate, which has hitherto been known only as a somewhat indefinite hydrate; it is readily attacked by water.

In addition to the crystalline products, a series of hydrated glasses was obtained, consisting of supercooled liquids, each of which represents the composition of a solution unsaturated under the conditions of experiment. They are perfectly hard, even though they contain up to 25% of water; when heated in the air, water is lost, and they swell up in the process to a sponge-like structure, often with extremely thin vesicular walls. T. S. P.

**Preparation of Potassium Manganifluoride.** I. BELLUCCI (*Atti R. Accad. Lincei.*, 1913, [v], 22, ii, 579—582).—This salt may be readily prepared in quantity by adding ether drop by drop, with constant stirring, to a solution of 2 grams of potassium permanganate in 20 c.c. of 40% hydrofluoric acid, the reaction being

carried out in a platinum dish. The addition of ether is continued until the solution has almost lost its purple tint. The product settles in the form of a yellow, microcrystalline precipitate.

R. V. S.

**The Preparation of Sodium.** BERNHARD NEUMANN and SIGURD GIERSTEN (*Zeitsch. angew. Chem.*, 1914, **27**, 65—70).—The authors have constructed a large, experimental apparatus, on the principle of the Castner apparatus, for the preparation of sodium by the electrolysis of fused sodium hydroxide, using, however, a special arrangement by which the water formed at the anode is evaporated largely by the heat of the fusion and is prevented from coming into contact with the sodium at the cathode.

The best conditions of current and temperature were investigated, and are discussed in detail, as also the various phenomena which occur during electrolysis. The most important factor for successful electrolyses is the temperature, which, in the catholyte, must be maintained very close to that of the melting point of the sodium hydroxide. Pure sodium hydroxide does not give such good results as the commercial substance, owing to its high melting point.

Current yields of 53% were obtained, whereas the average yield in the manufacturing process is 30—40%.

The details of the authors' experiments and considerations can only be appreciated by reference to the original paper.

T. S. P.

**The System Sodium Sulphate-Water.** J. P. WUITE (*Zeitsch. physikal. Chem.*, 1914, **86**, 349—382).—A résumé of the fusion curves of the system sodium sulphate-water is given, as far as this is known from previous work. The present paper gives an account of the determination of the missing details of these curves. The non-agreement of Tilden and Shenstone (A., 1884, 254) and Étard on the solubility at high temperatures is explained by the fact that some of the values of both are incorrectly determined. The transition point of the rhombic anhydrous salt into the monoclinic anhydrous salt is determined as 235° from solubility determinations on both sides of it. The *PT* curves for the different three-phase equilibria are drawn from the experimental data, and the two transition points at 24.4° and 32.4° accurately determined. The difference in the vapour pressure of pure water and that of the three-phase system at the equilibrium point 235° is experimentally shown.

J. F. S.

**Double Salts of Haloids with Silver Nitrate.** G. SCARPA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 452—459).—The paper deals with the thermal analysis of the systems  $\text{AgNO}_3\text{--AgCl}$ ,  $\text{AgNO}_3\text{--AgBr}$ , and  $\text{AgNO}_3\text{--AgI}$ .

Silver nitrate and silver chloride do not form any compound. There is an eutectic corresponding with 160° and about 75 mol. % of silver nitrate. Mixed crystals are formed between certain limits.

Silver nitrate and silver bromide form a compound,  $\text{AgNO}_3 \cdot \text{AgBr}$ , m. p.  $188^\circ$  (decomp.). There is an eutectic corresponding with  $155^\circ$  and 75 mol. % of silver nitrate. Mixed crystals are formed in mixtures rich in silver nitrate.

Silver nitrate and silver iodide form a compound,  $3\text{AgNO}_3 \cdot 2\text{AgI}$ , m. p. about  $105^\circ$ , which does not decompose on melting. There is an eutectic corresponding with about  $80^\circ$  and 45 mol. % of silver nitrate. Mixed crystals of each of the forms of silver iodide, with the compound  $3\text{AgNO}_3 \cdot 2\text{AgI}$ , are formed.

R. V. S.

**Tendency of Alkali Haloids to Combine with Silver Haloids.** II. C. SANDONNINI and G. SCARPA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 517—524. Compare Sandonnini, A., 1912, ii, 941).—This paper deals with the thermal analysis of the systems  $\text{LiBr}-\text{AgBr}$ ,  $\text{NaBr}-\text{AgBr}$ ,  $\text{LiI}-\text{AgI}$ , and  $\text{NaI}-\text{AgI}$ .

Lithium bromide and silver bromide form solid solutions which crystallise at temperatures intermediate between the melting points of the components.

Sodium bromide and silver bromide behave similarly.

Lithium iodide and silver iodide form solid solutions within very wide limits. The diagram of the system belongs to the fifth type of transformation of mixed crystals described by Roozeboom.

Sodium iodide and silver iodide are insoluble in the solid state, the eutectic mixture corresponding with  $394^\circ$  and about 60 mol. % of silver iodide.

R. V. S.

**The Binary Systems of Calcium Chloride with Barium Chloride and Strontium Chloride.** WALTER SCHAEFER (*Jahrb. Min.*, 1914, i, 15—23).—Calcium and barium chlorides form the double salt  $\text{CaCl}_2 \cdot \text{BaCl}_2$  (m. p.  $631^\circ$ ), but no mixed crystals. Calcium and strontium chlorides form a continuous series of mixed crystals with a minimum melting point at  $658^\circ$  with 66 mol. %  $\text{CaCl}_2$ .

L. J. S.

**Carbonate Fusions under Carbon Dioxide Pressure.** H. E. BOEKE (*Jahrb. Min.*, 1914, i, Ref. 9—10; from *Mitt. Naturf. Ges. Halle*, 1913, 3).—Barium carbonate undergoes two reversible transformations: at  $811^\circ$  passing from the  $\gamma$  form (witherite, orthorhombic and pseudo-hexagonal) to the  $\beta$  form (hexagonal), and at  $982^\circ$  to the  $\alpha$  form (cubic); m. p. about  $1740^\circ$ . The system barium carbonate-calcium carbonate (represented by the minerals alstonite and barytocalcite) gives isodimorphous mixed crystals with an eutectic at  $1139^\circ$  and  $52\frac{1}{2}$  mol. %  $\text{CaCO}_3$ . Up to 30 mol. %  $\text{CaCO}_3$  the orthorhombic alstonite is the stable form, but with more calcium carbonate this is replaced by trigonal barytocalcite. Monoclinic barytocalcite is not present in the fusions. Strontium carbonate shows an inversion at about  $929^\circ$  and melts at  $1497^\circ$ .

L. J. S.

**Magnesium Chloride as a Mineral Former; and Spectrochemistry of the Rare Earths.** K. A. HOFMANN and KURT HÖSCHELE (*Ber.*, 1914, 47, 238—247).—The authors have found that

fused, anhydrous magnesium chloride is an excellent solvent and crystallising medium for many inorganic oxides. In some cases interaction takes place with the oxides, or especially with the sulphates, if they are used, giving the volatile chlorides, for example, of glucinum, zinc, iron, and tin; in other cases spinelle-like compounds are formed, owing to the decomposition of the magnesium chloride by water vapour from the flame or by oxygen from the air, for example, magnesium ferrite,  $\text{Mg}(\text{FeO}_2)_2$ , and its transition products,  $(\text{Mg}, \text{Fe})(\text{FeO}_2)_2$ , towards magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ .

Magnesium orthoborate,  $3\text{MgO} \cdot \text{B}_2\text{O}_3$ , and magnesium uranate,  $\text{Mg}_3\text{U}_2\text{O}_9$ , were obtained by using boric and uranic acids respectively. Cerium and zirconium sulphates give the corresponding dioxides, the latter readily dissolving other rare earths, giving coloured crystals.

Erbium, neodymium, praseodymium, and samarium sulphates gave the corresponding oxychlorides, the spectra of which in reflected light were examined and compared with the spectra of other salts.

T. S. P.

**Equilibrium of the Double Salts of Cadmium-Sodium Chloride and Cadmium-Potassium Chloride with their Aqueous Solutions.** KÄTHE SUDHAUS (*Jahrb. Min.*, 1914, *Beil.-Bd.* 37, 1—50).—Crystallisation experiments and solubility determinations made for the ternary systems  $\text{CdCl}_2$ - $\text{NaCl}$ - $\text{H}_2\text{O}$  and  $\text{CdCl}_2$ - $\text{KCl}$ - $\text{H}_2\text{O}$  between  $19^\circ$  and  $55^\circ$  show that the following crystalline phases occur: the simple chlorides of sodium and potassium; two hydrates of cadmium chloride,  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  and  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ; and the three double salts  $\text{CdCl}_2 \cdot 4\text{KCl}$ ,  $\text{CdCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O}$ , and  $\text{CdCl}_2 \cdot 2\text{NaCl} \cdot 3\text{H}_2\text{O}$ .

L. J. S.

**Anhydrous Sulphates. VII. Cadmium Sulphate with Lithium, Sodium, and Potassium Sulphates.** G. CALCAGNI and D. MAROTTA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 442—445. Compare this vol., ii, 52).—Continuing this paper, the authors now give the results obtained in the thermal analysis of the system  $\text{CdSO}_4$ - $\text{K}_2\text{SO}_4$ . Two compounds are formed, namely,

$2\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4$  (at  $763^\circ$ ) and  $3\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4$  (at  $813^\circ$ ).

R. V. S.

**Crystallographic and Thermal Investigation of the Binary Systems of Thallous Chloride and Chlorides of Bivalent Metals.** E. KORRENG (*Jahrb. Min.*, 1914, *Beil.-Bd.* 37, 51—124).—The binary systems investigated were cuprous chloride with chlorides of the alkali metals lithium, sodium, and potassium, and thallous chloride with chlorides of the bivalent metals magnesium, calcium, strontium, barium, zinc, cadmium, tin, and lead. Mixed crystals were formed only with the systems  $\text{CuCl}$ - $\text{LiCl}$  and  $\text{TlCl}$ - $\text{ZnCl}_2$ ; in all other cases (except  $\text{CuCl}$ - $\text{NaCl}$  and  $\text{TlCl}$ - $\text{BaCl}_2$ ) double salts were obtained.

L. J. S.

**Allotropy of Copper.** I. ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 628—632).—From

dilatometric observations it has been found that there are two allotropic modifications of copper with a transition point at  $71.7^{\circ}$ . The experiments were made with electrolytic copper, which was melted in an electric furnace and poured out into cylinders of asbestos paper. As soon as the metal had solidified, the cylinders were chilled in water and turned into thin shavings on a lathe. If the copper is in a finely divided state, the reversible change takes place with considerable velocity, but the rate of change is very much smaller in the case of the solid metal. The experiments show that ordinary copper must be considered as a metastable mixture of  $\alpha$ - and  $\beta$ -copper which is continually changing into the stable modification ( $\alpha$ -copper) at temperatures below  $71.7^{\circ}$ .

That the allotropic transformation has not been previously observed is due to the extreme slowness of the change in the case of the compact metal. It is pointed out, however, that several observations recorded in the literature afford evidence of some change in copper at the ordinary temperature. Special reference is made to the experiments of Matthiessen and Bose (*Ann. Phys. Chem.*, 1862, 115, 353), who found changes in the electric conductivity (at  $0^{\circ}$ ) of pure copper wires after these had been heated for several days at  $100^{\circ}$ .  
H. M. D.

**Approximate Melting Points of Some Commercial Copper Alloys.** A. B. NORTON and H. W. GILLET (*J. Physical Chem.*, 1914, 18, 70—77).—The authors have determined the melting points of a number of ternary and quaternary alloys containing copper, zinc, tin, and lead. The following values are recorded, the numbers in brackets giving the percentage amounts of copper, zinc, tin, and lead, respectively, in the alloys: gun-metal (88, 2, 10, —),  $995^{\circ}$ ; leaded gun-metal (85.5, 2, 9.5, 3),  $980^{\circ}$ ; red brass (85, 5, 5, 5),  $970^{\circ}$ ; low-grade red brass (82, 10, 3, 5),  $980^{\circ}$ ; leaded bronze, (80, —, 10, 10),  $945^{\circ}$ ; bronze with zinc (85, 5, 10, —),  $980^{\circ}$ ; cast yellow brass (67, 31, —, 2),  $895^{\circ}$ ; half yellow, half red (75, 20, 2, 3),  $920^{\circ}$ ; naval brass (61.5, 37, 1.5, —),  $855^{\circ}$ ; manganese bronze (Cu 56, Zn 41, Fe 1.5, tin 0.9, Al 0.45, Mn 0.15),  $870^{\circ}$ . The recorded temperatures are those at which freezing begins, and measurements in duplicate were found to agree within  $\pm 5^{\circ}$ .  
H. M. D.

**Influence of Shaking on the Solution of Copper in Nitric Acid.** MAURICE DRAPIER (*Compt. rend.*, 1914, 158, 338—340).—For a given strength of nitric acid, the amount of copper dissolved in a given time is very considerably reduced by shaking or rotating the copper, and if the velocity of rotation is increased sufficiently, may be reduced practically to zero. This is not due to the destruction of local heating effects, since the flow of cold water through a copper tube has no effect on its rate of solution in nitric acid. The author considers that the effect is due to the distribution of the nitrous acid primarily produced at the surface of the metal, and to the consequent inhibition of its catalysing effect on the solution. The addition of increasing quantities of sodium nitrite to the nitric acid gradually nullifies the shaking effect. W. G

**Cupric Oxide Jellies.** L. S. FINCH (*J. Physical Chem.*, 1914, 18, 26—33).—Cupric oxide jellies have been prepared by the addition of a suitable quantity of ammonia to a saturated solution of copper acetate. The jellies are not permanent, cupric hydroxide separating out sooner or later. The stability of the jelly is increased if a small quantity of manganous sulphate, potassium sulphate, or sulphuric acid is added to the copper acetate solution previous to the addition of the ammonia. The best conditions are obtained by mixing together 50 c.c. of saturated copper acetate solution, 4 drops of concentrated sulphuric acid, and 3—4 c.c. of diluted ammonia (1:1). If such a jelly is allowed to dry up, it can be regenerated by shaking the dried mass with water. H. M. D.

**Modification of Lothar Meyer's Apparatus for the Purification of Mercury.** FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1914, 27, 24).—In this apparatus the mercury is allowed to fall through dilute nitric acid contained in a vertical tube about 1 metre in length, the lower end of the tube being connected with a capillary, which is bent upwards for a short distance and then outwards. The modification described consists in making a number of indentations at opposite sides of the vertical tube so that the drops of mercury are deflected from side to side and caused to take a longer passage through the nitric acid. The mercury is admitted to the top of the tube through a funnel, the stem of which is drawn out to a fine jet; the mercury may be filtered previously through muslin W. P. S.

**Mercuric Polyhaloids in Solution.** W. HERZ and W. PAUL (*Zeitsch. anorg. Chem.*, 1914, 85, 214—216).—The solubility of iodine and mercuric chloride, and of bromine and mercuric bromide, in water indicates the formation of readily soluble polyhaloids. Partition experiments, using carbon tetrachloride, indicate the existence of  $\text{HgBr}_2\text{I}_2$ ,  $\text{HgBr}_4$ , and  $\text{HgCl}_2\text{I}_2$ , and probably of other polyhaloids. C. H. D.

**Basic Compounds of Mercury and Copper.** B. FINZI (*Gazzetta*, 1913, 43, ii, 708—712. Compare A., 1912, ii, 158).—When yellow mercuric oxide is dissolved in a hot, almost saturated solution of copper nitrate, the compound  $\text{Cu}(\text{NO}_3)_2 \cdot \text{HgO} \cdot 3\text{H}_2\text{O}$  is precipitated (in small quantity) in the form of tufts of pale blue needles. R. V. S.

**The Preparation of Cerium and its Alloys.** MAX MOLDENHAUER (*Chem. Zeit.*, 1914, 38, 147).—Cerium oxide is not reduced to cerium by the Goldschmidt method, using either aluminium, magnesium, or calcium. Cerium fluoride is, however, readily reduced by excess of calcium, giving an alloy containing 12% Ca and about 86% Ce; it is necessary to cover the crucible with a layer of calcium fluoride during the reaction, in order to prevent oxidation. If the cerium fluoride is mixed with iron oxide, reduction with calcium



gives an alloy of cerium and iron containing 40% Ce. If the calcium is replaced by aluminium, an aluminium (10·2%)-cerium (25·3%)-iron (62·5%) alloy is produced.

All the above alloys show the properties of the ordinary iron-cerium alloy. T. S. P.

**Physical Nature of Colloidal Hydrous Aluminium Silicates.** H. STREMMER (*Centr. Min.*, 1914, 80—85).—A reply to R. Gans (this vol., ii, 55). L. J. S.

**The Transformation Points and the Structure of Nickel Chrome Steels.** LÉON GUILLET (*Compt. rend.*, 1914, 158, 412—414. Compare A., 1913, ii, 603).—The action of chromium on the transformation points of nickel steels by cooling is not proportional to the amount present. In a steel containing between 3 and 5% nickel the influence of chromium is very slight. Chromium in small amounts acts far less on nickel steels with low nickel content than on those with high nickel content.

Chrome nickel steels can be divided into three classes: (1) those in which the transformation point on cooling is but little different from that on heating; (2) those in which this difference increases proportionally with the chromium content up to a value of 500°; (3) those which still show this difference, but in which the influence of the chromium is only slight. This classification is in fairly close agreement with the structures of the alloys. Class (1) corresponds with perlitic structure; (2) corresponds with steels containing martensite; (3) corresponds with steels containing carbide, and in which, in consequence, all the chromium is not in solution.

The martensite structure commences when the transformation point on cooling is about 350°. W. G.

**Ternary Alloys of Nickel, Copper, and Gold.** P. DE CESARIS (*Gazzetta*, 1914, 44, i, 27—35. Compare A., 1913, ii, 1061; 1914, ii, 57).—A description of the space diagram of this system based on the diagrams of the constituent binary systems (*loc. cit.*, and Kurnakov and Shemtschuschny, A., 1907, ii, 525), and on further experimental results here recorded. R. V. S.

**Peroxides.** S. TANATAR (*Ber.*, 1914, 47, 87—89).—A reply to Tubandt and Riedel (A., 1911, ii, 987). The author has carried out repeated experiments which show that a solution of nickel peroxide in sulphuric acid contains, not only persulphuric acid, but also hydrogen peroxide. The greatest amount of hydrogen peroxide is produced when the nickel peroxide is dissolved in a solution of hydrogen cyanide containing potassium cyanide; this cannot be due to the autoxidising action of the nickel-cyanogen complex produced, since neither nickel hydroxide nor nickel salts, when free from cobalt, give rise to hydrogen peroxide under the same conditions. The different results obtained by Tubandt and Riedel were probably due to the fact that the nickel peroxide used by them contained cobalt, it being well known that hydrogen

peroxide is produced during the oxidation of potassium cobaltocyanide (compare Manchot and Herzog, A., 1900, ii, 546).

T. S. P.

**The Apparent Explosibility of Uranyl Nitrate.** WALTER EICHHORN (*Chem. Zeit.*, 1914, 38, 139).—A 3—4 year old specimen of uranyl nitrate showed triboluminescence, but no explosions could be heard on shaking it in a flask (compare Ivanov, A., 1912, ii, 455). Uranyl nitrate obtained by the extraction of a concentrated aqueous solution with ether contains less water of crystallisation than the ordinary nitrate. No explosions could be obtained with such a product (compare Andrews, A., 1913, ii, 60).

T. S. P.

**Isolation and Separation of Thorium from Other Rare Earths.** DEUTSCHE GASGLÜHLICHT AKT.-GES. (AUERGESELLSCHAFT) (D.R.-P. 268866).—Solutions containing thorium and other rare earths, such as are obtained in the working up of monazite sand, and containing an excess of hydrochloric acid, are treated with hypophosphoric acid or its sodium salt, whereby thorium hypophosphate separates in a pure state.

J. C. C.

**Iridium Chlorides.** MARCEL DELÉPINE (*Compt. rend.*, 1914, 158, 264—267.\* Compare A., 1911, ii, 806).—The author has submitted the yellow powder obtained by the action of sulphuric acid on iridochlorides to the action of dry hydrogen chloride at 200°, 300°, 400°, 450°, and 500°. The colour remains practically the same, but there are progressive variations in composition, which approaches nearer and nearer to that of  $\text{IrCl}_3$ , there being probably traces of hydrogen chloride and water still retained. The chlorides so obtained are distinguished from the anhydrous chloride by being hygroscopic and soluble in water. On evaporating the aqueous solution, redissolving the residue, and again evaporating the solution, there is obtained a black, feebly hygroscopic mass having the composition  $\text{IrCl}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  after desiccation at 100°. It is soluble in water and alcohol to a greenish-yellow solution, giving with silver nitrate a precipitate having the composition  $\text{IrCl}_3 \cdot \text{AgOH}$  at 110°. Anhydrous iridous chloride is rapidly transformed by concentrated alkalis on a water-bath into the blue oxide of iridium.

W. G.

**Is there a New Element in the Platiniferous Minerals of the Urals?** ANGEL DEL CAMPO Y CERDAN and SANTIAGO PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1913, 11, 562—599).—Holtz (A., 1913, ii, 143) suspected the existence of a new metal in the copper-palladium fraction of the platiniferous Ural minerals.

The authors have made a spectrographic analysis, not of the fraction examined by Holtz, but of a small specimen of metal "black" arising from the same mineral. Two spectrographs gave 360 and 600 lines respectively, but no new lines were observed.

Tin, lead, chromium, and magnesium were found to be present in addition to the metals observed by Holtz.

G. D. L.

\* and *Bull. Soc. chim.*, 1914, [iv], 15, 231—241.

## Mineralogical Chemistry.

**Tables for Crystallochemical Analysis.** E. VON FEDOROV (*Zeitsch. Kryst. Min.*, 1914, 53, 337—388. Compare A., 1913, ii, 393).—Further remarks and conclusions based on the author's tables. Not suitable for abstraction. L. J. S.

**Temiskamite, a New Nickel Arsenide from Ontario.** T. L. WALKER (*Amer. J. Sci.*, 1914, [iv], 37, 170—172).—This mineral occurs with niccolite, bismuth, and silver in calcite veins in the Moose Horn Mine, Elk Lake, Ontario. It is silver-white with a tinge of red and a metallic lustre; on exposure it tarnishes quickly to madder-grey; streak, brownish-black.  $H\ 5\frac{1}{2}$ ,  $D\ 7.901$ . It forms radiating fibrous masses with a botryoidal or arborescent surface. It is slowly attacked by hydrochloric acid, but readily by nitric acid, and is easily fusible. Analysis gives the formula  $Ni_4As_3$ , which is near to that of maucherite (A., 1913, ii, 516).

Ni.	Co.	Fe.	As.	S.	Sb.	Bi.	Total.
49.07	1.73	trace	46.34	1.03	n.d.	0.55	98.72

L. J. S.

**Syngenite from Sondershausen.** HENRICO SCHREIBER (*Jahrb. Min.*, 1914, *Beil.-Bd.* 37, 247—284).—A detailed review of the literature is given. Crystals from Sondershausen, Germany, are tabular parallel to the ortho-pinacoid, with  $a : b : c = 1.352 : 1 : 0.871$ ;  $\beta = 75^\circ 55'$  at the ordinary temperature ( $20^\circ$ ), and  $a : b : c = 1.359 : 1 : 0.894$ ;  $\beta = 76^\circ 3'$  at  $200^\circ$ . Analysis agrees with the usual formula,  $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ .

CaO.	K <sub>2</sub> O.	SO <sub>3</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
17.20	28.80	48.40	5.41	99.81	2.579

The crystals commence to become cloudy, owing to loss of water, at  $220$ — $250^\circ$ , minute crystals (probably of anhydrous calcium potassium sulphate) being formed. Detailed determinations were made of the optical constants at various temperatures up to  $230^\circ$ . With rise in temperature the optic axial plane changes from being perpendicular to parallel to the plane of symmetry. L. J. S.

**Carphosiderite and Hydrozincite from Mexico.** ERNESTO WITICH (*Jahrb. Min.*, 1914, i, Ref. 28—29; from *Bol. Soc. Geol. Mexicana*, 1913, 8, 47—51).—Carphosiderite occurs in fair amount at several localities in the State of Chihuahua, forming straw-yellow to dark yellow, crystalline masses with silky lustre, and consisting of minute, six-sided plates with basal cleavage, optically uniaxial character, and strong negative birefringence. The mineral has been deposited from solutions formed by the decomposition of

sulphides in mineral veins. Analyses approximate to the formula  $3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 10\text{H}_2\text{O}$ .

$\text{SO}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}$	Total.
28.73	51.68	0.12	—	19.42	99.95
26.18	53.59	—	0.17	20.01	99.95
32.83	47.07	—	0.10	19.90	99.90

Hydrozincite occurs as fibrous, silky aggregates and as white crusts on calamine and other zinc minerals. Analysis gave:

$\text{ZnO}$	$\text{CO}_2$	$\text{H}_2\text{O}$
13.50	69.17	17.10
15.01	68.09	16.80

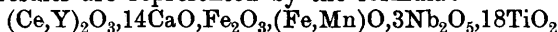
Aurichalcite is also recorded from Chihuahua.

L. J. S.

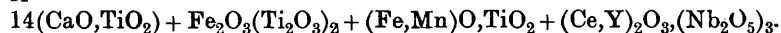
**Chemical Investigation of Certain Minerals from Ceylon Gravel.** V. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 41—50).—Gravel from the Uva Province contains variegated pebbles showing a large number of shining inclusions, some of which are well-developed cubical crystals. These crystals are steel-black, and those in the interior of the pebbles have a metallic, diamond-like lustre, whilst those near the surface are duller. In mass, the crystals are opaque, but the edges of thin sections transmit a faint brownish-red light. The mineral exhibits marked cleavage, and readily scratches apatite;  $D=4.13$ . Its chemical composition is:

$\text{CaO}$	$\text{Ce}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{Nb}_2\text{O}_5$	(+ $\text{Ta}_2\text{O}_5$ )	$\text{TiO}_2$	$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{MgO}$	Total.
21.69	8.80	4.76	1.81	0.17	22.32	(trace)	39.90	trace	trace	trace	99.05

These results are represented by the formula:



or



The physical and chemical properties indicate the mineral to be a modification of dysanallyte.

The methods of analysis are described in detail. T. H. P.

**Optical Study of the Amphiboles.** W. E. FORD (*Amer. J. Sci.*, 1914, [iv], 37, 179—193).—The materials analysed by Penfield and Stanley (A., 1907, ii, 102) were examined optically. The mean index of refraction ranges from 1.61 to 1.71, increasing in a more or less regular manner with the percentages of iron and aluminium, and decreasing with increased amounts of silica and magnesia. In the tremolite-actinolite series (with  $\text{SiO}_2$ , 51—58%) the angle of optical extinction on the plane of symmetry ranges from  $8^\circ$  to  $20^\circ$ , and in the hornblende series ( $\text{SiO}_2$ , 36—44%) it is 9— $33^\circ$ ; in both series the value of the extinction-angle increases with the percentage of iron present.

L. J. S.

**Decomposition and Isomorphism of the Felspars.** J. ŠPLIČAL (*Jahrb. Min.*, 1914, i, Ref. 12—15; from *Abh. böhm. Akad.*, 1913, No. XII, 1—20).—Orthoclase from Kragerö ( $D\ 2.549$ , analyses I—III) and anorthite from Miyake Island, Japan ( $D\ 2.69$ , anal. IV and V), were treated at the ordinary temperature for several

weeks with various acids (concentrated sulphuric, dilute hydrochloric, formic, and carbonic acids), and the amounts of the several oxides dissolved were determined. The mineral acids and formic acid extract silica and alumina in amounts comparable with the lime and alkalis; but with carbonic acid the amounts of the latter are much greater, indicating that the reaction here tends to the formation of kaolin. The action of sodium hydroxide solution, chloric, perchloric, and acetic acids, was also determined. The character of the gelatinous silica obtained from anorthite varies greatly with the nature and the concentration of the acid employed.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss on ignition	Total.
I.	65.48	18.07	0.93	0.58	1.03	11.91	2.14	0.20	100.34
II.	65.32	18.13	0.62	0.78	0.94	10.83	3.47	0.15	100.24
III.	65.75	17.84	1.08	0.53	0.99	11.68	2.35	0.25	100.47
IV.	44.17	34.53	1.47	19.50	0.44	trace	0.60	0.35	101.01[?]
V.	44.90	34.90	1.39	18.32	0.72	trace	0.50	2.25	100.93[?]
VI.	68.87	20.30	0.62	1.32	1.07	—	7.06	0.25	99.49
VII.	63.30	23.44	0.73	4.83	0.25	1.30	6.74	0.55	101.14

Experiments were also made with a view to determine whether the solubility of mixed crystals of plagioclase is an additive character of the solubilities of albite and anorthite. Albite ("tschermakite") from Bamle (D 2.585, anal. VI) and oligoclase from Arendal (D 2.627, anal. VII) were used. It was found that hydrochloric acid extracts only 6.21% of the lime from oligoclase, whilst from anorthite the whole of the lime is extracted. The conclusion is therefore drawn that plagioclase does not represent mechanical mixtures of albite and anorthite. L. J. S.

**Montmorillonite in the Granulites of Cala Francese (Island of Maddalena).** DOMENICO LOVISATO (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 670—675).—The author describes a sample of montmorillonite of a peach-red to almost white colour occurring in a small pocket in a mass of granulites. It is greasy to the touch, can be scratched with the nail, and its lustre is faintly resinous, or, in its more compact portions, almost vitreous; D<sup>14</sup> 2.027. Its composition is:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Loss at 130°.	Total.
42.12	21.98	5.90	0.84	1.88	2.77	0.42	22.37	98.28

T. H. P.

**Allophane-like Clays.** B. AARNIO (*Centr. Min.*, 1914, 69—75).—A greenish-grey talcose clay, from Transylvania, which becomes soapy in water, gave analysis I. A yellowish-brown, greasy clay from Galicia gave II. A white to yellowish, gelatinous substance ("rock-butter") formed in the mine levels traversing pyritiferous chlorite-schist at Canezza, in southern Tyrol, gave III.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>2</sub> .	H <sub>2</sub> O at 105°.	Loss on ign.	Total.
I.	57.58	trace	14.01	2.65	2.60	2.95	1.69	0.96	0.12	—	14.60	3.29	100.45
II.	50.17	trace	15.58	2.18	2.51	3.95	0.96	0.16	0.16	—	19.13	4.75	99.55
III.	7.48	—	10.86	1.96	0.20	0.48	0.11	0.35	trace	0.44	71.93	5.94	99.75

In analysis I,  $\text{Al}_2\text{O}_3 : \text{SiO}_2 = 1 : 7$ ; and in III the ratio is  $1.17 : 1.0$ , corresponding with allophane. Hydrochloric acid (D 1.19) dissolved from these three clays, 21.95, 27.81, and 92.89% respectively.

L. J. S.

**Meteoric Iron from Durango, Mexico.** JUAN S. AGRAZ (*Zeitsch. Kryst. Min.*, 1914, 53, 405; from *Bol. Soc. Geol. Mexicana*, 1909, 6, 9—91).—Analysis of this octahedral iron gave:

Fe.	Ni.	Co.	C.	Total.	Sp. gr.
96.60	0.99	2.39	0.13	100.11	7.782

L. J. S.

**Meteoric Iron from Muonionalusta, North Sweden.** A. G. HÖGBOM (*Zeitsch. Kryst. Min.*, 1914, 53, 408; from *Bull. Geol. Inst. Univ. Upsala*, 1910, 9, 229—238).—This iron, found in 1906, weighs 7.53 kilos. and has D 7.9. It consists of kamacite, taenite, and plessite, together with grains of troilite, the latter with a nucleus of daubreelite. The structure is octahedral with fine lamellæ. The nickel-iron, which forms more than 99% of the mass, gave, on analysis by R. Mauzelius:

Fe.	Ni.	Co.	Cu.	Cr.	P.	Total.
91.20	8.02	0.69	0.01	0.01	0.05	99.88

L. J. S.

**Composition of the Water of Lake Huacachina (Peru).** M. EMM. POZZI-ESCOT (*Bull. Soc. chim.*, 1914, [iv], 15, 96—100).—The author has analysed the water of Lake Huacachina and, in addition, has investigated the mud from the bottom of the lake, the more or less crystalline efflorescence from the shores, and the subsoil at a distance of 25 metres from the shore. The waters are rich in sodium and potassium salts, chiefly the chlorides, sulphates, and carbonates; thiosulphates are present in sensible amount together with traces of phosphates, bromides, and iodides; iron, nitrites, or nitrates are not present.

The formation of the lake appears to be due to the infiltration of water from the subsoil of the region which accumulates in a depression without outlet and becomes progressively charged with saline matter from the neighbourhood. Production of hydrogen sulphide and of thiosulphates is due to the reduction of the sulphates by the living matter which pollutes the water. H. W.

### Analytical Chemistry.

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**An Improved Absorption Tube for Spectral Analysis.**  
ULRICH MÜLLER (*Chem. Zeit.*, 1914, 38, 116).—Near the one end of the tube a narrow side-tube is fused in; on the opposite side, at the other end, a bulb tube with stopcock is fused. The ends of

the main tube are covered with glass plates as usual. By dipping the narrow side-tube in the solution to be investigated, and applying suction at the bulb tube, the main tube can be filled without loss of liquid, and is, of course, equally readily emptied. T. S. P.

**Modified Hempel's Gas Pipette.** R. P. ANDERSON (*Zeitsch. angew. Chem.*, 1914, 27, 23—24).—In order to prevent drops of the absorption solution which may collect in the capillary from passing over into the burette, a small bulb, 3 mm. in diameter, is blown on the capillary. When using fuming sulphuric acid in the pipette, the ends of the latter may be closed with glass caps during the time the pipette is not in actual use. W. P. S.

**Determination of Weight by Titration.** HUGO DUBOVITZ (*Chem. Zeit.*, 1914, 38, 222).—It was necessary to determine the weight of a quantity of oil which was to be refined. The acid number of the oil was determined, and then a known quantity of sodium hydroxide, insufficient for complete neutralisation added, and the acid number again determined. From the results the weight of the oil was readily calculated. T. S. P.

**Filtration and Extraction Tubes.** R. PETERS (*Zeitsch. angew. Chem.*, 1914, 27, 64).—The tube described by the author is very similar to the tube ordinarily used for collecting cuprous oxide in quantitative sugar estimations, except that a lipped funnel is fused on to the top, so that liquid in the tube can be poured out readily. Cotton wool is used as the filter medium. The tube is recommended for filtration of solutions in benzene, ether, light petroleum, etc., since the evaporation of the solvent, and also creeping, are prevented. T. S. P.

**The Detection of Hydrochloric Acid in Medicine.** O. KRUMMACHER (*Zeitsch. Biol.*, 1914, 63, 275—304).—This is an experimental investigation of the value of Günzberg's reagent (phloroglucinol-vanillin; A., 1888, 617) as a test for hydrochloric acid in the stomach contents, and a discussion of the meaning of the reaction. The conclusions drawn are that the reagent in question is a delicate indicator for hydrogen ions, and that its range of delicacy corresponds with a concentration of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  gram ions of hydrogen per litre. W. D. H.

**Detection of Bromides in Presence of Thiocyanates and of Ferrocyanides. Action of Chromic Acid on Cyanogen Bromide.** VI. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1914, 49, 15—21. Compare A., 1913, ii, 333).—The detection of bromine in presence of thiocyanates by the ordinary analytical methods is difficult, and the author formerly experienced difficulties with his method also in these circumstances. He now finds, however, that if the substance to be tested is in solid form or in concentrated solution, and if an excess of chromic acid is added to destroy the thiocyanate, it is possible by his method to detect very small quan-



tities of bromide in the presence of much thiocyanate. The same modification of experimental conditions is effective also in the case of bromide in the presence of ferrocyanide or ferricyanide.

The use of potassium permanganate instead of chromic acid for the liberation of bromide in these cases is undesirable as it leads to the evolution of ammonia, which reacts with the test paper used.

Cyanogen bromide is decomposed by chromic acid with formation of bromine, chromium sesquioxide, carbon dioxide, and ammonia.

R. V. S.

**Estimation of Total Sulphur in Commercial Benzene.** KONRAD SCHENK (*Chem. Zeit.*, 1914, 38, 83—84).—The author recommends the combustion of benzene from a specially constructed apparatus, absorption of the sulphur dioxide in 1% hydrogen peroxide solution, and estimation of sulphuric acid by titration with *N*/10-alkali, using methyl-orange as indicator. The acidity of the hydrogen peroxide is separately determined.

To volatilise the benzene, the author uses a flask with a broad base. It is provided with two tubulures which can be closed by stopcocks; through one tubulure a tube passes to the bottom of the flask, whilst the other carries a glass tube drawn out to a fine point. To increase the surface of the benzene, the flask is loosely filled with cotton wool. To carry out the experiment, the flask is weighed, and a suitable quantity of the sample introduced. A regulated stream of air is passed through it, and the mixture of benzene vapour and air ignited at the fine jet. The size of the flame should be about 0.5—0.7 cm., and the rate of air supply can easily be so controlled that deposition of soot does not take place. The products of combustion are drawn through three washbottles each containing 30 c.c. of 1% hydrogen peroxide solution, the arrangement of the apparatus being similar to that used in determining sulphur in coal gas. To aid the volatilisation of the sample, the flask is immersed in a water-bath the temperature of which is raised during the course of the experiment from 30° to 75°. Even at the latter temperature, commercial benzene is not completely vaporised, but this is of no consequence since the sulphur compounds are completely removed with the more volatile portions. In practice, therefore, the temperature is not raised above 75°, and the experiment is discontinued as soon as combustible products are no longer obtained. Explosions, owing to striking back of the flame, are not to be feared.

The accuracy of the method is indicated by a series of experiments on the combustion of pure benzene to which thiophen and carbon disulphide have been added. About 1—1.5 grams of benzene per hour can thus be burnt.

H. W.

**New Method of Analysis by Reduction of Nitrates, Chlorates, and Peroxides.** C. RUSSO and G. SENSI (*Gazzetta*, 1914, 44, i, 9—15).—The estimations depend on the mode of titration of ferric salts described in a preceding paper (this vol., ii, 222).

Nitrates are estimated in the following way: two flasks are connected together by corks and tubes so that a current of carbon dioxide can be passed through both in series. In the first flask is placed the weighed quantity of nitrate, an excess (3 grams) of Mohr's salt (ferrous ammonium sulphate), and, when all the air has been expelled, 10 c.c. of concentrated hydrochloric acid. In the second flask are placed 120 c.c. of water and a solution of two drops of methylene-blue (1%) which has been decolorised by boiling with one drop of  $N/5$  stannous chloride. The contents of the first flask are now boiled, carbon dioxide passing meanwhile, until all nitrogen peroxide has been driven off. The water in the second flask is brought to the boiling point by the time this has been effected. Both flames being now extinguished, the aqueous solution of indicator in the second flask siphons back into the first, into which the tubes are also washed. The ferric salt in the first flask is then titrated with stannous chloride.

For the estimation of chlorates, it is not necessary to work in the absence of air. The chlorate solution is boiled with an excess of Mohr's salt and hydrochloric acid, and the ferric salt formed is titrated with stannous chloride.

Manganese dioxide and lead peroxide can be analysed in the same way.  
R. V. S.

**Volumetric Estimation of Nitro- and Nitroso-compounds by means of Titanium Trichloride.** HEINRICH SALVATERRA (*Chem. Zeit.*, 1914, 38, 90—91).—Knecht's process of determining nitro- and nitroso-compounds by reduction with titanium trichloride at the boiling point, and subsequent estimation of the excess of reagent with ferric alum solution at the ordinary temperature, suffers from the defects that the end point is not sharp, and that the solutions must be allowed to cool before the experiment can be finished. The author proposes the following modification: the solution of the nitro- or nitroso-compound is treated at its boiling point with a measured excess of titanium trichloride solution; after a short time, a known volume of methylene-blue solution (previously standardised against the titanium chloride solution) is introduced, and the process finished by gradual addition of titanium chloride solution. The end point, from green to pale yellowish-brown or yellow, is very distinct, and the accuracy of the process is established by experiments with known quantities of picric acid.

A slight modification of the apparatus is recommended, in which the lip of the burette is connected with a tube bent twice at right angles. This tube is first somewhat constricted, then allowed to retain its normal diameter for a length of 1 cm. and, finally, drawn out to a point. In this manner, the burette is not placed directly over the boiling liquid, whilst, also, the addition of the reagent can be accurately controlled.  
H. W.

**Solubility of Calcium Phosphates in Ammonium Citrate Solution.** T. WARYNSKI and J. LANGE (*Ann. Chim. anal.*, 1914, 19, 1—6).—Since mono-, di- and tri-basic calcium phosphates are soluble

in both water and ammonium citrate solution to an appreciable extent, the method of separating these salts, which depends on the insolubility of tribasic calcium phosphate in ammonium citrate solution and on the insolubility of dibasic and tribasic calcium phosphates in water, yields only approximately trustworthy results. The solubility of the salts in ammonium citrate solution reaches an equilibrium in about one hour at 30°, but this does not apply in the case of manures where the phosphates may be coated with other substances. The best separation is attained by treating the phosphates for one hour with a cold, saturated ammonium citrate solution. It may be noted that the solubility of the monobasic and tribasic phosphates varies with the concentration of the citrate solution, and reaches a maximum with a concentration of from 10% to 15%.  
W. P. S.

**Rapid Estimation of Boric Acid, Normal, or Introduced, in Foodstuffs.** GABRIEL BERTRAND and H. AGULHON (*Compt. rend.*, 1914, **158**, 201—204).—The authors have applied their colorimetric method for the rapid estimation of minute quantities of boric acid (compare this vol., ii, 146) to the analysis of a number of fruits, vegetables, meats, and other common articles of food. It is necessary in such cases to distil off the methyl borate in order satisfactorily to apply the test.  
W. G.

**The Estimation of Boric Acid in Substances, Alimentary or Otherwise.** JAY (*Compt. rend.*, 1914, **158**, 357—358. Compare A., 1896, ii, 76).—A claim for priority over Bertrand and Agulhon (compare this vol., ii, 146) for the estimation of boric acid in vegetables, fruits, and other foodstuffs, and in animal secretions.  
W. G.

**The Estimation of Carbon by the Wet Method. Simultaneous Estimation of the Halogens.** F. H. THIES (*Chem. Zeit.*, 1914, **38**, 115—116).—The author has improved his method (compare A., 1912, ii, 1001) in such a way that halogens can be estimated simultaneously with carbon. The products of oxidation with the dichromate mixture are passed through a heated lime tube to absorb the halogen and part of the carbon dioxide, and then through a weighed soda-lime tube to absorb the remaining carbon dioxide. The halogens and the carbon dioxide are then estimated in the lime tube. If iodine is present, silver nitrate is added to the oxidation flask in order to retain the iodine as silver iodide; bromine and chlorine are not thus retained.

The results given are satisfactory.

T. S. P.

**Combustions with Tellurium Dioxide.** R. GLAUSER (*Chem. Zeit.*, 1914, **38**, 187).—The author recommends the use of tellurium dioxide for combustions in dealing with substances such as aluminium nitride, calcium cyanamide, ferrochrome, certain hard steels,

etc. The tellurium dioxide melts to a mobile, heavy liquid, in which the substances mentioned readily dissolve. T. S. P.

**Carbon Dioxide Apparatus. III. Another Special Apparatus for the Estimation of Very Minute Quantities of Carbon Dioxide.** SHIRO TASHIRO (*J. Biol. Chem.*, 1914, 16, 485—494. Compare A., 1913, i, 313; ii, 725).—The author has modified his previous apparatus (*loc. cit.*) to make it suitable for a complete determination of the carbon dioxide production from a single tissue, the metabolic rate of which is constantly changing, and the available amount of which is not great. There is a device by which the air can be withdrawn into a tube from the respiratory chamber, and can be analysed subsequently. By this means it is possible, not only to make a complete analysis with one sample of the tissue, but also to make several complete estimations with it. A sketch of the apparatus is given and full details for using it.

W. G.

**Titration of Small Quantities of Carbon Dioxide.** ALFRED DORNER (*Zeitsch. physiol. Chem.*, 1913, 88, 425—429. Compare Warburg, A., 1909, ii, 830).—In this method, the heating of the barium hydroxide previously recommended has been given up because it leads, in glass vessels, to appreciable changes of titre of the barium hydroxide. In the modified process here described, good results are obtained by absorbing the carbon dioxide with cold *N*/100 barium hydroxide, using an apparatus (which is figured) which permits of a prolonged contact between the gas and the absorbing solution.

R. V. S.

**Method of Correcting Silica for Included Salts.** S. B. KUZIRIAN (*Amer. J. Sci.*, 1914, 37, 61—64).—The silica is ignited, treated with a few drops of sulphuric acid, again ignited over a Bunsen flame, and weighed. After the silica has been removed by treatment with hydrofluoric acid, the residue is treated with sulphuric acid, ignited at the same temperature and for the same duration of time as was the silica, and weighed. The weight of this residue is deducted from the weight of the silica found in the first instance.

W. P. S.

**Estimation of Free Alkali Hydroxide in Soaps.** E. BOSSHARD and W. HUGGENBERG (*Zeitsch. angew. Chem.*, 1914, 27, 11—20).—Five grams of the soap are dissolved in 100 c.c. of 50% alcohol, the mixture being heated gently under a reflux apparatus to accelerate the solution of the soap; after cooling, the solution is treated with from 15 to 20 c.c. of 10% barium chloride solution, and the mixture is titrated with *N*/40-alcoholic stearic acid solution, using  $\alpha$ -naphtholphthalein as indicator. This titration gives the quantity of free alkali present as hydroxide. When free alkali carbonate is also present, a further quantity of 5 grams of the soap is dissolved in 100 c.c. of 50% alcohol, and the cold solution is titrated with *N*/40-stearic acid solution, the indicator being phenol-

phthalein or  $\alpha$ -naphtholphthalein; the difference between the two titrations gives the quantity of alkali carbonate. W. P. S.

**Estimation of Alkalis in the Blood.** MAX FEDERER (*Zeitsch. physiol. Chem.*, 1914, 89, 232—235).—Certain details of procedure in the estimation of the blood-ash of the alkalis present are given, which have for their object the increase of accuracy in the results. W. D. H.

**Estimation of Calcium in Solid Substances and Fluids Derived from the Animal Organism.** S. GUTMANN (*Biochem. Zeitsch.*, 1914, 58, 470—471).—In Aron's method of estimating calcium (A., 1907, ii, 652), in which the calcium salts are precipitated by alcohol after destruction of the organic matter by a mixture of nitric and sulphuric acids, there is a source of error, due to the adherence of calcium sulphate to the flask. This is obviated if alcohol is added (after eliminating the excess of nitric acid by boiling the contents of the incinerating flask with water), and the precipitate formed is filtered off after remaining for a day. The precipitate is then returned to the flask and dissolved in 10% sodium carbonate solution, with which it is heated for half-an-hour. The sulphate adhering to the flask as well as the precipitate is thereby converted into carbonate, which can then be dissolved in acetic acid. From the neutralised solution, the calcium can be precipitated as oxalate. S. B. S.

**Separation of Calcium from Magnesium.** FRANZ HALLA (*Chem. Zeit.*, 1914, 38, 100).—The following method is recommended for the separation of very small quantities of calcium in the presence of large amounts of magnesium: the neutral solution containing the chlorides of the two metals is heated to boiling, and solid ammonium oxalate is added until the magnesium oxalate, at first precipitated, re-dissolves; the calcium oxalate remains insoluble. After a few hours, the calcium oxalate is collected on a filter, washed with hot water, then with cold water, ignited, sulphated, and weighed as calcium sulphate. The magnesium oxalate may be precipitated from the filtrate by the addition of acetic acid. W. P. S.

**Method for Determining the Amount of Zinc Chloride in Treated Wood.** ERNEST BATEMAN (*J. Ind. Eng. Chem.*, 1914, 6, 16—18).—Five grams of the ground wood or sawdust are treated in a 500 c.c. flask with 50 c.c. of concentrated nitric acid saturated previously with potassium chlorate; when the reaction has subsided, 10 c.c. of sulphuric acid are added, the solution is boiled, a further quantity of nitric acid containing chlorate is added, and the boiling is continued until the solution is clear and practically colourless when all the nitric acid has been expelled. Either of two volumetric methods may now be employed for the estimation of the zinc in this solution. (1) The solution is boiled for five minutes

after the addition of 0.5 gram of sodium sulphite, cooled, diluted with 100 c.c. of water, and the ferrous iron in solution is oxidised by the addition of 25 c.c. of bromine water. The excess of bromine is expelled by boiling, the ferric salts are precipitated with ammonia, and the filtered solution is neutralised with hydrochloric acid. Five c.c. of concentrated hydrochloric acid are now added, the mixture is diluted to 175 c.c., heated to  $80^{\circ}$ , and titrated with standardised potassium ferrocyanide solution, using uranium acetate as an outside indicator. It is advisable to add 25 c.c. of hydrogen sulphide solution immediately before the titration in order to ensure that the titration is carried out in a reducing solution. (2) The acid digestion solution is diluted with 100 c.c. of water, 10 c.c. of 2% ferric chloride solution, and 1 gram of citric acid are added, the mixture is rendered slightly alkaline with ammonia, diluted to 200 c.c., and titrated at  $80^{\circ}$  with potassium ferrocyanide solution. The end of the titration is reached when a drop of the mixture yields a blue coloration with a drop of a solution consisting of equal volumes of glycerol and glacial acetic acid. Control estimations, using untreated sawdust or filter-paper, should be made at the same time.

W. P. S.

**Application of a New Reaction of Copper, Cobalt, and Nickel.** GIUSEPPE MALATESTA and ETTORE DI NOLA (*Boll. Chim. farm.*, 1913, 52, 819—823).—Uhlenhuth's reaction for copper (A., 1910, ii, 898) is given also by cobalt and nickel. All three reactions are modified, but in different ways, by the addition of electrolytes such as ammonium chloride, of ammonia or of sodium hydroxide. Details are given of the alterations in the nature and sensibility of the reaction so obtainable, and in this way it is possible to differentiate between the three metals. The reaction can be applied to solutions in test-tubes, to drops of suspected liquids on filter-paper or even to metal objects direct. The following modified reagent is recommended: 1:2-diaminoanthraquinone-3-sulphonic acid (0.5 gram), concentrated ammonia solution (100 c.c.), water (360 c.c.), sodium hydroxide  $40^{\circ}$  Be. (40 c.c.). With this reagent, a blue coloration is obtained with all three metals. If it is due to nickel it turns reddish-violet on adding concentrated ammonia solution, if due to copper it becomes red on adding ammonium chloride, whilst a coloration due to cobalt is not changed by either of these substances.

R. V. S.

**Analysis of Bronze, German Silver, and Brass.** L. BERTIAUX (*Ann. Chim. anal.*, 1914, 19, 6—14. Compare A., 1913, ii, 731, 1078).—The following is an outline of the method proposed for the estimation of copper, lead, tin, iron, nickel, cobalt, manganese, aluminium, zinc, arsenic, and antimony in these alloys. Five grams of the sample are dissolved in a mixture of sulphuric and nitric acids, and the copper is deposited electrolytically from the solution; after the nitric acid has been removed by evaporation, the tin is precipitated from the solution as sulphide, the filtrate from this precipitate is oxidised with hydrogen peroxide, and the iron, alum-

inium, and manganese are precipitated as hydroxides. The iron is then estimated by titration with permanganate, the manganese colorimetrically, and the aluminium is taken by difference. Nickel and cobalt, and subsequently zinc, are deposited electrolytically from the residual solution. Lead is estimated by dissolving 5 grams of the alloy in copper nitrate solution, adding nitric acid, and depositing the metal as peroxide; when antimony is present, the lead must first be separated as sulphate. For the estimation of tin, the alloy is dissolved in nitric acid, and the insoluble metastannic acid is collected and weighed. Arsenic and antimony are estimated by the distillation method. W. P. S.

**New Method of Quantitative Estimation of Mercury in the Solid State.** C. DUCINI (*Gazzetta*, 1913, 43, ii, 693—699).—The method depends on the separation of metallic mercury when solutions containing it are treated with a hydrazine salt in presence of alkali. Instead of measuring the volume of nitrogen produced (Rimini, A., 1904, ii, 207), the author weighs the mercury on a tared filter-paper. The results are accurate (0.10% error, using about 0.25 gram of substance). It is of general application, and is not affected either by the presence of free acid in solution or by the concentration of the solution. R. V. S.

**Detection of Traces of Aluminium.** G. H. PETIT (*J. Pharm. Chim*, 1914, [vii], 9, 66—69).—The test depends on the solubility of barium aluminate, and is capable of detecting a quantity of 0.005 gram of aluminium in the presence of 5 grams of iron. The precipitate of ferric, chromium, and aluminium hydroxides, obtained in the usual way, is washed until quite free from ammonium salts, then rinsed into a beaker with water, 2 grams of barium hydroxide are added, and the mixture is boiled. After filtration, a slight excess of sulphuric acid is added to the filtrate, which is then evaporated to about 30 c.c., the barium sulphate is separated, and the solution is rendered faintly ammoniacal. On boiling, aluminium hydroxide is precipitated. W. P. S.

**Analysis of Aluminium.** HARI PADA BHATTACHARYYA (*Chem. News*, 1914, 109, 38).—Silicon is estimated by dissolving the metal in nitric acid and evaporating with hydrochloric acid; copper is precipitated as sulphide from the filtrate from the silica, and the aluminium is precipitated as phosphate in the presence of sodium thiosulphate. The zinc present is precipitated as sulphide in the filtrate from the aluminium phosphate. Iron is estimated by dissolving the metal in sodium hydroxide solution, collecting the ferric hydroxide on a filter, dissolving it in hydrochloric acid, and reprecipitating it by the addition of ammonia. Sodium is estimated in the usual way, and carbon by the sodium copper chloride method. W. P. S.

**The Estimation of Iron According to Neumann.** G. FENDLER (*Zeitsch. physiol. Chem.*, 1914, 89, 279—288. Compare Neumann, A., 1902, ii, 176, 583).—The author's experiments show that this

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method fails when applied to products rich in the phosphates of the alkali earths and even in other cases is not very exact. The modification of Edelstein and v. Csonka (A., 1912, ii, 184) gives more trustworthy results. R. V. S.

**New Method of Titration of Ferric Salts by Reduction.** C. Russo (*Gazzetta*, 1914, 44, i, 1—8).—The method depends on the use of a standard solution ( $N/5$ ) of stannous chloride to reduce the ferric salt present. The end-point is recognised with the aid of a 1% solution of methylene-blue; two drops of this are added to the solution and, when most of the ferric salt is reduced, the liquid is boiled, and the addition of stannous chloride is continued drop by drop until the blue coloration shows signs of disappearing. After boiling for two or three minutes, another drop of stannous chloride is added, and so on until decolorisation occurs. The solution must not contain more than a certain amount of acid, so that, if necessary, the liquid must previously be made just alkaline with ammonia, and then re-acidified with hydrochloric acid. R. V. S.

**Volumetric Estimation of Titanium.** B. NEUMANN (*Zeitsch. angew. Chem.*, 1914, 27, 56).—A reply to Knecht (this vol., ii, 73). W. P. S.

**Loss of Noble Metals during Cupellation.** J. LOEY (*Chem. Zeit.*, 1914, 38, 82—83).—Loss of metals during cupellation is attributed to evaporation and absorption by the cupel. The former cause is operative only in the case of silver, since the highest temperature reached in the muffle is insufficient to volatilise gold to an appreciable extent. Loss of the latter is, therefore, solely due to absorption by the cupel.

The author has examined the capacity of absorbing gold of a large number of cupels obtained from different firms, and finds the loss of gold to vary from 0.197 to 0.370%, whilst the loss in silver varies between 1.190 and 1.710%, and, even with the most careful work, is partly due to volatilisation. Contrary to the opinion of the Commission of the Chem. and Metal. Soc. of South Africa (1899), he finds that French cupels possess no superiority over those of German manufacture. In agreement with F. K. Rose (*ibid.*, 1905), he finds that the quality of any batch of cupels obtained from any particular firm is very uneven, and that the absorptive capacity of any one kind can only be accurately estimated by repeated determinations after definite intervals of time. H. W.

**The Use of Pyridine as a Solvent in the Estimation of Hydroxyl Groups by means of Magnesium Alkyl Haloids.** ARTHUR P. TANBERG (*J. Amer. Chem. Soc.*, 1914, 36, 335—337).—It is stated that the use of pyridine as recommended by Zerevitinov (A., 1907, ii, 509; 1908, i, 593; 1911, i, 101; 1912, i, 841) as a solvent for the estimation of hydroxyl groups by magnesium methyl iodide is not generally satisfactory; with  $\alpha$ -naphthol, for example, more than twice the theoretical volume of methane is produced.



The excess is at least in part due to the pyridine, for this substance in blank experiments at room temperature immediately gave rise to a considerable amount of gas. This result is the more surprising as the pyridine employed was of a higher degree of purity than that used by Zerevitinov. D. F. T.

[**Estimation of Methoxyl Groups.**] GUIDO GOLDSCHMIEDT (*Ber.*, 1914, **47**, 389—392).—The addition of acetic anhydride or of phenol in the estimation of methoxyl by Zeisel's method, condemned by Manning and Nierenstein (this vol., ii, 150), is strongly recommended by the author. In blank experiments in Meyer's apparatus, the amount of silver iodide produced after five to twelve hours' boiling is only a few mg., a quantity which is quite negligible in comparison with the experimental error of the method. C. S.

**A Microanalytical Method for Estimation of the Sugar in the Blood.** L. MICHAELIS (*Biochem. Zeitsch.*, 1914, **59**, 166—172).—For the method, about 1.5 c.c. of blood suffice. It depends on two processes. (1) Separation of the proteins by a combination of heat coagulation with iron hydroxide precipitation (according to the method of Michaelis and Rona). (2) Estimation of the sugar in the filtrate by Bertrand's method. For the latter purpose, the cuprous oxide precipitated is separated by centrifugalisation, dissolved in Bertrand's ferric sulphate solution, which is then titrated from a small 3 c.c. burette with *N*/100-permanganate solution. The method is described in detail, and yield results which are accurate to within 3 or 4%. S. B. S.

**The Picrate Colorimetric Method for the Estimation of Carbohydrates.** WILLIAM M. DEHN and FRANK A. HARTMAN (*J. Amer. Chem. Soc.*, 1914, **36**, 403—409).—The reddish-brown colour which develops on warming solutions of sugars with picric acid and alkali, and was first noticed by Braun (*Zeitsch. anal. Chem.*, 1865, **4**, 185), can be adapted to the colorimetric estimation of the sugars provided that sodium carbonate is used in place of sodium hydroxide.

Details as to the solutions and procedure are given. The standard for comparison is prepared from a known weight of a pure sugar, preferably sucrose, the colour being fairly permanent if the solution is kept in the dark. D. F. T.

**Hydrogen Ion Concentration in Beer and in its Preparation.** FRITZ EMSLANDER (*Kolloid. Zeitsch.*, 1914, **14**, 44—48).—A method for the estimation of the acidity of beer is described which consists in the electrometric measurement of the hydrogen ion concentration in the original beer and of the concentration after the addition of 10 c.c. of 0.1*N*-alkali to 100 c.c. of beer. If, on a diagram, in which  $\log[H^+]$  is plotted as ordinate against volume of added alkali as abscissa, a straight line is drawn through the two experimental points, the point at which this intersects the horizontal line drawn through the ordinate  $\log[H^+] = -7.0$ , gives a measure of the acidity.

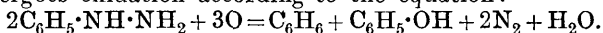
The relation between the albumin content of the beer and its acidity is discussed, and it is shown that the inclination of the titration line towards the abscissa diminishes as the relative amount of albumin increases. The slope of this line affords, therefore, some indication of the albumin content of the beer.

It is also shown that the "keeping power" of a beer is related to the slope of the titration line, the "keeping power" increasing with the inclination of this line to the abscissa. H. M. D.

#### Estimation of Lactic Acid in Fluids containing Proteins.

MAX OPPENHEIMER (*Zeitsch. physiol. Chem.*, 1914, 89, 39—44).—The method suggested by Mondschein for the liberation of the lactic acid from the proteins by means of boiling 10% sodium hydroxide solution is open to serious objection, and the author recommends the precipitation of the proteins with hydrochloric acid and mercuric chloride as proposed by Schenk. In comparative experiments with blood, muscle- and yeast-juice, it was found possible to determine, by the latter method, upwards of 96% of the lactic acid added to the original fluids. Precipitation by means of colloidal iron failed to give satisfactory results, about 30% of the lactic acid being retained by the proteins. H. B. H.

**Estimation of Pyruvic Acid.** IDA SMEDLEY MACLEAN (*Biochem. J.*, 1913, 7, 611—615).—Pyruvic acid cannot be quantitatively estimated by precipitation as a hydrazone, owing to the solubility of the latter. In dilute solutions of the acid, a method involving such a process is useless. If a solution containing the acid is kept for half-an-hour with phenylhydrazine, the excess of the latter used can be estimated by treatment with Fehling's solution in the cold. It undergoes oxidation according to the equation:



It is not convenient to measure the nitrogen evolved, but the amount of phenylhydrazine in the solution can be determined by filtering off the precipitated cuprous oxide, dissolving this in Bertrand's ferric sulphate solution, and titrating the ferrous salt thus formed with permanganate. By the difference in the titration numbers of the phenylhydrazine solution in the presence and absence of pyruvic acid, the amount of the latter can be calculated. The method is also available in the presence of dextrose, which does not reduce the Fehling solution in the cold. S. B. S.

**A Reaction of Succinic and Malic Acids.** W. CECHNER DE CONINCK (*Bull. Soc. chim.*, 1914, [iv], 15, 93—94).—When a concentrated aqueous solution of succinic acid is added to a suspension of several grams of calcium salicylate in a little cold water and the mixture gently warmed, a pale pink coloration is quickly developed which persists for several days, even on exposure to direct sunlight. In similar circumstances, malic acid develops a fugitive, delicate pink coloration which gradually disappears on gently boiling the mixture, and is completely destroyed after several hours, the liquid becoming yellowish-brown. H. W.

**Triketohydrindene Hydrate. A Method for the Quantitative Estimation of the  $-\text{NH}_2\cdot\text{CO}_2\text{H}$  Group.** E. HERZFELD (*Biochem. Zeitsch.*, 1914, 59, 249—259).—If ninhydrin (triketohydrindene hydrate) solution is evaporated on a water-bath to dryness, a coloured residue is obtained, which gives an almost colourless solution in water or alcohol. If, however, an amino-acid is present in the solution, the residue dissolves in alcohol with practically no diminution of the colour intensity, although the colour diminishes perceptibly when it is dissolved in boiling water. When the solution in alcohol has a reddish shade, the latter can be converted into the violet shade by addition of traces of ammonia. The evaporation to dryness of the ninhydrin solution with the substance under investigation, and the solution of the residue in hot alcohol, is now suggested as a technique for the use of the ninhydrin reaction. Several substances have been investigated in this way. Ammonium oxalate gives a violet solution, and ammonium thiocyanate a red one. In most of the other substances investigated a negative result was obtained. The reaction is, however, very sensitive to amino-acids, and a method is described for the application to quantitative estimation of these substances (or  $-\text{NH}_2\cdot\text{CO}_2\text{H}$  groups) by measuring the extinction coefficient of the solution produced when 0.5 c.c. of a 1% ninhydrin solution is evaporated to dryness with the solution under investigation on a water-bath, and the residue is dissolved in alcohol. For this purpose, a spectrophotometer is employed. It was found that the percentage of  $-\text{NH}_2\cdot\text{CO}_2\text{H}$  groups was  $\epsilon/0.046$ , where  $\epsilon$  is the extinction coefficient, under the described conditions of the experiment. The method has been applied by the author with satisfactory results to Abderhalden's pregnancy reaction. The sera of pregnant individuals alone was found to give dialysates with higher ninhydrin values than normal sera. S. B. S.

**The Solidifying and Melting Points of Mutton Tallow and Its Fatty Acids.** ROBERT MELDRUM (*Chem. News*, 1914, 109, 49—51).—Results of determinations of the solidifying and melting points of various samples of tallow and of the fatty acids obtained from the same are recorded. The difference between the lowest temperature to which a tallow falls during solidification and its melting point varies from  $12^\circ$  to  $13^\circ$ ; in the case of the fatty acids, this difference amounts to from  $2^\circ$  to  $4^\circ$ . W. P. S.

**Estimation of the Reichert-Meissl and Polenske Numbers (of Fats).** A. GOSKE (*Zeitsch. Nahr. Genussm.*, 1913, 26, 651—652).—The following method is recommended for the saponification of the fat: Five grams of the sample are placed in a flask, together with 6 c.c. of glycerol-potassium hydroxide solution (1 : 2), two small fragments of pipe-clay are added, and the flask is then heated on an air-bath so that its contents attain a temperature of  $200^\circ$  within about ten minutes; the burner is now removed from beneath the air-bath, whilst the flask is allowed to remain until the temperature of the contents rises to  $215^\circ$ . Saponification will

then be complete, and the method is proceeded with in the usual way. A thermometer having a small bulb bent at a right-angle to the stem, so that the bulb may be immersed completely in the liquid, is employed; an ordinary thermometer will indicate the temperature of the mixture to be about  $20^{\circ}$  lower than the points mentioned.

W. P. S.

**Quantitative Analyses of Artificially-prepared Mixtures of Ethereal Oils.** CANILL HOFFMEISTER (*Chem. Zentr.*, 1913, ii, 2062; from *Arb. Pharm. Inst. Univ. Berlin*, 1913, 10, 147—154).—Benzaldehyde may be quantitatively estimated in the presence of alcohol by converting it into the osazone by means of a solution of phenylhydrazine in acetic acid. The osazone can be estimated gravimetrically (Dumer, *Zeit. anal. Chem.*, 1889, 29, 228) or volumetrically (A. von Mayer, *Monatsh.*, 1891, 12, 525). Eugenol is determined under similar circumstances by transformation into benzoyl-eugenol.

Benzaldehyde in the presence of oil of turpentine is estimated by conversion into its bisulphite compound. The latter is purified by repeated extraction with ether; benzaldehyde is liberated by successive addition of sodium hydroxide and acetic acid, and converted into its osazone. Eugenol is separated from oil of turpentine by repeated extraction with sodium hydroxide, and estimated by the method of Thoms (A., 1904, ii, 93). In a mixture of benzaldehyde, eugenol, and oil of turpentine, the former is removed in the form of its bisulphite compound, and the eugenol is then extracted with sodium hydroxide, the two substances being then estimated as above described.

In the estimation of linalool and linalyl acetate in oil of lavender, the total linalool content is determined by acetylation, and the linalyl acetate originally present (determined by saponification) is deducted. In this manner, 41.861% of the latter and 7.505% of the former were found in oil of lavender.

Benzaldehyde, eugenol, linalool, linalyl acetate, alcohol and palmitic acid are determined as follows in the presence of oil of turpentine: The specimen is shaken three times with sodium hydrogen sulphite, and the bisulphite compound freed from the other substances by repeated treatment with ether. The benzaldehyde is estimated as previously described. Palmitic acid is then removed by cold 10% potassium carbonate solution, the solution is acidified, and the palmitic acid quantitatively extracted with ether. The ethereal solution of the remaining components is agitated with six portions each of 5 c.c. of cold 15% sodium hydroxide, and allowed to remain for an hour after each agitation. Eugenol is determined in the alkaline solution according to Thoms. The residue is made up to a definite volume with ether, and the linalool and linalyl acetate determined in aliquot portions. The content in oil of turpentine is estimated by difference. The estimation of alcohol in the mixture is not described in the original paper. The accuracy of the processes is shown by a series of tables. H. W.

**Analysis of Fertilisers Containing Cyanamide.** H. W. HILL and W. S. LANDIS (*J. Ind. Eng. Chem.*, 1914, 6, 20—22).—The authors discuss the reactions which take place between calcium cyanamide and “acid phosphates,” and show that, in the case of a fertiliser containing these two substances, the American Official Method of Analysis in no way gives results indicative of the character of the sample as taken when free calcium hydroxide or cyanamide are present in the mixture.

W. P. S.

**Estimation of Creatine in Muscle.** LOUIS BAUMANN (*J. Biol. Chem.*, 1914, 17, 15—17).—Hashed muscle is boiled with 5*N*. sulphuric acid for three hours in a flask with reflux condenser. The product is filtered, and a measured amount of the filtrate after dilution is mixed with 10% sodium hydroxide, and the creatine + creatinine estimated by Folin's method. The results are accurate, and the whole process is rapidly performed.

W. D. H.

**Detection of “Saccharin” in Foods with a Modification of Schmidt's Methods.** HALSEY DURAND (*J. Ind. Eng. Chem.*, 1913, 5, 987—989).—The following modification of Schmidt's method, in which the “saccharin” is converted into salicylic acid by heating with sodium hydroxide, was found to be trustworthy. An aqueous extract of the sample to be tested is acidified with phosphoric acid and extracted with ether. The ethereal solution is filtered, evaporated to dryness in a nickel basin, and a portion of the residue is tested for salicylic acid; if this acid is present, the residue is dissolved in hydrochloric acid, an excess of bromine is added, and the mixture filtered; the salicylic acid is thus removed completely as a bromine derivative. The filtrate is then rendered strongly alkaline with sodium hydroxide, evaporated, and the residue treated as described below. In the absence of salicylic acid, the residue obtained on evaporating the ethereal solution is moistened with 1 c.c. of saturated sodium hydroxide solution, the basin is placed on a piece of asbestos board, and heated for ten minutes over a Bunsen flame. After cooling, the mass is dissolved in dilute hydrochloric acid, the solution extracted with ether, and the ethereal solution is shaken in a test-tube with dilute ferric chloride solution. A violet coloration is obtained in the aqueous layer.

W. P. S.

**Microchemical Reaction for Caffeine, Theobromine, Theophylline, and Their Derivatives with Mercuric Chloride.** M. WAGENAAR (*Pharm. Weekblad*, 1914, 51, 23—24).—Mercuric chloride is a delicate, microchemical reagent for the detection and identification of purine derivatives containing one or more methyl groups. It yields characteristic crystals with caffeine, theobromine, theophylline, and their derivatives.

A. J. W.

**Estimation of Creatinine and Creatine in Muscle.** VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1914, 17, 65—69).—See this vol., i, 351.

**Estimation of Tannin in Cider.** C. W. SPIERS (*J. Agric. Sci.*, 1914, 6, 76—83).—A modification of Körner and Nierenstein's method (detannising the solution with casein), in which the tannin removed is estimated by the difference in the permanganate titrations.

The cider (5 c.c.) is added to 750 c.c. of water in a shallow porcelain dish, with 20 c.c. of indigo solution (5 grams of indigo-carmin per litre). The permanganate solution (1 gram per litre) is run in slowly and well stirred for five to ten seconds after each c.c. Afterwards it is added more slowly, until the liquid becomes a clear, golden-yellow, with a tinge of pink round the edge of the dish. At least three titrations should be made.

For detannising, Kahlbaum's pure casein is employed. It is first extracted with ether for thirty-six hours, and is added in two portions of 1 gram, the liquid being filtered after each addition, the second time through a barium sulphate filter.

The permanganate is standardised with Schering's tannin leviss. puriss.

It was found that the commercial pure tannins are not homogeneous, different samples of the same tannin giving somewhat different figures. Taking the average value of the tannins, it was found that 1 gram of ammonium oxalate = 0.4648 gram tannin.

N. H. J. M.

**Detection of Albumin in Urine.** ADOLF JOLLES (*Zeitsch. angew. Chem.*, 1914, 27, 20—22).—With regard to a test described recently by O. Mayer (this vol., ii, 80), the author refers to similar tests proposed previously by himself (A., 1896, ii, 344; 1900, ii, 516); a modification of the test has been given recently (A., 1913, ii, 83). Mayer's test is trustworthy only in the case of urines containing small quantities of albumin.

W. P. S.

**A Modification of Teichmann's Test for Blood.** CLAUDE TREVINE SYMONS (*Biochem. J.*, 1913, 7, 596—598).—The use of a mixture of sodium iodide and lactic acid is recommended in place of sodium chloride and acetic acid for the preparation of Teichmann's hæmin crystals. The benzidine test for blood is not characteristic.

W. D. H.

**The American Method of Standardising Tetanus Antitoxin.** ALFRED MACCONKEY (*J. Hygiene*, 1914, 13, 467—493).—This investigation confirms the statement that the American method is simple, accurate, and trustworthy. The deterioration in samples examined over two years is absent or almost negligible. Tetanus antitoxin can be heated at 57° for one hour on each of three successive days without loss of power, provided no antiseptic is added. In the presence of preservative there is a loss of 12%, and this occurs during the first hour.

W. D. H.

## General and Physical Chemistry.

**The Refractive Indices and Dispersion of Liquid Hydrogen.** H. W. W. AUGUSTIN (*Chem. Zentr.*, 1914, i, 609; from *Ber. K. Sächs. Ges. Wiss.*, 1913, 65, 229—236).—The following values for the refractive index of liquid hydrogen were obtained by Liveing and Dewar's method, and are correct to two units in the last place:

$\lambda$ .....	656.3	579.0	546.1	435.9	404.7
$n-1$ ...	0.10924	0.10974	0.10003	0.11179	0.11262

The value for the density was  $D=0.07086$ .

J. C. W.

**Selective Reflexion of Solutions of Nitrides.** A. K. ÅNGSTRÖM (*Zeitsch. physikal. Chem.*, 1914, 86, 525—528).—The infra-red reflexion of saturated solutions of the nitrides of sodium, potassium, ammonium, calcium, and barium has been investigated by means of a spectroscope and a Nichol's radiometer. It is shown that in the region  $1-10\mu$  there is only one selective reflexion position for the nitrides of sodium, potassium and ammonium, and this lies approximately at  $4.9\mu$ . It is shown from the reflexion curves that these nitrides have a strong absorption band between  $4.6\mu$  and  $4.8\mu$  which can be regarded as characteristic of the  $N_3$  group. This band is not exhibited by the saturated solutions of calcium and barium nitride, but its absence is attributed to the small concentration of the salts in saturated solution. These nitrides show the characteristic reflexion at  $4.9\mu$ .

J. F. S.

**Determination of Tertiary Normals in the Region  $\lambda$  2987 to  $\lambda$  4118 in the Arc Spectrum of Iron.** HEINRICH VIERHAUS (*Zeitsch. wiss. Photochem.*, 1914, 13, 209—234, 245—264).—Recent work on the arc spectrum of iron, which has been carried out by different observers with the object of determining the wave-lengths of lines which may be used as tertiary normals in spectroscopic investigations, indicates that the conditions of the arc discharge have not been sufficiently sharply defined in the recommendations of the International Union. The requirement that the strength of the current should be from 5 to 10 amperes is quite insufficient, and a more complete specification of the conditions of the discharge is found to be essential to the attainment of agreement between the results of different observers. The author's own measurements were made with an arc between cylindrical iron rods of about 1 cm. diameter, the strength of the current being 7 amperes.

Each line on the photographic plates was measured eight times under stipulated conditions, and from these data the wave-lengths and the probable error of the measurements are deduced. Those lines for which the mean error does not exceed 0.003 Å. are recommended for use as tertiary normals. The whole of the lines are grouped in a series of tables according to the magnitude of the mean error.

A comparison of the results with those obtained by Burns (A., 1913, ii, 541, and following abstract) shows that the agreement between the wave-length values of lines which have been measured by both observers is not nearly so good as would be expected from the magnitude of the errors which are assigned to the measurements by the individual observers. H. M. D.

**Arc Spectrum of Iron.** H. BURNS (*Zeitsch. wiss. Photochem.*, 1914, 13, 235—244. Compare A., 1913, ii, 541).—Further measurements of wave-lengths have been made by the method described previously. The recorded data have reference to lines between  $\lambda 5434$  and  $\lambda 8824$ .

From observations made with an arc between two nickel electrodes, and also with an arc between a nickel and an iron electrode, it has been found that the nickel lines obtained under the latter conditions are too diffuse for use as normal lines.

From the measurements of barium lines in the iron arc, it is found that the wave-lengths are shorter than those recorded for the same lines in a carbon arc.

Similarly, it is found that the manganese lines measured by the author in the iron arc spectrum have wave-lengths greater than those recorded by Kilby (*Astrophys. J.*, 1909, 30, 243) in the case of 75% of the lines examined. In some few cases, however, the author's values indicate that the lines are displaced towards the violet end. H. M. D.

**The Optical Effect of the Different Alkali and Alkaline Earth Metals in Salt Formation in the Ultra-violet.** A. HANTZSCH (*Zeitsch. physikal. Chem.*, 1914, 86, 624—632. Compare Hantzsch, Garrett and Gajevski, A., 1913, ii, 893).—The absorption spectra of the acetates and trichloroacetates of the metals of the alkalis and alkaline earths have been determined in various solvents at a series of concentrations in the neighbourhood of  $\lambda 4000$ . It is shown that ionisation, even in the extreme ultra-violet, is an optically indifferent process, and that sometimes, but not always, the solvate formation, preceding ionisations, as well as the salt formation of carboxylic acids, bring about small optical and chemical changes. Normal salt formation is also an optically indifferent process, and the hypsochromatic and bathochromatic effects sometimes produced are due to a difference in constitution between the acid and its alkali salt. All alkali and alkaline earth salts of the same acid possess an identical absorption. From the last fact the conclusion is drawn that every noticeable difference in the absorption of alkali and alkaline earth salts of the same acid, even in the presence of two polychromatic forms of the same salt, is a direct proof that the salts in question can exist in two chemically different chromatic isomerides. J. F. S.

**Influence of the Ethenoid Linking and the Carbonyl and Carboxyl Groups on the Absorption of Ultra-violet Rays.** JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1914, 158, 567—570. Compare this vol., ii, 7).—In continuation of the study of the



influence of constitution on the absorption of the ultra-violet rays, the authors have now obtained the following results. The band characteristic of the carbonyl group is displaced towards the red by a carboxyl group in a conjugated position, whilst if it is in the  $\gamma$ -position there is no displacement of the band, but an increase in the absorption. Similar results are obtained by an ethenoid linking in a conjugated and a  $\gamma$ -position, and, at the same time, in the first position a new band appears in the extreme ultra-violet towards  $\lambda=2350$ . If the molecule contains a carbonyl group and two ethenoid linkings, which latter occur, either one or both, in conjugated positions, in the first case the band characteristic of the carbonyl group is displaced slightly towards the red, whilst in the second case this displacement is twice as great. In both cases the band due to the ethenoid linking is present, but in the second case it also is displaced towards the red.

When a molecule contains two chromophores, they influence one another mutually. If they are not too close to one another in the molecule, there is simply an increase in the absorption or a hyperchrome effect, whilst if they are in conjugated positions there is a displacement of the characteristic bands of each chromophore towards the red, or a hypsochrome effect.

W. G.

**Absorption Spectra and Constitution of Benzene Derivatives. IV. Binuclear Compounds: Diphenylamine, Diphenyl Ether, and Diphenylmethane.** N. A. VALIASCHKO and G. M. DRUSHININ (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 2014—2063).—Investigations similar to those previously published (A., 1913, ii, 367) have been made on aniline, methylaniline, diphenylamine, *p*-aminodiphenylamine, *p*-phenylenediamine, acetanilide, methylacetanilide, diacetanilide, acetyldiphenylamine, anisole, diphenyl ether, toluene, and diphenylmethane.

The results obtained show that aniline, methylaniline, dimethylaniline, and *p*-phenylenediamine are completely analogous to the alkali derivatives of phenols, their molecules existing in a strongly developed phenolic form in dynamic equilibrium with a feeble  $\alpha$ -modification. Acetanilide, methylacetanilide, and diacetanilide possess molecules oscillating between very weak phenolic and  $\alpha$ -forms. Toluene exhibits an absorption band intermediate to that of benzene, on the one hand, and those of anisole and phenol on the other, and must be regarded as feebly phenolic.

With binuclear benzene derivatives, two similar forms,  $\alpha$  and  $\phi$ , exist. The presence of the two rings favours increased development of the two forms, each ring inclining alternately to one or the other; at one and the same time the two rings are in different forms,  $\phi_1 + \alpha_2 \rightleftharpoons \alpha_1 + \phi_2$ . When the two rings are united by way of an imino-group or an oxygen atom, the conditions exist for the development of a strongly phenolic form; the absorption spectra of diphenylamine and acetyldiphenylamine are perfectly analogous to those of aniline and acetanilide, and the spectrum of diphenyl ether to that of anisole.

Connexion of the two benzene rings through a methylene group

creates conditions favouring the development of the  $\alpha$ -modification, determined by the so-called quinonoid character of the compound; introduction of a third benzene ring intensifies this modification.

The above results have an intimate bearing on the various hypotheses which have been advanced concerning the origin of the triphenylmethane colouring matters. They do not, for example, confirm von Baeyer's hypothesis (A., 1907, i, 757), since they indicate that even mononuclear, non-colouring benzene compounds give rhythmic motion and possess characteristic absorption spectra, the presence of two nuclei united by carbon atoms only resulting in conditions especially favourable for the development of such motion.

The authors' results also lead further than the conclusions of Meyer and Fischer (A., 1913, ii, 167), who compared the absorption spectra of fuchsone and benzaurin, and those of fuchsonimonium chloride and Döbner's violet, and found that no fundamental difference exists between simple quinones and quinones containing an auxochrome group. The observations described above show that the absorption spectra of triphenylmethane colouring matters exhibit no essential difference from that of diphenylmethane. The introduction of a third benzene ring or of an amino- or hydroxyl group, or the conversion into carbinol and the removal of water from the latter with the formation of a quinonoid structure—if this really occurs—exerts an intensifying influence on the motion already in existence in the molecule, and at the same time retards it, and consequently displaces the absorption spectrum towards the red. The spectrum of diphenylmethane is, indeed, the forerunner or original type of the spectra of the triphenylmethane colouring matters, differing from these especially in the pronounced development of its  $\alpha_2$ -band and in the marked displacement of the whole spectrum towards the red.

The chromogen must be regarded as a simpler compound than triphenylmethane, namely, either diphenylmethane or, to go further back, the benzene ring itself.

These considerations are advanced in opposition to Hantzsch's fundamental theorem, stating that the typical chromophore of colouring matters arises only on conjugation of a quinonoid chromophore by means of supplementary valencies with a second unsaturated aniline or phenol residue, in which the benzene rings play a quite subordinate part (*Zeitsch. Elektrochem.*, 1912, **18**, 478).

The suggestion cannot be excluded that compounds containing no benzene ring may, under certain conditions, give absorption spectra similar to those of benzene derivatives. Indeed, Hantzsch has pointed out the similarity between the absorption spectra of nitrobarbituric acid and *p*-nitrophenol. Under the influence of substituent groups, the benzene nucleus may so change that its properties approximate to those of unsaturated aliphatic compounds.

Kaufmann's hypothesis of the constitution of triphenylmethane dyes (A., 1912, i, 397) regards all the three nuclei as of the same

kind, and denies their conversion into the quinonoid form; this, too, is not in accord with the authors' observations.

Baly and Tuck (T., 1908, **93**, 1902) have shown that the absorption spectrum of diphenylmethane is quite similar to that of anthracene, so that diphenylmethane is also the chromogen of anthraquinone compounds. The relation between the latter and triphenylmethane dyes is thus established, and the similarity between their absorption spectra explained. T. H. P.

**Production of a Very Intense Sodium Flame.** R. W. WOOD (*Phil. Mag.*, 1914, [vi], **27**, 530—531).—If a small fragment of a Welsbach mantle is laid upon the grill of a Meker burner, and two or three pieces of fused sodium chloride are placed on this, a sodium flame of great brilliancy is obtained. The intensity is comparable with that of the oxy-hydrogen sodium flame. The effect is due to the spreading of the material over a large surface of very small heat capacity. H. M. D.

**Photometric Study of the Fluorescence of Iodine Vapour.** R. W. WOOD and W. P. SPEAS (*Phil. Mag.*, 1914, [vi], **27**, 531—538.\* Compare A., 1911, ii, 82, 169, 950).—Further experiments on the fluorescence of iodine vapour have been made with the object of determining to what extent the luminosity due to a molecule of iodine is diminished by the proximity of other iodine molecules. From observations of the intensity of the fluorescence at different pressures, it is found that this increases rapidly with the pressure, attains a maximum at a pressure of 0.2 to 0.3 mm., and then decreases gradually. At the lowest pressures the intensity is directly proportional to the number of iodine molecules, but at higher pressures the intensity is diminished, in consequence of the interaction of the separate molecules. This intermolecular effect has already been observed when other gases are present in the tube containing the iodine vapour, and on comparing the action of iodine with that of other gases and vapours, it is found that the intensity of the fluorescence is reduced to the same extent by hydrogen at 24 mm., air at 11 mm., carbon dioxide at 7 mm., ether vapour at 3 mm., iodine chloride at 1.8 mm., and by iodine at a pressure of only 0.4 mm. The high activity of iodine vapour is to be attributed to its strongly electronegative character.

The colour of the fluorescent light changes from yellow to red as the density of the iodine vapour increases, and this is probably due to absorption, for it has been found that the fluorescent light is more strongly absorbed by iodine vapour than light of the same colour which was obtained by filtering the light from a Welsbach burner through suitable colour-filters. The effect of absorption is, however, small in comparison with that which results from the mutual action between the molecules. H. M. D.

**Solubility and [Optical] Activity.** G. PELLINI and A. COPPOLA (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 144—150) —The data hitherto available do not suffice to show the nature of inactive alanine. By

\* and *Physikal. Zeitsch.*, 1914, **15**, 317—321.

simultaneous measurements of solubility and rotatory power in various mixtures of *d*-alanine and *l*-alanine in water at 0°, 17°, and 30°, the authors obtain material for the construction of diagrams which indicate that inactive alanine is a true racemic compound, and in a discussion of the curves obtained the authors show that they afford at least a partial confirmation of Meyerhoffer's rules regarding the solubility of optically active substances.

The specific rotatory power of alanine hydrochloride in aqueous solution is independent of the concentration. R. V. S.

**Discovery of the Sensitiveness of Silver Salts to Light.** FELIX FRITZ (*Chem. Zeit.*, 1914, 38, 246—247).—Historical. Schulze is generally believed to have been the first to discover, in 1727, the action of light on silver salts. The author points out, however, that W. Homberg, in 1694, showed that when bones were immersed in a solution of silver nitrate, they blackened on exposure to sunlight. The reference is found in "*Regiae Scientiarum Academiae Historia*," by Joanne-Baptista du Hamel. T. S. P.

**Chemical Action of Light. XXIX. Autoxidations. VII.** G. CIAMICIAN and P. SILBER (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 113—119; *Ber.*, 1914, 47, 640—646. Compare A., 1913, ii, 545).—Acetic acid undergoes slow autoxidation when exposed to light, formic acid being formed.

Glycollic acid in the light in the presence of oxygen is almost completely oxidised to carbon dioxide and formaldehyde.

Oxalic acid in similar circumstances yields carbon dioxide.

Malonic acid yields carbon dioxide, formaldehyde, and acetic acid.

Succinic acid yields carbon dioxide, acetaldehyde, acetic acid, possibly propionic acid, and glyoxal.

Pyrotartaric acid is but little affected by oxygen and light.

Glyceric acid yields carbon dioxide, formaldehyde, and glyoxal.

Saccharic acid is oxidised to a considerable extent, with formation of carbon dioxide and formic acid.

Coumarin yields principally the polymeride, Dyson's dihydrocoumarin, which is formed in the absence of oxygen in smaller quantity, salicylic acid, and a substance of m. p. 163°.

Oleic acid yields formic acid, nonoic acid, azelaic acid, dihydroxystearic acid, a substance of m. p. 56°, and some of the lower members of the fatty acid series. R. V. S.

**Syntheses in Organic Chemistry by means of Light. VIII. Various Experiments.** E. PATERNÒ [with G. CHIEFFI and G. PERRET] (*Gazzetta*, 1914, 44, i, 151—164. Compare A., 1909, i, 393; 1910, i, 41).—In the experiments here described, the reagents were subjected to the action of light for periods varying from a few months to two or three years.

Acetaldehyde and alcohol seem to give butane- $\beta$ -diol (see Eltekov, A., 1883, 566), which was, however, not isolated in a pure state.

Benzaldehyde and acetophenone give a polymeride of benz-

aldehyde, and benzaldehyde and benzophenone apparently yield the trimeric benzaldehyde described by Mascarelli (A., 1906, i, 962).

Salicylaldehyde and amylene do not react.

*p*-Tolualdehyde and decane (diisoamyl) give *tolupinacone*, which forms colourless needles, m. p. 155—157°.

*p*-Tolualdehyde and amylene yield hydrotoluylide,  $C_{16}H_{18}O_2$ , and an additive compound,  $C_{13}H_{18}O$ , b. p. 250—252°,  $D_0^{20}$  0.9714,  $D_0^{20}$  0.9646,  $D_0^{38.6}$  0.9424,  $D_0^{100.24}$  0.8955,  $n_D^{17.2}$  1.5081, which has the normal molecular weight in freezing benzene.

Acetone with either amylene or acetic or butyric acid gives no products which could be readily isolated.

Acetophenone and benzyl alcohol give  $\alpha\beta$ -diphenylpropanediol. Tiffeneau and Dorlencourt (*Ann. Chim. Phys.*, 1909, [viii], 16, 252) prepared a compound, m. p. 192°, which they described as the carbazone of this glycol, but the action of semicarbazide hydrochloride on the glycol obtained by the author yields acetophenone semicarbazone, m. p. 200°, the glycol thus undergoing resolution into its components.

Anisaldehyde and toluene give only a little hydroanisoin, benzylphenol and benzophenone only benzopinacone, and oxalic acid and amylene traces of polymerides of amylene.

Benzil reacts with decane, but no product could be isolated; with amylene, benzil gives a pasty resin of liquid crystals, having the composition of a compound of the two components.

Saligenin gives: (1) with benzophenone, only benzopinacone; (2) with acetophenone, salireton (compare Giacosa, A., 1880, 716); (3) with amylene, no additive product, the phenolic hydroxyl, like that of salicylaldehyde, hindering the reaction.

Deoxybenzoin and alcohol yield the  $\alpha$ - and  $\beta$ -pinacones of deoxybenzoin, described respectively by Limpricht and Schwanert (*Annalen*, 1870, 155, 60), and by Wislicenus and Blank (A., 1889, 261). Deoxybenzoin and toluene give benzoic acid and the  $\alpha$ -pinacone of deoxybenzoin, which is also obtained, together with another crystalline compound and a resin, from deoxybenzoin and ethylbenzene. Deoxybenzoin and phenylacetic acid seem to form a complex acid, which could not be purified.

In presence of chloroform, xanthone and amylene give a compound,  $C_{13}H_{18}O$  (?), crystallising in dark orange-red needles, m. p. 190—192°.

With toluene or acetophenone, piperonaldehyde yields a compound (C 58.85%, H 4.39%), forming colourless crystals, m. p. 226—228°.

In presence of amylene, dimethylpyrone is converted into a *dimeride*, m. p. 183°. This polymerisation of dimethylpyrone occurs also under the influence of the sun's rays alone, but does not take place in alcoholic solution, whilst in aqueous solution it proceeds to a slight extent.

In aqueous solution, pyrone undergoes no sensible alteration, but alone or in presence of amylene it is converted into a rust-red, amorphous polymeride, which is virtually insoluble in water or organic solvents. This polymeride resembles some of the pentosans,

and, like pyrone itself, gives some of their reactions, although it yields no furfuraldehyde. Phloroglucinol gives with arabinose a red coloration, which is also obtained less intensely with pyrone, and still less intensely with the polymeride. With orcinol, arabinose gives a violet-green coloration, whilst pyrone and its polymeride yield orange-red colorations, changing to greenish. With 1:3-dihydroxynaphthalene, arabinose gives a violet-blue coloration and a precipitate, whilst pyrone and the polymeride form intense blue colorations, and also precipitates.

From their composition, pyrone and its polymeric modification may be regarded as dehydration products of pentosans.

T. H. P.

**Fitful Point Discharges and the Electric Method of Counting  $\alpha$ - and  $\beta$ -Particles.** L. MYSSOVSKI and K. NESTURCH (*Ann. Physik*, 1914, [iv], **43**, 461—472).—The "natural disturbances" in counting  $\alpha$ -particles by the electric method, which Rutherford and Geiger ascribed to the natural radioactivity of the walls of the cylindrical condensers, were found to depend on the unevennesses of the electrode-surfaces. Such natural disturbances often exceed in magnitude those produced by  $\alpha$ -rays, and because of them no electrical method of counting  $\alpha$ -particles can be used as a control of the optical or scintillation method.

F. S.

**Fresh Verifications of the Laws of Transparency of Matter to X-rays, in the Special Case of Inorganic Complexes.** LOUIS BENOIST and HIPPOLYTE COPAUX (*Compt. rend.*, 1914, **158**, 559—561. Compare A., 1901, ii, 215).—The authors have examined three inorganic complexes, namely, potassium ferricyanide, purpureo-cobalt chloride, and potassium silicomolybdate, and find a close agreement between the values calculated and found for  $E$ , the equivalent of transparency. The calculation is made from the equivalents of transparency of the elements in the complexes, according to the formula  $M/E = \sum m/e$ .

W. G.

**Long-waved Residual Rays (Reststrahlen).** H. RUBENS and H. VON WARTENBERG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, **7**, 169—190. Compare *ibid.*, 1913, 530; A., 1910, ii, 172).—Seven new groups of residual rays, with wave-length in the neighbourhood of  $50 \mu$ , from ammonium chloride and bromide, thallium chloride, bromide and iodide, silver cyanide and mercuric chloride, have been examined, and their mean wave-length determined and compared with the frequency formulæ of Madelung and of Lindemann. The plates are prepared between steel dies in a hydraulic press under 3000 at. pressure, and are turned in the lathe. An unpolished surface is advantageous, as after three or four reflections all shorter waves are scattered and eliminated. Measurements are made with the quartz interferometer, through a total thickness of 2 mm. of quartz, in a desiccator when necessary to avoid absorption of the rays by water vapour, a common Auer burner being the source of light. For ammonium chloride, the mean wave-length

is  $51.5\ \mu$ , which is almost exactly that of rock salt. For the other substances, the wave-lengths found were: ammonium bromide,  $59.3$ ; thallium chloride,  $91.6$ ; silver cyanide,  $93$ ; mercuric chloride,  $95$ ; thallium bromide,  $117$ ; and thallium iodide,  $151.8$ . A comparison of the results with theoretical formulæ showed general agreement, but the data are insufficient to decide between them.

F. S.

**Extraction of Radium from the Olary Ores.** S. RADCLIFF (*J. Soc. Chem. Ind.*, 1914, **33**, 229—232).—An analysis of the Olary ore has already been published by Crook and Blake (*A.*, 1910, ii, 308); even when concentrated, it contains only 8 mg. of radium, calculated as bromide, per ton.

After dry-crushing and sieving, the ore is concentrated magnetically. The concentrates, amounting to about 30% of the ore crushed, give the following analysis:

CaO.	PbO.	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	ThO <sub>2</sub> , Ce <sub>2</sub> O <sub>3</sub> , (La, Di, Y) <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	U <sub>3</sub> O <sub>8</sub> .	V <sub>2</sub> O <sub>5</sub> .	TiO <sub>2</sub> .	SiO <sub>2</sub> .
0.55	0.16	17.4	16.9	trace	3.27	0.85	1.6	0.86	45.85	12.70

After fusion with sodium hydrogen sulphate, the fused product is crushed, and then agitated in a continuous current of water in such a way that the coarse material which separates is almost free from radium and uranium. The turbid liquid carries in suspension the radium, lead, and barium as sulphates, together with a considerable amount of finely divided silica; in solution are the uranium rare earths and part of the iron and acid earths contained in the ore. The "slimes" from the turbid liquid, when dry, form about 10% of the weight of the concentrates, and are treated for the recovery of radium; the clear liquid from the slimes is treated for uranium.

To recover the uranium, the clear liquid is treated with an excess of a mixture of sodium carbonate and hydrogen carbonate, whereby the iron and most of the other bases are precipitated. After collecting the precipitate, the filtrate is made acid with sulphuric acid, the carbon dioxide expelled with a current of air, and the uranium precipitated with ammonia. After collecting the precipitate, drying, crushing, and washing it to remove sodium salts, a residue is obtained which, when dry, contains about 75% of U<sub>3</sub>O<sub>8</sub>.

The radium is recovered from the slimes as follows. They are treated with sulphuric acid to form the insoluble sulphates of barium, lead, and radium. After washing free from sulphuric acid, the sulphates are converted into the carbonates by boiling with a solution of sodium carbonate, a large amount of the silica being thereby dissolved. The washed carbonates are then converted into chlorides by treatment with hydrochloric acid, and the sulphates again precipitated from the solution. The crude sulphates thus obtained are fused with sodium carbonate in graphite pots, and the product digested with hot water. The insoluble residue, after picking out the metallic lead, is heated with hydrochloric acid, the solution evaporated to dryness to dehydrate the silica, the residue treated with acid and hot water, and the

silica collected. The chloride solution is then saturated with hydrogen chloride, whereby barium and radium chlorides are precipitated nearly free from the other elements (Soddy's method). The chlorides are then converted, through the carbonates, into the bromides for the purpose of fractionation.

About 1500 grams of dry chloride, which when freed from radioactive substances other than radium have an equilibrium activity of 40 to 50, are obtained weekly.

T. S. P.

**Uranium-Y.** OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1914, 15, 236—240. Compare this vol., ii, 89).—The existence of uranium-Y has been put beyond doubt. It gives low-velocity  $\beta$ -rays, and its half-period is given as 25.5 ( $\pm 0.5$ ) hours. In chemical properties it is the same as uranium-X or thorium, and it results either from uranium-I together with uranium-X, or from uranium-II together with ionium.

In several experiments on the decay of uranium-X + uranium-Y preparations, the value for the half-period varied between twenty-one and twenty-six hours. The recovery curve of uranium, purified with great care from uranium-X + uranium-Y, showed the effect of uranium-Y, and the period calculated from this curve agreed with that found for the decay curves. Uranium-Y was shown to be non-separable from uranium-X by adding thorium to the mixture and precipitating it by characteristic reactions, which failed to alter the ratio between uranium-X and uranium-Y.

F. S.

**The Action of the Electric Discharge in Helium on the Radium Emanation.** L. BRUNER and E. BEKIER (*Physikal. Zeitsch.*, 1914, 15, 240—241).—With the idea of ascertaining whether the rate of disintegration of the radium emanation would be affected by increase of the concentration of one of the reaction products, namely, charged helium atoms, the rate of decay of the  $\gamma$ -rays from a tube containing radium emanation and helium through which a discharge was kept passing was measured. The result was negative, and no alteration of the disintegration constant of the emanation under these conditions was observed.

F. S.

**Decomposition of Ammonia Gas under the Action of Radium Emanation, and Influence of the Temperature on the Chemical Effects Produced by the Radiations from Radioactive Substances.** EUGÈNE WOURTZEL (*Compt. rend.*, 1914, 158, 571—573).—The results obtained with hydrogen sulphide as to the influence of temperature and pressure on the decomposition produced by radium emanation (compare this vol., ii, 18) being inconclusive owing to the possibility of re-combination of the hydrogen and sulphur under the experimental conditions, the author has repeated the work with ammonia, and obtained more conclusive results.

Ammonia is decomposed by the emanation into nitrogen and hydrogen without any other reaction taking place. The quantity of gas decomposed for destruction of unit radiation increases with



the pressure, but approaches a limit, the pressure effect being solely one of improving the absorption of the radiation of the gas. The amount of ammonia decomposed by 1 curie of emanation at the ordinary temperature is 219.2 c.c. (compare Usher, T., 1910, **97**, 389, 1193). Rise in temperature favours the destruction of the ammonia, being twice this amount at 108° and more than three times it at 220°.

W. G.

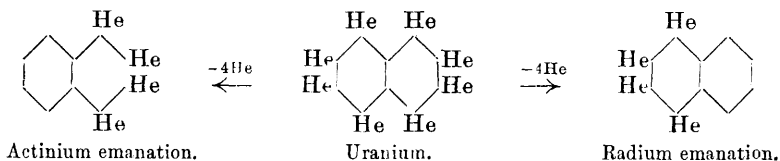
**Helium of Coal Mine Gases and Radioactivity of Coals.** CHARLES MOUREU and ADOLPHE LÉPAPE (*Compt. rend.*, 1914, **158**, 598—603. Compare A., 1911, ii, 1087).—In view of the fact that the various samples of coal mine gases examined (*loc. cit.*) were found to contain appreciable quantities of helium, the authors have examined samples of coal from the same sources as the natural gases, for the presence of thorium and radium. Minute quantities of these two elements were invariably present, but these were far too small to account for the amount of helium evolved. The source of the helium in the coal is not at present solved.

W. G.

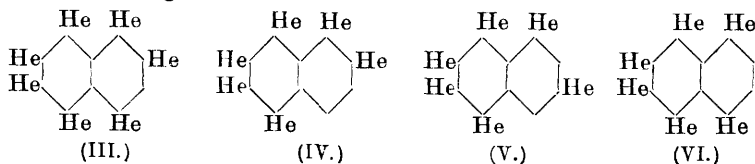
**Radioactivity and Atoms.** GIUSEPPE ODDO (*Gazzetta*, 1914, **44**, i, 200—218).—Historical account of radioactivity since Röntgen's discovery in 1895.

T. H. P.

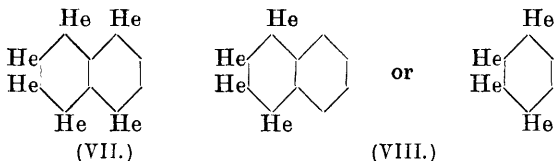
**Molecular Structure of Radioactive Atoms.** GIUSEPPE ODDO (*Gazzetta*, 1914, **44**, i, 219—235).—In order to explain the loss of helium atoms during the disintegration of radioactive elements, the author suggests that these atoms are arranged in the form of one or of two contiguous hexagons, in the same way as the carbon atoms of the benzene or naphthalene molecule. The uranium atom would thus contain eight helium atoms in two hexagons, which must differ in some way one from the other, loss of four helium atoms occurring in two modes to yield actinium emanation and radium emanation:



The loss of He from the  $\alpha'$ -position would give an unknown term, which undergoes transformation into (III), representing uranium-2, whilst further loss of He would yield uranium-Y (IV), uranium-X (V), and ionium (VI), three, and only three, such isomerides being known:



Elimination of He from (VI) gives only one product, radium (VII), which, in its turn, gives only radium emanation or niton (VIII):



Continuing the elimination, and indicating the positions by the numbers 1, 2, 3, 4, we get: 1:2:3 (?); 1:2:4, radium-*A*; 1:2, radium-*B*; 1:3, radium-*C*; 1:4, radium-*C*<sub>2</sub>; 1, radium-*D*; 2, radium-*E*; 3, radium-*F*=polonium. Complete elimination would render the material residue of the new atom (? lead) non-radioactive.

Thus, of the sixteen elements which should exist according to the author's hypothesis, fourteen are known, the positions of the heliums in the two as yet unknown being 1:2:3:4:5:6:7 and 1:2:3. The analogies between these two structures suggest that there is no tendency to form such elements, so that in nuclei containing four atoms of helium, the elimination commences at the  $\beta$ - rather than at the  $\alpha$ -position; it may be, however, that such elements are formed, but that they give no rays, and are of short duration.

For the other two series of radioactive elements we have, similarly: Actinium series: 1:2:3:4:5:6:7:8, uranium-1; 1:2:3:5:6:7:8, ?; 1:2:4:5:6:7:8, homouranium-2 (?); 1:2:5:6:7:8, homouranium-*y* (?); 1:3:5:6:7:8, actinium (?); 1:4:5:6:7:8, radioactinium; 1:5:6:7:8, actinium-*x*; 5:6:7:8, actinium emanation; 6:7:8, ?; 5:7:8, actinium-*A*; 7:8, actinium-*B*; 6:8, actinium-*C*; 5:8, actinium-*C*<sub>2</sub>; 8, actinium-*D*; complete elimination, lead (?). Here, too, all the known terms are foreseen by the hypothesis, there being four gaps.

Thorium series: 1:2:3:4:5:6:7:8, anthorium(?); 1:2:3:4:6:7:8, ?; 1:2:3:4:5:7:8, thorium; 1:2:3:4:7:8, mesothorium-1; 1:2:3:4:6:8, mesothorium-2; 1:2:3:4:5:8, radiothorium; 1:2:3:4:8, thorium-*x*; 1:2:3:4, thorium emanation; 1:2:3, ?; 1:2:4, thorium-*A*; 1:2, thorium-*B*; 1:3, thorium-*C*; 1:4, thorium-*C*<sub>2</sub>; 1, thorium-*D*.

A table is given showing, in parallel columns, for the corresponding members of each of the three series, the atomic weight, the nature of the rays emitted, and the time in which one-half of the element undergoes transformation.

Taking the table given by F. W. Clarke to show the percentages of the twenty elements occurring in the largest proportions in the earth's crust, the author calculates in each case by how much the atomic weight differs from a multiple of 4. Thus, the first few elements are: oxygen, 49.78%,  $16=4 \times 4+0$ ; silicon, 26.08%,  $28.3=4 \times 7+0.3$ ; aluminium, 7.34%,  $27.1=4 \times 7-0.9$ ; and so on. These twenty elements together make up 99.54% of the earth's

crust, and with only five of them, namely, sodium, barium, manganese, nitrogen, and fluorine, which give a total of 2.54%, is this atomic-weight difference equal to or greater than 1; with three, namely, aluminium, potassium, and phosphorus, the total percentage content is 9.73, and the difference equals or exceeds 0.9; then follow chlorine (0.21%), 0.54; strontium (0.03%), 0.37; and magnesium (2.24%), 0.32. So that, with the elements constituting 86.5% of the earth's crust, the differences of the atomic weights from multiples of 4 are not greater than 0.3. This may be mere coincidence, or it may be that non-radioactive atoms, or at least certain of them, are to be regarded as stable condensation terms of helium atoms (compare Collins, A., 1913, ii, 313).

T. H. P.

**The Amount of Radioactive Products in the Atmosphere.** SHINZÔ SATÔ (*Sci. Reports, Tôhoku Imp. Univ.*, 1913, 2, 171—174).—Details are given of experiments at the Tôhoku University on the amount of active deposit obtained from the atmosphere upon a negatively charged wire. The mean ratio of the effect due to radium to that due to thorium was 9.7, which corresponds with the ratio of 5000 to 1 for the relative concentrations of the two emanations in the atmosphere. Expressed in terms of curies per cubic metre, the mean value for the radium emanation was  $83 \times 10^{-12}$ , which agrees with results obtained in Montreal, Chicago, and Cambridge, but is greater than that found in Tokio. F. S.

**Acceleration of Electrical Conductors.** RICHARD C. TOLMAN, EARL W. OSGERBY and T. DALE STEWART (*J. Amer. Chem. Soc.*, 1914, 36, 466—485).—In an earlier paper (A., 1911, ii, 248) attention was directed to the fact that there is a difference of electrical potential between the two ends of a vertical tube of a salt solution, which is due to the effect of gravitation, and experiments were described on the measurement of the *E.M.F.* produced by centrifugal force.

It is now pointed out that a tube of a salt solution, when subjected to acceleration, should show a difference of potential between the two ends, and a theory is developed leading to an expression for calculating the value of this potential difference. Experiments are described in which an apparatus was employed which consisted essentially of a glass tube provided with electrodes, and bent to fit into the rim of an ordinary bicycle wheel. The tube was filled with the electrolyte, the wheel given a sudden acceleration, and the current noted which flowed through a galvanometer placed in the external circuit which connected the two electrodes. The electrolytes used were solutions of potassium, sodium, and lithium iodides, containing 1 mol. of the salt and 1/100 mol. of iodine per kilogram of water. The results afford conclusive proof that potential differences are developed at the ends of a column of accelerated electrolyte, and they agree fairly well with the requirements of the theory.

Experiments have also been made with metallic conductors.

Insulated copper was wound in a groove cut in the edge of a disk of an aluminium alloy, the ends of the wire being connected with insulated binding posts at the centre of the disk. The disk was caused to rotate very rapidly, and was then suddenly stopped, and observations were made of the pulse of electricity through the galvanometer, which was connected directly in series with the rotating coil. The results show that the mass of the mobile carrier of electricity in metals is probably less than  $1/200$  of that of the hydrogen atom. It is considered that it would be possible to increase the sensitiveness of this method to a point at which the electron, if it really is the carrier of electricity in metals, with a mass of  $1/1800$  of that of the hydrogen atom, should produce an appreciable effect. E. G.

**The Specific Inductive Power of Liquids.** C. GUTTON (*Compt. rend.*, 1914, **158**, 621—623).—The specific inductive power of liquids, such as toluene, in which the value is low, shows no variation with increase in intensity of the electric field. For liquids of higher specific inductive power, such as  $\alpha$ -bromonaphthalene, there is a feeble decrease with increase in the magnetic field. For the specific inductive powers at  $15^\circ$  the following values were obtained: toluene, 2.36; carbon disulphide, 2.61;  $\alpha$ -bromonaphthalene, 4.72—4.69, varying with the intensity of the field. W. G.

**Passivity of Metals.** WILHELM RATHERT (*Zeitsch. physikal. Chem.*, 1914, **86**, 567—623).—The author has examined the metals iron, nickel, and chromium in solutions of sulphuric acid and several sulphates during anodic polarisation. It is shown that the potential at which the passive metal becomes active is not the same as that at which the active metal becomes passive, and that the point of sudden change of potential observed by Flade (A., 1912, ii, 558) does not represent the boundary potential below which the metal is active and above which it is passive. It is shown that a metal may be active or passive on both sides of this point, depending on its previous treatment. The potential at which iron becomes passive is dependent in a marked degree on the concentration of the electrolyte in which the anodic polarisation is effected, whilst the potential at which passive iron becomes active is not. The appearance of the passivity potential and the activity potential during anodic polarisation is dependent on the current density, and consequently on the oxygen concentration on the electrode. These various facts are not to be explained on the oxide theory of passivity, but they find an easy explanation on the hydrogen theory. The passage of the one form into the other, under stated conditions, takes place at definite potentials in the case of iron and chromium, but there is no such definite potential in the case of nickel, the passage of the one form into the other taking place gradually. Polished chromium is not active in hydrogen, as is demanded by the oxide theory; this fact is, however, in accord with the hydrogen theory. Nickel is also not active after polishing in hydrogen, and

then dipping into a liquid which has the property of rendering metals passive. Passive chromium becomes active when it is charged electrolytically with hydrogen; the potential of nickel is also very much reduced by charging with hydrogen, and in a solution which ought to render it passive in these circumstances it becomes active. Molecular hydrogen has hardly any action on the potential of a passive chromium electrode. It is also shown that passive iron, which does not pass into solution electrolytically, on the absorption of hydrogen ions by diffusion becomes active, and then dissolves strictly in accordance with Faraday's law. The same fact is also observed in the case of chromium, which is further evidence in favour of the hydrogen theory. J. F. S.

**A Scheme for the Dissociation of Ternary Electrolytes.** CARL DRUCKER (*Zeitsch. Elektrochem.*, 1914, 20, 83—84).—Polemical; an answer to Wegscheider's (this vol., ii, 95) criticism of the author's previous paper (A., 1913, ii, 1015). J. F. S.

**Influence of a Magnetic Field on the Electromotive Force of Elements and on Chemical Processes.** W. RATHERT (*Zeitsch. Elektrochem.*, 1914, 20, 145—151).—The effect of a magnetic field on the element  $\text{Fe} \mid \text{FeSO}_4 \mid \text{CuSO}_4 \mid \text{Cu}$  is investigated; it is shown that there is no difference in the *E.M.F.* set up, whether a magnetic field is applied or not. The experiments of Remsen (*La Lumière Électrique*, 1882, 4, 126) show that when a solution of copper sulphate is placed on an iron plate lying across the poles of a magnet the copper is deposited in different thicknesses on the plate, thinner just above the poles and thicker further away. The author is able to confirm these results, and offers the following explanation. The copper is at first uniformly deposited, with the formation of ferrous sulphate; this substance, being more magnetic than copper sulphate, is held to the surface of the iron over the poles, and so fresh copper sulphate cannot diffuse to the plate, and so react, whereas in the regions remote from the magnetic poles the iron sulphate is free to diffuse, and in consequence the layer of copper in these places can become thicker. Similar results are observed with other metals, and this appears to be a complete proof that the phenomena observed by Remsen are not due to a change in the solubility of iron under the influence of a magnetic field. It is shown that if the susceptibility of the salt produced in reactions, similar to that described above, is greater than that of the original salt, then the deposit of metal will be thinner in positions of great magnetic intensity and thicker in positions of weaker magnetic intensity, and if, on the other hand, the susceptibility of the original salt is the greater, then the metal will be deposited in greatest thickness in the regions of greatest magnetic intensity. This explanation also makes it clear why an *E.M.F.* is set up in cells of the type  $\text{Fe}$  (magnetised),  $\text{H}_2\text{SO}_4$ ,  $\text{Fe}$  (non-magnetised). In the case of the magnetised iron, the ferrous sulphate produced is held to the metal, whereas in the case of the non-magnetised iron the ferrous sulphate diffuses, so that the element resolves itself into a concentration cell. It is also

shown that a magnetic field is unable to bring about a separation of a liquid mixture even when the salts in solution have very different susceptibility. A magnet, which is protected from chemical action (that is, by covering with varnish), when placed in a magnetic solution is also unable to effect a change in the concentration of the solution. This is only possible when the magnetic substance is being produced by chemical action on the magnet itself. J. F. S.

**Transition Temperatures of the Hydrates of Sodium Carbonate as Fixed Points in Thermometry.** THEODORE W. RICHARDS and AUGUSTUS H. FISKE (*J. Amer. Chem. Soc.*, 1914, **36**, 485—490).—In earlier papers (A., 1898, ii, 555; 1899, ii, 354; 1903, ii, 411; 1906, ii, 727; 1908, ii, 16; 1911, ii, 695) it has been shown by Richards and his co-workers that the transition temperatures of certain hydrated, crystalline salts form convenient fixed points for standardising thermometers.

Attention has now been directed to the use of sodium carbonate for this purpose. The work of previous observers, especially that of Wells and McAdam (A., 1907, ii, 542), has been confirmed, which shows that the stable hydrates of this salt are: between  $-2.1^{\circ}$  and  $32.0^{\circ}$ , the decahydrate; between  $32.0^{\circ}$  and  $35.4^{\circ}$ , the heptahydrate; and above  $35.4^{\circ}$ , the monohydrate. The transition temperature between the decahydrate and the heptahydrate has been carefully determined, and found to be  $32.017^{\circ}$  on the hydrogen scale, as compared with the value  $32.00^{\circ}$  obtained by Wells and McAdam (*loc. cit.*). When the hydrates are left at the ordinary temperature in air dried by sulphuric acid, they all easily lose water, and become converted into the anhydrous salt. E. G.

**Specific Heat  $c_p$  of Air between 1 and 200 Atmospheres.** L. HOLBORN and M. JAKOB (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 213—219).—Measurements of the specific heat of air have been made at pressures of 1, 25, 50, 100, 150, and 200 atmospheres by the continuous-flow method described by Callendar. Observations at each of these pressures were taken with three, and in some cases four, different rates of flow of air.

Over this range of pressure, the specific heat (at  $59^{\circ}$ ) increases from 0.2415 to 0.2925. The experimental values are satisfactorily represented by the equation

$$10^4 c_p = 2413 + 2.86p + 0.0005p^2 - 0.00001p^3.$$

The increase in the specific heat with increase of pressure is much smaller than that indicated by Lussana's measurements. The authors' results are, however, in good agreement with those calculated from the Thomson-Joule effect on the basis of Linde's theory.

H. M. D.

**Specific Heat of Solids. III.** H. VON JUPTNER (*Zeitsch. Elektrochem.*, 1914, **20**, 105—109. Compare A., 1913, ii, 921; this vol., ii, 99).—A mathematical paper in which formulæ are deduced giving the atomic and molecular heat of solid substances. The author deduces the equations from the idea of an energy value under

which the atoms just fail to vibrate, and from this it is shown that the mean vibrational energy,  $E$ , of a solid substance is of the same dimensions as the mean kinetic energy,  $E_0$ , of a gas, the ratio between the original energy value,  $\epsilon'$ , and the mean energy,  $E_0$ , is given by  $\epsilon'/E_0 = \beta\nu/T$ , whereby  $\beta\nu$  has a value twice as large as the value  $\beta\nu'$  of the previous publications (*loc. cit.*). Also  $\beta\nu$  (Jüptner)  $= 4/5\beta\nu$  (Nernst and Lindemann)  $= 8/15\beta\nu$  (Einstein). On the above expression,  $N_0 e^{-\beta\nu/T}$  gives the number of atoms in vibration.

J. F. S.

**Variation with Temperature of the Specific Heat of Sodium in the Solid and the Liquid State; also a Determination of its Latent Heat of Fusion.** EZER GRIFFITHS (*Proc. Roy. Soc.*, 1914, A, 89, 561—574).—The method described in a previous paper (A., 1913, ii, 753) has been employed in the determination of the specific heat of sodium in the solid state between 0° and 94°, and in the liquid state between 100° and 140°. About 350 grams of sodium were employed in the measurements, the solid being enclosed in a copper envelope, which was filled while the sodium was in the molten condition.

The specific heat of solid sodium increases with temperature, but its absolute value at a given temperature has been found to depend on the previous thermal treatment of the metal. At temperatures below about 60°, the specific heat is greater in the “quenched” condition than in the “annealed” condition, and from measurements of the density by a differential method it has been found that the density of annealed sodium is greater than that of the quenched metal to the extent of 1 part in 7000. The specific heat of liquid sodium varies with the temperature according to a linear equation, the temperature-coefficient being equal to  $-0.00034$  per 1°.

By a slight variation in procedure, the method has been applied to the determination of the latent heat of sodium, giving a mean value of 27.52 cal. The melting point of the metal was found to be 97.61°.

H. M. D.

**The Heat of Fusion of Hydrated Salts and of Hydrates in General.** CH. LEENHARDT and A. BOUTARIC (*Compt. rend.*, 1914, 158, 474—477).—A theoretical paper in which the authors show that, as a first approximation, in the majority of cases the heat of fusion of a hydrate is equal to the heat of fusion of the water it contains. If a greater precision is desired, the authors do not think that it is at present possible to affirm that the heat of fusion of the hydrate is the sum of the heats of fusion of the anhydrous substance and the water at the temperature of fusion of the hydrate. The chemical affinity between the anhydrous substance and the water does not appear to be necessarily the same in the solid and liquid states.

W. G.

**Properties of Iodine as a Cryoscopic Solvent.** F. OLIVARI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 41—45. Compare this vol., ii, 168).—The results obtained in the case of sulphur confirm those

previously published (A., 1909, ii, 37). The numbers obtained for the molecular weight of selenium dissolved in iodine are intermediate between those required by Se and Se<sub>2</sub>, except in very concentrated solutions, where the values approximate to Se<sub>2</sub>. Tellurium dissolves in iodine, with development of heat. It yields depressions corresponding very nearly with those calculated for monatomic molecules.

The alkali iodides, KI, RbI, NH<sub>4</sub>I, and the organic ammonium iodides, NH<sub>2</sub>Ph, HI, NMe<sub>4</sub>I, NMe<sub>3</sub>PhI, C<sub>6</sub>H<sub>4</sub>Me·NMe<sub>3</sub>I, show a characteristic anomalous behaviour in fused iodine. In very dilute solutions the molecular weights are almost normal. They increase rapidly with the concentration up to a certain point, then decrease again until, in some cases, at very high concentrations values below the theoretical are found.

R. V. S.

**An Efficient Boiling Rod.** GREGORY TOROSSIAN (*J. Amer. Chem. Soc.*, 1914, **36**, 513—514).—A piece of an alundum crucible or porous porcelain plate is crushed to fragments about 0.5 mm. in diameter, and heated to redness. The end of a glass rod, 10—12 cm. long, is softened by heat and dipped into the coarse powder, so that some of the particles adhere to it. This is repeated until a suitable quantity has been collected on the end of the rod. The rod is then heated to make the fragments adhere, and when it has cooled all the loose particles are rubbed off.

Another form of rod can be prepared by fusing one end of a narrow rectangular or triangular piece of alundum or porous porcelain into the end of a glass rod, and bending the latter so that the piece of alundum or porcelain will lie on the bottom of the beaker or flask. The boiling rod should not be placed in the liquid until it reaches the boiling point.

E. G.

**The Binary Systems Cyanamide–Water, Cyanamide–Carbamide and Cyanamide–Dicyanodiamide.** M. PRATOLONGO (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 46—52).—The thermal analysis of these systems shows that in all three cases simple eutectics exist, corresponding with 37.8% of cyanamide and –16.6°, 63.9% of cyanamide and 17.4°, and 85.0% of cyanamide and 35.6° respectively.

R. V. S.

**Thermodynamical Calculation of Chemical Affinities.** W. NERNST (*Ber.*, 1914, **47**, 608—635).—A lecture delivered before the German Chemical Society.

D. F. T.

**Thermodynamics of Calcium Hydride Formation.** J. N. BRÖNSTED (*Zeitsch. Elektrochem.*, 1914, **20**, 81—83).—The author has determined the dissociation pressure curve of calcium hydride between the temperatures 641° and 747°, and has shown that the values of  $\log_e p$ , calculated from the expression  $\log_e p = -Q_0/RT + \{(C_p - C_H)/R\} \log_e T + i$ , agree well with the observed values.  $C_p$  is the molecular specific heat of gaseous hydrogen at constant pressure, and  $C_H$  the specific heat of solid hydrogen, to which the



value 2.3 is attributed.  $Q_0$  and  $i$  are determined from the curves, and have values 42710 and 6.21. The equation therefore becomes  $\log_e p = -42710/RT + 4.2 \log_e T/R + 6.21$ , and from this the heat of formation of calcium hydride at  $18^\circ$  is found to be 43930 cal. The heat of formation is determined experimentally from calorimetric experiments on the heat of solution of calcium and calcium hydride in hydrochloric acid. At  $18^\circ$  these values are found to be per gram 3280 cal. and 2110 cal. respectively, or 135,400 cal. and 90,300 cal. per molecule respectively. The heat of formation of calcium hydride is therefore 45,100 cal. at  $18^\circ$  (compare Guntz and Bassett, A., 1905, ii, 300). Moldenhauer and Roll-Hansen (A., 1913, ii, 705) have shown the probability of the existence of a lower hydride of calcium, and in connexion with this the author shows that the heat of combination of each hydrogen atom is about the same,  $\text{Ca} + \text{H} \rightarrow \text{CaH} + 23,100 \text{ cal.}$  and  $\text{CaH} + \text{H} \rightarrow \text{CaH}_2 + 22,000 \text{ cal.}$  J. F. S.

**The Heat of Formation of Manganese Sulphide.** S. WOLOGDINE and B. PENKIEVITSCH (*Compt. rend.*, 1914, 158, 498—499).—A determination by two methods of the heat of formation of manganese sulphide,  $\text{MnS}$ . The first, which did not give concordant results, consisted in oxidation of the sulphide in a calorimeter filled with oxygen. The mean value for the molecular heat of formation in this case was 70,535 cal.

The second method consisted in measuring the heat evolved by the direct combination of finely powdered manganese and sulphur in an atmosphere of nitrogen in a Mahler bomb. The two substances were compressed into a pastille, and lit by a known quantity of a mixture of aluminium and potassium chlorate with a fuse of fulminating cotton. The values obtained in this way were, with one exception, concordant, and gave, for the molecular heat of formation, the mean value 62,901 cal. W. G.

**Heats of Combustion of Phototropic Substances.** M. PADOA and B. FORESTI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 95—98).—The two forms of salicylidene- $\beta$ -naphthylamine are found to have the same heats of combustion within the limits of experimental error, as also have the two forms of benzaldehydephenylhydrazone. R. V. S.

**Apparatus for the Determination of the Density of Gases.** M. HOFSSASS (*Zeitsch. angew. Chem.*, 1914, 27, 136).—The apparatus makes use of the principle of the Bunsen diffusimeter. It consists essentially of a U-tube, the limbs of which are in connexion with a straight tube, through which the main current of gas flows. By means of appropriate stop-cocks in the U-tube and the straight tube, the current of gas, for example, in a lighting system, can be deflected through the U-tube, which is thereby filled with gas under the pressure in the system. The U-tube is fitted with a manometer, and also with a Bunsen diffusion plate, the latter being cut off from the U-tube by means of a stop-cock. When this cock is

opened, the gas passes through the plate, and the time necessary for a given fall in the manometer reading to take place is noted. The apparatus having been previously calibrated with air, the density of the gas can thus be found. T. S. P.

**Molecular Attraction.** X. J. E. MILLS (*J. Physical Chem.*, 1914, **18**, 101—117).—A reply to Mathews' criticism (A., 1913, ii, 674) of the author's views on molecular attraction. It is pointed out that the equation  $\lambda = k(\sqrt[3]{d} - \sqrt[3]{D})$ , where  $\lambda$  is the internal heat of vaporisation,  $d$  the density of the liquid, and  $D$  that of the saturated vapour, is not empirical in the ordinary sense of the word, but was derived by the author as the final result of a definite theoretical argument. It is not to be expected that the above equation will agree with van der Waals' equation of condition, for this is known to be contradictory to observed facts. If the masses of the attracting molecules are supposed to be constant, the law of gravitational attraction leads directly to the equation  $\lambda = k(\sqrt[3]{d} - \sqrt[3]{D})$ . The assumption that the molecular attraction is not determined by the product of the masses of the molecules was not made, as alleged by Mathews, because of the disagreement of the author's equation with experimental data. H. M. D.

**Viscosity of Some Protein Solutions.** HARRIETTE CHICK and EVA LUBRZYNSKA (*Biochem. J.*, 1914, **8**, 59—69. Compare A., 1912, ii, 1042).—The authors have investigated the influence of concentration and of temperature on the viscosity of solutions of crystallised egg-albumin and (horse) serum-albumin.

The data for egg-albumin indicate that for solutions which contain less than about 9% of protein, the relation between viscosity and concentration can be approximately represented by a linear equation. At higher concentrations, the slope of the viscosity-concentration graph increases rapidly, until, at a concentration of 28%, the viscosity reached the value 10 ( $H_2O = 1$ ). Between 0° and 40°, the relative viscosity of solutions which contain less than 20% of egg-albumin falls to a slight extent only, but there is a much greater decrease in the case of a 28% solution. Measurements made with solutions prepared from dialysed and undialysed material show that the ammonium sulphate associated with the undialysed substance has no influence on the nature of the solution.

The data for (horse) serum-albumin show that the relative viscosity of its solutions is much greater than that of corresponding solutions of egg-albumin, and that the influence of temperature on a 20% solution is also much larger in the case of the serum-albumin.

Similar relations are exhibited by solutions of whole serum (horse). The relative position of the viscosity-concentration curve shows that proteins of higher viscosity than egg- or serum-albumin are present in the whole serum. H. M. D.

**Viscosity of Binary Mixtures.** EUGENE C. BINGHAM (*J. Physical Chem.*, 1914, **18**, 157—165).—A criticism of Kendall's view that the

logarithmic viscosity (or fluidity) is the property of a binary mixture which shows additive relations (this vol., ii, 109). The fact that the average percentage deviation between the calculated and observed viscosity, according to Kendall's formula, is smaller than that shown by any of the formulæ which have been previously put forward, is said to be due to the circumstance that contraction and heat development are characteristic of the majority of the mixtures which were submitted to examination. The fact that the specific volume of a liquid has been shown recently to be a linear function of its fluidity (Batschinski, A., 1913, ii, 26) is distinctly in favour of the view that the additive property is the fluidity.

H. M. D.

**Viscosity of Liquid Mixtures.** I. A. SACHANOV and N. RJACHOVSKI (*Zeitsch. physikal. Chem.*, 1914, 86, 529—537).—It is shown that the viscosity and fluidity of binary liquid mixtures is not a linear function of the composition, and consequently the viscosity and fluidity of mixtures cannot be represented by an equation of the form  $\eta = \eta_1(100 - p)/100 + \eta_2 p/100$ . The author deduces the following expression

$$\eta = \eta_1(100 - p)^2/(100)^2 + \eta_2 \cdot (p/100)^2 + n \sqrt{\eta_1 \eta_2} [(100 - p)p/(100)^2]$$

to represent the viscosity of mixtures. In this expression  $p$  is the molecular percentage of one constituent,  $\eta_1$ ,  $\eta_2$ , and  $\eta$  the viscosities of the two constituents and the mixture respectively, and  $n$  is a constant varying between 1.43 and 2.08. This equation is applied to mixtures benzene-chloroform, chloroform-bromobenzene, chloroform-phenetole, chloroform-diphenyl ether, and ethyl iodide-phenetole, which have been determined by the author. By suitable choice of the value of  $n$ , an agreement is obtained which is always within 3%. Similar agreement is also found with the measurements of Linebarger (A., 1897, ii, 247), Dunstan (T., 1905, 85, 222), and Faust (A., 1912, ii, 333). Some mixtures do not agree with the above expression, but the divergence is only found in those cases where one of the liquids has an abnormally high viscosity and an abnormally high viscosity temperature-coefficient.

J. F. S.

**The Absorption of Gases by Coal.** F. LEPRINCE-RINGUET (*Compt. rend.*, 1914, 158, 573—576).—A study of the absorption of gases, such as methane, carbon dioxide, air, or oxygen, by different kinds of coal under different conditions of temperature and pressure. There is a state of equilibrium for each temperature and pressure, the absorption decreasing rapidly with rise in temperature, and increasing at first rapidly, and then more slowly, with increase in pressure. The absorption is slow. The evolution of the gases absorbed occurs in puffs, like small explosions, even when the phenomenon is made extremely slow.

W. G.

**Relationship between Surface Tension and Adsorption.** WALTER A. PATRICK (*Zeitsch. physikal. Chem.*, 1914, 86, 545—563).—The surface tension of mercury in solutions, of various concentra-

tions, of mercurous sulphate, salicylic acid, picric acid, new magenta, morphine hydrochloride, and caffeine has been determined by allowing mercury to fall in small drops into the various solutions. In each case 60 drops were collected and weighed, and from the weight the surface tension was calculated. The value of the surface tension in each case diminishes with increasing concentration. The reduction of the surface tension is greatest in the case of mercurous sulphate and least in the case of caffeine, the other substances effecting it in the order given above. The adsorption of the above-mentioned substances on the surface of mercury was also determined, by allowing a finely divided stream of mercury to fall through a solution of the substance in question which was flowing in the opposite direction. The concentration of the solution was determined before and after the adsorption. It is shown that mercurous sulphate is most strongly adsorbed, and the other substances are adsorbed in the order of their influence on the surface tension. Curves are given for the influence of concentration on the surface tension and on the adsorption. It is clear from these that the adsorption is similar to that obtained with solid adsorbents—a large increase in the adsorbed amount from weak solutions and a saturation value from concentrated solutions. No satisfactory quantitative relationship could be found between the adsorption and the surface tension.

J. F. S.

**Adsorption of Colloidal Ferric Hydroxide.** PAUL ROHLAND (*Zeitsch. physikal. Chem.*, 1914, **86**, 633—634).—Carli (A., 1913, ii, 1029) has shown that kaolin does not adsorb ferric hydroxide; the author points out that there is a non-plastic form of kaolin which contains no colloidal substance, and consequently cannot exhibit any adsorptive properties. This variety only forms colloids on long keeping in moist air, and then it possesses strong adsorptive properties and reacts with hydroxyl ions.

J. F. S.

**Theory of Dyeing. II.** WILDER D. BANCROFT (*J. Physical Chem.*, 1914, **18**, 118—151. Compare this vol., ii, 178).—Further observations recorded in the literature have been examined, and further conclusions are drawn relative to the behaviour of dyes towards cotton, wool, and silk fibres.

Basic dyes are taken up most readily from an alkaline solution, although dyeing may occur in both neutral and acid solution. Readily adsorbed anions increase the quantity of basic dyes which are taken up by the fibre, whilst readily adsorbed cations have the opposite effect. For this reason, basic dyes are taken up by wood to a greater extent on the addition of sodium sulphate to the dye-bath, and the effect produced by sulphuric acid is found to be much greater than that produced by an equivalent quantity of hydrochloric acid.

H. M. D.

**Compounds of Dissolved Substance and Solvent in Solution.** NILRATAN DHAR (*Zeitsch. Elektrochem.*, 1914, **20**, 57—79).—The author gives a survey of the evidence on which the explanation

that the discontinuity in the physical properties of a series of solutions of a given substance in a given solvent is due to the formation of one or more compounds between molecules of the solvent and the dissolved substance. A very complete critical account is given of the work in this connexion with respect to the following physical properties of solutions: (1) abnormal electrical conductivity; (2) Kohlrausch's hypothesis on viscosity and electrical conductivity; (3) transport numbers; (4) osmotic pressure; (5) influence of other substances on solubility; (6) boiling point; (7) vapour pressure; (8) freezing point; (9) refractivity and molecular refraction; (10) absorption spectra; (11) density and volume relationships; (12) viscosity; (13) surface tension; (14) magnetic rotation; (15) anomalous electric absorption; and (16) specific heat.

J. F. S.

### Compounds of Dissolved Substance and Solvent in Solution.

C. DRUCKER (*Zeitsch. Elektrochem.*, 1914, **20**, 79—81. Compare preceding abstract).—The author adds several points, as an addendum to Dhar's paper, which tend to show the presence of compounds of the dissolved substance with the solvent in solution.

J. F. S.

**Ideal Concentrated Solutions.** J. N. BRÖNSTED (*Zeitsch. Elektrochem.*, 1914, **20**, 151—153).—Polemical. The author criticises statements of Nernst ("Theoretische Chemie," 1913) on his work in connexion with ideal concentrated solutions (A., 1910, ii, 112). It is maintained that Nernst's criticism is unjustified, and that the condition for an ideal concentrated solution,  $dU/dx = dA/dx$ , as given by Nernst, must be replaced by  $(dU/dx)_{x_1}^{x_2} = (dA/dx)_{x_1}^{x_2}$ . Ideal solutions are those which conform to the equations  $A_1 = -RT \log_e x$ ,  $A_2 = -RT \log_e(1-x)$ , where the symbols have their usual meanings. It is also held that Nernst's proof of his heat theory for sulphuric acid solutions is imperfect, because he applies the Thomsen formula outside the range in which it is strictly true, and because he has only made use of older data, taking no account of the newer data. Further, the calculation of the temperature relationship of the heat change is also open to criticism.

J. F. S.

[Ideal Concentrated Solutions.] W. NERNST (*Zeitsch. Elektrochem.*, 1914, **20**, 153—156. Compare preceding abstract).—Polemical; an answer to Brönsted's criticism. It is shown that Brönsted's condition for an ideal concentrated solution is identical with that of Nernst, but is written in an unusual way.

J. F. S.

**Determinations of the Degree of Hydration of Salts in Concentrated Solutions.** E. H. RIESENFELD and C. MILCHSACK (*Zeitsch. anorg. Chem.*, 1914, **85**, 401—429).—When the number of mols. of water per mol. of anhydrous salt in a saturated solution is plotted against the temperature, all salts, acids, and bases which contain water of crystallisation give similar curves, with maxima

at the number of mols. of water which enter into the crystalline hydrate. Dissociation in solution is indicated by a flattening of the maximum. Away from the maximum, the curves are nearly straight lines, so that the theoretical melting point of the undissociated compound may be found by extrapolation, and the dissociation of the hydrate at its melting point may then be computed. The degree of dissociation of a number of hexahydrates of metallic nitrates has been calculated in this way. Cobalt nitrate hexahydrate is much more dissociated than the nickel salt, although they both have the same melting point. Copper gives curves deviating widely from a straight line, probably owing to complex formation.

The heat of fusion of a number of nitrates and chlorides has been determined in a calorimeter composed of two concentric vacuum vessels, the salt being melted in a small silver shell by means of a vapour-bath. Toluene is the most suitable calorimetric liquid. The latent heat of fusion is then compared with the "total heat of fusion" computed from the solubility curves, the latter being always greater. The difference between the two values may be accounted for by assuming a higher molecular weight for water in the solutions. Walden's rule is confirmed, that the molecular heat of fusion, divided by the absolute melting point, is a constant. Good agreement is also found when the specific heat of the solid salt is calculated by Nernst's method from the specific heat of the liquid, the latent heat of fusion, and the temperature of fusion.

C. H. D.

**Surface Tension and Hydration in Solution.** M. PADOA and G. TABELLINI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 88—94).—The paper records the results of measurements of the surface tension of solutions by the method of Morgan and Higgins (A., 1908, ii, 668) with a view to the detection of association or hydration. The solutions dealt with included aqueous solutions of ammonium chloride ( $N$  and  $3N$ ), cobaltous chloride ( $N$ ), sodium bromide ( $N$ ), magnesium chloride ( $N$ ), and hydrogen chloride ( $N$ ,  $2N$ , and  $3N$ ). The results are most striking in the case of the solutions of hydrogen chloride, which give values indicating a very high degree of association.

R. V. S.

**Decline of the Hypothesis of Ionic Dissociation.** F. P. WORLEY (*Phil. Mag.*, 1914, [vi], 27, 459—467).—A criticism of the ionic theory, with special reference to the connexion between the chemical activity of electrolytes and their presumed degree of ionisation. The assumption that the hydrolytic activity of acids is partly due to the action of the non-ionised molecules is supposed to remove one of the strongest arguments in support of the theory. If applied to the interpretation of the author's observations on the rate of inversion of sucrose in presence of hydrochloric acid, it is found that the activity of the non-ionised acid is about twelve times as great as that of the hydrogen ion.

In the author's opinion, the known facts relating to the chemical

activity of electrolytes are not in favour of the ionic theory, and merely serve to show the existence of a close connexion between chemical and electrolytic activity.

H. M. D.

**Crystallisation Phenomena in Binary Systems of the Chlorides of the Univalent and Bivalent Metals.** TH. LIEBISCH and E. KORRENG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 192—212).—The authors give a summary of the results which have been obtained in the investigation of the crystallisation of forty-two pairs of chlorides by thermal and microscopic methods. The chlorides of the following metals were used: lithium, sodium, potassium, rubidium, copper, silver, thallium, magnesium, calcium, strontium, barium, zinc, cadmium, tin, and lead. The various binary systems are grouped according to the behaviour which is found on solidification, and in these tables are recorded the data characteristic of the various systems, such as crystallisation temperatures, eutectic temperatures and composition, transition temperatures, and formulæ of compounds.

The following pairs of chlorides form neither compounds nor mixed crystals: LiCl with KCl, SnCl<sub>2</sub>, PbCl<sub>2</sub>; NaCl with CuCl, CaCl<sub>2</sub>, SrCl<sub>2</sub>, BaCl<sub>2</sub>, SnCl<sub>2</sub>, PbCl<sub>2</sub>; TiCl—BaCl<sub>2</sub>, AgCl—PbCl<sub>2</sub>.

Binary systems characterised by the formation of compounds which melt without decomposition are indicated by the formulæ of these compounds: KCl, MgCl<sub>2</sub> (487°), KCl, CaCl<sub>2</sub> (740°), 2KCl, BaCl<sub>2</sub> (663°), TiCl, CaCl<sub>2</sub> (683°), 2TiCl, ZnCl<sub>2</sub> (352°), TiCl, 2ZnCl<sub>2</sub> (226°), TiCl, CdCl<sub>2</sub> (436°), 3TiCl, SnCl<sub>2</sub> (310°), TiCl, SnCl<sub>2</sub> (244°), 3TiCl, PbCl<sub>2</sub> (407°), TiCl, 2PbCl<sub>2</sub> (435°), 2KCl, SrCl<sub>2</sub> (597°), KCl, 2SrCl<sub>2</sub> (638°), KCl, 3SnCl<sub>2</sub> (208°), KCl, SnCl<sub>2</sub> (224°). The numbers in brackets represent the melting points of the respective compounds.

Other pairs of chlorides also form compounds, but these are decomposed below the melting point. The formulæ of the compounds and the transition temperatures characteristic of these are indicated in the following list: 2NaCl, CdCl<sub>2</sub> (425°), 2KCl, CuCl (244°), TiCl, 2MgCl (499°), TiCl, SrCl<sub>2</sub> (569°), CaCl<sub>2</sub>, BaCl<sub>2</sub> (631°).

In three cases it has been found that compounds belonging to both the above classes are formed; the compounds with melting points are: KCl, CdCl<sub>2</sub> (431°), KCl, 2PbCl<sub>2</sub> (440°), RbCl, 2PbCl<sub>2</sub> (423°), RbCl, PbCl<sub>2</sub> (440°); those which exhibit transition points are: 4KCl, CdCl<sub>2</sub> (461°), 2KCl, PbCl<sub>2</sub> (490°), 2RbCl, PbCl<sub>2</sub> (448°). The compound RbCl, PbCl<sub>2</sub> changes from a rhombic into a regular modification at about 310°.

From an examination of the compounds which the chlorides of the bivalent metals form with those of the alkali metals, it is found that the calcium and barium compounds contain only 1 molecule of the alkaline earth metal chloride, whilst the corresponding double chlorides of magnesium, strontium, zinc, cadmium, and lead may contain one or more molecules of the bivalent metal chloride. The alkali metal chlorides do not form compounds with one another, and, except in the case of the pair CaCl<sub>2</sub>—BaCl<sub>2</sub>, this is true for the chlorides of the alkaline earth metals.

Pairs of chlorides which form complete series of mixed crystals are:  $\text{LiCl}-\text{NaCl}$ ,  $\text{NaCl}-\text{KCl}$ ,  $\text{NaCl}-\text{AgCl}$ ,  $\text{CaCl}_2-\text{SrCl}_2$ ,  $\text{SrCl}_2-\text{BaCl}_2$ . In consequence of the dimorphism of barium chloride, the series of singly refracting mixed crystals, which are formed when mixtures of this with strontium chloride are allowed to crystallise, is transformed into a series of doubly refracting mixed crystals as the temperature falls. The fact that complete series of mixed crystals are formed in the system  $\text{CaCl}_2-\text{SrCl}_2$  is worthy of note, in view of the circumstance that calcium chloride is monoclinic, whilst strontium chloride is regular. The mixed crystals separate into the components when the temperature is lowered.

Tables are given in which the degree of miscibility of the components in the various binary systems is indicated. These show that there is a marked difference in the behaviour of sodium chloride and potassium chloride towards other chlorides.

H. M. D.

**Preparations of Colloidal Solutions by Mechanical Subdivision.** GUSTAV WEGELIN (*Kolloid. Zeitsch.*, 1914, **14**, 65—69).—Colloidal solutions of silicon, antimony, tungstic acid, titanitic acid, molybdic acid, vanadium trioxide, and vanadium pentoxide have been prepared by reducing the substances to a finely divided condition in an agate mortar. The time required for this varies with the substance; in some cases the process is accelerated by the addition of a little water. The results were quite negative in the case of a large number of other substances which were subjected to this mechanical treatment. The colloidal solutions of the above-mentioned substances show great differences in stability. In all cases the particles are negatively charged, and coagulation occurs on the addition of sodium chloride.

If the colloidal solution of vanadium pentoxide is coagulated by adding a small quantity of sodium chloride, the precipitate shows little change of colour on keeping, but if a larger amount of sodium chloride is used in the coagulation, the resulting precipitate changes its colour in the course of a few days from yellow to reddish-brown. Further observations have shown that this is probably connected with the existence of two modifications of the vanadium pentoxide.

The black solution of vanadium trioxide is very stable in the absence of air. On standing in the air, oxidation occurs, and the solution becomes green, a green precipitate being thrown down later, which probably consists of  $\text{V}_2\text{O}_4$ .

H. M. D.

[The Condition Diagram of Water.] P. B. BRIDGMAN (*Zeitsch. physikal. Chem.*, 1914, **86**, 513—524. Compare Tammann, A., 1913, ii, 935; Bridgman, *Proc. Amer. Acad.*, 1912, **47**, 441—558).—Polemical. The author doubts the existence of a second form of ice II, and attributes the results on which Tammann (*loc. cit.*) bases his assumption that such a form exists to insufficiently accurate measurements.

J. F. S.



**The Laws of Displacement of Chemical Equilibrium.** A. ARIÈS (*Compt. rend.*, 1914, 158, 492—494. Compare Raveau, *ibid.*, 1909, 148, 767).—A theoretical paper in which the author deduces a law which combines into one the two laws of Le Chatelier, and van't Hoff's two laws. He enunciates it as follows: In a transformation where the temperature, the entropy, the pressure, or the volume remain invariable, all the reactions are produced in the sense which exalts the change of volume or entropy foreseen by the laws of displacement of thermo-elastic equilibrium.

W. G.

**Theory of Heterogeneous Chemical Equilibria.** A. THIEL (*Chem. Zentr.*, 1914, i, 211—212; from *Sitzungsber. Ges. Bef. Naturw. Marburg*, 1913, reprint, 16 pp.).—The apparent discrepancy in the results obtained by the application of the mass law and the phase rule on the one hand, and the molecular theory on the other, to the equilibrium in systems with two solid phases and a gas phase, such as that represented by  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ , is due to the assumption of a relation between the masses of the reacting substances and the free surfaces.

The apparent contradiction which a racemic compound offers to the requirements of the phase rule is shown to disappear if the system is regarded as a special case of one in which the *d*- and *l*-forms are separate components. The discrepancy met with in the case of sodium chlorate, which exists in a rhombic and in two enantiomorphic rhomboidric-tetartroedric forms, disappears in like manner if the enantiomorphic forms are counted as a single phase.

H. M. D.

**Equilibria in Ternary Systems. XII.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 739—754. Compare this vol., ii, 113, 184).—A further discussion of possible types of equilibrium in ternary systems.

H. M. D.

**Physical Chemistry of Magmas.** P. NIGGLI (*Zeitsch. Elektrochem.*, 1914, 20, 156—159).—A theoretical paper in which the constitution of magmas of silicates in the presence of volatile substances, such as carbon dioxide, hydrogen chloride, hydrogen fluoride, and other gases, is considered from the point of view of the phase rule. The object of the paper is mainly geological, and is concerned with the conditions of formation of rocks from the molten magma.

J. F. S.

**Photochemical Decomposition of Hydrogen Peroxide. I.** J. HOWARD MATHEWS and HARRY A. CURTIS (*J. Physical Chem.*, 1914, 18, 166—178).—The rate of decomposition of aqueous solutions of hydrogen peroxide has been investigated when the solutions, contained in a quartz tube provided with a quartz stirrer, are subjected to the influence of the light emitted by a "uvioi" lamp of constant intensity, which is set up in close proximity and parallel to the tube containing the hydrogen peroxide solution. After

measured time intervals, a sample is removed and titrated with standardised potassium permanganate. The decomposition follows the course of a unimolecular reaction, and ceases abruptly when the light is cut off. Between 20° and 45° the velocity of decomposition increases in the ratio 1:1.5 for a rise of temperature of 10°. On addition of small quantities of sulphuric acid, sodium chloride, acetanilide, sodium, calcium and barium hydroxides, the velocity of decomposition is retarded, and these substances may consequently be regarded as negative catalysts in respect of the photolytic reaction.

H. M. D.

**Velocity of Diazotisation of Some Amines.** E. TASSILLY (*Compt. rend.*, 1914, 158, 489—491. Compare this vol., ii, 42).—In the case of the various amines previously examined, the author now shows that their diazotisation is sensibly regulated, as in the case of aniline, by the formula  $dx/dt = k(100 - x)^2$ , the variations between calculated and found values for  $x$  coming within the range of experimental error.

W. G.

**Pseudo-Ternary Systems of Acid Anhydrides and Water.**  
**I. Phthalic Anhydride.** H. R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 712—718).—If the solution obtained by shaking water in contact with phthalic anhydride is titrated with standard alkali hydroxide, after measured time intervals, it is found that the acid titre increases to a maximum, and then falls to a constant value. Further experiments, in which the water was shaken with both phthalic anhydride and phthalic acid, and in which the electrical conductivity of the solution was measured from time to time, show that the above variation in the acid titre of the solution is due to the dissolution of the anhydride, which subsequently undergoes rapid hydration, with the formation of a supersaturated solution of the acid. The fall in the titre indicates the gradual attainment of an equilibrium condition, in which the solution is in equilibrium with both acid and anhydride. The solubility of the acid is increased somewhat in the presence of the anhydride.

H. M. D.

**Mechanism of the Acid Formation of Aliphatic Acid Anhydrides in an Excess of Water.** J. BÖESEKEN and P. E. VERKADE (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 718—726).—The velocity of hydration of a number of acid anhydrides has been measured at 0° and at 25° by the conductivity method. The following represent the unimolecular velocity-coefficients which have been obtained for the several anhydrides, the non-bracketed figures giving the value of  $0.4343k$  for 0°, and the figures in brackets the value for 25°: acetic anhydride, (0.0713); propionic anhydride, 0.00700, (0.0372); *n*-butyric anhydride, 0.00471, (0.0243); *iso*-butyric anhydride, 0.00454, (0.0227); acetic propionic anhydride, (0.0522). Since previous observations have shown that the velocity of hydration is determined by the magnitude of the ionisation coefficient of the acid, the authors seek to eliminate this influence

by dividing the hydration-coefficients by the corresponding ionisation-coefficients. The numbers obtained in this way are found to diminish as the aliphatic series is ascended, whilst the equality of the numbers for *n*- and *iso*-butyric acids shows that the branching of the carbon chain has no measurable influence on the rate of hydration.

In the case of *isovaleric* anhydride, the rate of hydration does not fit in with the unimolecular formula. The actual behaviour can be explained if it is assumed that the reaction occurs in two stages, in the first of which a hydrate is formed by addition of water, this hydrate being split up into two molecules of acid in the second stage. Whereas the first stage is relatively very rapid in the case of the lower anhydrides, this does not hold for *isovaleric* anhydride, and the values obtained for the unimolecular velocity-coefficient decrease as the hydration proceeds. H. M. D.

**Union of Hydrogen with Acetylenic  $\gamma$ -Glycols in Presence of Palladium or Platinum.** Y. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1875—1895).—Previous investigations on the partial hydrogenation of compounds with an acetylenic linking have usually been limited to interruption of the reaction when the amount of hydrogen absorbed has reached that calculated for the conversion of the triple into a double linking. Arrest of the reaction at this stage is, however, only possible if the conditions are such that the velocity of combination of hydrogen at the triple bond is considerably greater than at the double bond. If the reverse is the case, a mixture of saturated and acetylenic compounds is obtained, whilst if the two velocities are more or less of equal magnitude, a mixture of saturated, ethylenic and acetylenic compounds is naturally formed.

It is hence of interest to study the velocities of such reactions under different conditions, for instance, in presence of different catalysts, and this the author has done for  $\gamma$ -glycols of the acetylene series, making use of platinum black, prepared according to Willstätter and Hatt's method (A., 1912, i, 545), and of colloidal palladium, made in the manner indicated by Paal and Amberger (A., 1905, ii, 397).

With the latter of these catalysts, hydrogenation of  $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol (compare Iocitsch, this vol., i, 405) proceeds with extreme slowness after two atoms of hydrogen have been combined. When platinum black is used, however, the hydrogenation not only proceeds as far as the conversion of the triple linking into a simple one, but also leads to reduction of the hydroxyl groups. For each of these cases calculations have been made of the velocity constants of the conversion of the triple into the double linking,  $k_1$ , and of those of complete hydrogenation,  $K$ . With palladium  $k_1$  remains virtually constant, whereas  $K$  rapidly diminishes, so that almost all of the hydrogen first reacts with the acetylenic glycol, the ethylenic glycol thus formed subsequently undergoing but slow reduction. With platinum,  $k_1$  exhibits a marked increase, whilst  $K$  remains constant until near the end of the experiment,

where it shows a slight increase, which is probably caused by the reduction of the hydroxyl groups; here, then, the hydrogenation of triple and double linkings proceeds with approximately the same velocity.

These results show that if a saturated glycol is desired, hydrogenation should be effected in presence of platinum black, whereas when an ethylenic glycol is required, colloidal palladium should be employed. In either case, it is necessary to measure the quantity of hydrogen absorbed and to stop the reaction at the proper time, but there is no necessity to hasten the removal of the hydrogen from the vessel in which the reaction is taking place.

In the above case, the individuality of the  $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol and the  $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexene- $\beta\epsilon$ -diol obtained was established.

Preliminary experiments have also been similarly made on the hydrogenation of  $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol (compare Iocitsch, this vol., i, 375). The results obtained are analogous to those given by the dimethyl glycol, the hydrogenation, as shown by the values of  $k_1$  and  $K$ , varying markedly according as platinum black or colloidal palladium is present. With the former catalyst, reduction of the hydroxyl groups proceeds more energetically than with  $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol.

Further investigations are in progress.

T. H. P.

**Union of Hydrogen with  $\alpha\delta$ -Diphenyl- $\Delta\gamma$ -butinene- $\alpha\delta$ -diol.** Y. S. ZALKIND and E. D. ISAKOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1896—1903).—Experiments similar to those previously described (see preceding abstract) have been made with  $\alpha\delta$ -diphenyl- $\Delta\beta$ -butinene- $\alpha\delta$ -diol,  $\text{OH}\cdot\text{CHPh}\cdot\text{C}:\text{C}\cdot\text{CHPh}\cdot\text{OH}$  (compare Iocitsch, this vol., i, 404). The curves representing the course of the hydrogenation in presence of platinum black or colloidal palladium, and also the values of  $k_1$  and  $K$ , are closely analogous to those obtained with  $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol.

$\alpha\delta$ -Diphenylbutane- $\alpha\delta$ -diol,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$ , the product obtained when platinum black is used, forms crystals, m. p. 113—113.5°. Like its *diacetyl* derivative,  $\text{C}_{20}\text{H}_{22}\text{O}_4$ , m. p. 99—99.5°, it has the normal molecular weight in boiling ether.

$\alpha\delta$ -Diphenyl- $\Delta\beta$ -butene- $\alpha\delta$ -diol,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}:\text{CH}\cdot\text{CHPh}\cdot\text{OH}$ , obtained when colloidal palladium is used, forms acicular crystals, m. p. 150—152°, and decolorises bromine water and dilute permanganate solution; it exhibits normal ebullioscopic behaviour in acetone.

T. H. P.

**Demonstration of the Velocity of Chemical Reaction by means of the Galvanometer.** M. CENTNERSZWER (*Chem. Zentr.*, 1914, i, 330; from *Zeitsch. physikal.-chem. Unterr.*, 1913, 26, 344—349).—The velocity of the reaction between methyl sulphate and methyl alcohol (compare Kremann, A., 1907, ii, 157) has been calculated on the assumption that the conductivity of the mixture is approximately proportional to the concentration of the methyl hydrogen sulphate. The mean values for the constant obtained in two

experiments at 25° were 0.00154 and 0.00141. In the original it is described how the reaction may be used to demonstrate the laws of the velocity of reactions. In one experiment it may be shown by galvanometer deflections that the velocity decreases with time, and, in a parallel experiment, that it is proportional to initial concentration, and that a rise of 20° increases the speed about five times. The influence of catalysts cannot be demonstrated, for the reaction is indifferent towards water, acids, alkalis, or platinum.

J. C. W.

**Determination of the Velocity of Reactions in Solution from the Change in Density.** ERNEST ANDERSON and J. L. HOLDEN (*J. Physical Chem.*, 1914, 18, 152—156).—It is shown that the inversion of sucrose can be followed by measuring the density of the solution after measured intervals of time. Data are given for experiments in which hydrochloric, sulphuric, and oxalic acids were employed as catalysts. The values obtained for the velocity coefficient are in good agreement.

H. M. D.

**Chemical Kinetics. I. The Influence of Synchronous Changes in Concentration on the Course of a Unimolecular Reaction.** JULIUS HIRNIAK (*Chem. Zentr.*, 1914, i, 3—5; from *Ukrain. Ševčenko-Ges. Wiss. Lemberg*, 1911, 1—101).—Formulæ have been deduced which represent the course of unimolecular reactions, in which the concentration of the reacting substance increases as a function of the time. The equations for concurrent and consecutive reactions of the first and second order are also discussed, and reference made to periodic chemical changes (compare A., 1911, ii, 196).

In the experimental portion of the paper the author gives the results of measurements of the velocity of reaction of ethyl iodide with heterocyclic bases, and of the temperature-coefficients of these reaction velocities.

The temperature-coefficient of the reaction between dimethylaniline and ethyl iodide in dimethylaniline solution is less than in methyl alcohol solution. Since the reaction proceeds according to the unimolecular formula in the former case, and according to the bimolecular formula in the latter, it is suggested that this is an exception to Halban's rule, according to which unimolecular reactions have a higher temperature-coefficient than reactions of the second and third order.

From experiments with *p*-toluidine, pyridine,  $\alpha$ -picoline, quinoline, collidine, and  $\alpha$ -naphthaquinoline, it is found that the temperature-coefficient increases as the reaction velocity diminishes. The data obtained for *isoquinoline*,  $\beta$ -naphthaquinoline, and 2-methylquinoline indicate that the speed of the reaction falls as the nitrogen becomes more enclosed by other groups of atoms. At the same time the temperature-coefficient increases, as is shown by the data obtained for the members of the three following groups: (1) dimethyl-*p*-toluidine, dimethyl-*o*-toluidine; (2) pyridine,  $\alpha$ -picoline, collidine; (3) *isoquinoline*, quinoline,  $\alpha$ -naphthaquino-

line, 2-methylquinoline. In the case of the two pairs of bases (1) pyridine and *iso*quinoline, (2) quinoline and  $\beta$ -naphthaquinoline, where the nitrogen is subjected to the same steric influence, the temperature-coefficients are equal. An explanation of the steric influence is put forward. H. M. D.

**Reactions with Halogen Substituted Acids.** Action of Aqueous Sodium Hydroxide on Bromomalonic Acid and on Alkylbromomalonic Acids. E. HÖST MADSEN (*Zeitsch. physikal. Chem.*, 1914, **86**, 538—544).—Velocity reactions have been carried out with sodium hydroxide solution and solutions of bromomalonic acid, bromobenzylmalonic acid, bromoethylmalonic acid, and bromoisopropylmalonic acid. In every case the reaction is unimolecular, which indicates that the hydrolysis is brought about by undissociated water molecules, and that the sodium hydroxide only serves to combine with the liberated hydrogen bromide. The relative velocities of hydrolysis of the four acids are bromoisopropylmalonic acid, 4165; ethyl bromomalonic acid, 555; bromobenzylmalonic acid, 307; and bromomalonic acid, 1. The influence of the substituting alkyl group on the velocity is of the same nature as that found by Senter for the action of silver nitrate on bromine-substituted fatty acids (T., 1910, **97**, 346). J. F. S.

**Catalytic Influence of Kaolin on the Combination of Hydrogen and Oxygen.** JACQUES JOANNIS (*Compt. rend.*, 1914, **158**, 501—504).—Kaolin has a marked catalytic influence on the combination of hydrogen and oxygen at temperatures when there is no combination under the influence of the glass vessel alone. The effect was noticeable at 230°, and up to 280° was proportional to the time of contact of the gases with the kaolin. The temperature to which the kaolin had been previously heated had a decided influence on its activity, this diminishing as the temperature of preliminary heating increased. This effect was also noticeable after a short time in the results obtained in the cases where the kaolin was kept at 300° or over without the preliminary heating, the rate of combination slowly diminishing as the experiment progressed. W. G.

**Catalysis of the Addition of Halogens.** L. BRUNER and J. FISCHLER (*Zeitsch. Elektrochem.*, 1914, **20**, 84—88).—The author has investigated the catalytic action of halogen carriers on the addition of chlorine and bromine to unsaturated compounds. The experiments are carried out with acetylene dichloride and ethyl cinnamate in carbon tetrachloride and nitrobenzene solutions. It is shown that acetylene dichloride does not combine with bromine in either carbon tetrachloride or nitrobenzene solutions when the halogen is present in 1/20 molecular quantity, and that the catalysts, iodine, stannic bromide, and ferric bromide are inactive when in carbon tetrachloride solution, but antimony tribromide is markedly active. On the other hand, antimony tribromide has no action in nitrobenzene solution. There is no addition of chlorine either when

alone or in the presence of iodine chloride in these solutions. The catalysis is not strictly proportional to the concentration of the catalyst. The addition of chlorine and bromine to ethyl cinnamate is strongly catalysed by the addition of iodine, and here also the velocity of the reaction is not strictly proportional to the concentration of the catalyst. Antimony tribromide is a good catalyst for the addition of bromine to ethyl cinnamate in carbon tetrachloride solution, and the reaction is shown to be apparently simpler than a first-order reaction.

J. F. S.

**A New Gas-Generating Apparatus.** MAX BRAUN (*Chem. Zeit.*, 1914, **38**, 320).—An apparatus of the Döbereiner-Mohr type is described and figured.

L. DE K.

**Lecture Experiment on the Chlorination of Iron.** O. OHMANN (*Chem. Zentr.*, 1914, i, 331; from *Zeitsch. phys.-chem. Unterr.*, 1913, **26**, 365—366).—A tuft of steel wool will ignite in chlorine if sprinkled with powdered antimony.

J. C. W.

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## Inorganic Chemistry.

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**Compressibility of Ice.** THEODORE W. RICHARDS and CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1914, **36**, 491—494).—Determinations of the compressibility of ice have been made by means of the piezometer described previously (A., 1912, ii, 896), dilute alcohol being used above the mercury instead of water. It has been found that the compressibility between 100 and 500 megabars is 0.0000120 at  $-7.03^{\circ}$ , or about one-fourth of the compressibility of water at neighbouring temperatures, and that it does not decrease greatly with increasing pressure. This is probably the first direct determination which has been made of this constant, but Bridgman (A., 1913, ii, 39), by indirect calculation, has obtained the value 0.000036 for the compressibility of common ice at  $0^{\circ}$ . The discrepancy between the observed and calculated values is probably partly due to the temperature-coefficient of the compressibility of ice being abnormally high. E. G.

**The Decomposition of Chlorine Water by Light.** JAROSLAV MILBAUER (*Zeitsch. physikal. Chem.*, 1914, **86**, 564—566).—Ten c.c. of chlorine water of known concentration were placed into each of a series of test-tubes, and to these tubes 0.001 gram of a number of substances was added as catalyst. The catalysts include iodine, bromine, sulphuric acid, selenic acid, arsenic acid, boric acid, the chlorides of lithium, sodium, potassium, copper, rubidium, silver, caesium, gold, glucinium, magnesium, calcium, zinc, strontium, cadmium, barium, mercury, aluminium, thallium, carbon, tin,



cerium, lead, vanadium, antimony, bismuth, chromium, manganese, iron, nickel, cobalt, platinum and palladium, sodium tungstate, sodium molybdate, and uranyl sulphate. The tubes were then exposed to light, and the change in the chlorine concentration determined. It is shown that, with the exception of bromine, none of these substances shows a positive catalytic effect; in most cases a negative catalysis is observed. Chlorine and bromine are shown mutually to catalyse the reactions  $\text{Br}_2 + \text{H}_2\text{O} = 2\text{HBr} + \text{O}$ ,  $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{O}$ . Iodine has no accelerating effect on either reaction, but rather a retarding effect, which is probably due to the formation of relatively stable iodine compounds. J. F. S.

**Ozonisation of Air.** L. SCHWARZ and G. MÜNCHMEYER (*Chem. Zentr.*, 1914, i, 56; from *Zeitsch. Hyg. Infekt. Krankh.*, 1913, 75, 81—100).—In continuation of their previous investigations (A., 1913, ii, 73), the authors have examined the action of ozone on a number of substances which might occur as impurities in air.

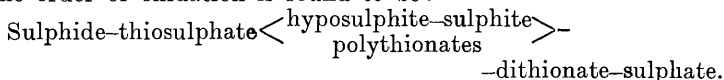
Under the experimental conditions adopted, hydrogen sulphide is more or less rapidly oxidised by ozone, according to the activity of the latter. Ammonia is not affected, whilst carbon monoxide does not react within twenty-four hours. Sulphur dioxide is only partly acted on. Mercaptan is rapidly oxidised by a large excess of ozone; scatole and indole are similarly decomposed, yielding products of pleasant, ester-like odour.

For the detection of ozone, the authors recommend neutral potassium iodide, or the alkaline solution prepared according to Lechner (A., 1911, ii, 822), which is acidified immediately previous to titration; the latter should be performed as rapidly as possible. In using chemically prepared ozone, or that obtained from air, the possible presence of oxides of nitrogen must be taken into account.

H. W.

**The Action of Ozone on Inorganic Sulphur Compounds.** E. H. RIESENFELD and TH. F. EGIDIUS (*Zeitsch. anorg. Chem.*, 1914, 85, 217—246).—Ozone may react in one of two ways. One atom of oxygen may be given up to the reducing agent, the remaining two forming gaseous oxygen, or the whole molecule may be added to form an ozonide. More complicated ratios are probably due to combinations of these two reactions. Solutions of inorganic sulphur compounds have now been treated with ozonised oxygen.

The order of oxidation is found to be:



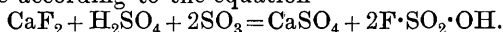
Sodium sulphide and polysulphide are directly oxidised by ozone to sulphite, some thiosulphate and a little hyposulphite being also formed. Sodium hydrogen sulphide evolves free hydrogen sulphide, and the sodium sulphide is oxidised as before.

Neutral solutions of thiosulphates form chiefly sulphate and dithionate, whilst in alkaline solution oxygen is evolved, and only two atoms of the ozone molecule are active. A neutral solution

of a sulphite reacts similarly, whilst sodium hydrogen sulphite is oxidised to sulphate and a little dithionate without liberation of oxygen. The results suggest that ozonides are first produced by simple addition, and then undergo decomposition. C. H. D.

**Hydrofluoric Acid and Fluorosulphonic Acid.** OTTO RUFF and HANS JULIUS BRAUN (*Ber.*, 1914, **47**, 646—656).—The reaction between fluorspar and sulphuric acid has been investigated in order to determine the effect of varying conditions on the results obtained. In the preparation of hydrofluoric acid from these reagents, it is best to use 90% sulphuric acid. When 97—100% sulphuric acid is used, a yield of 60% of hydrofluoric acid is obtained; this acid is of 95—96% strength, but is never anhydrous. The distillation residues contain, not only calcium sulphate and unchanged calcium fluoride, but also some calcium fluorosulphonate.

When sulphuric acid containing a high percentage (50—60%) of sulphur trioxide is used, the product no longer contains hydrofluoric acid, but consists only of fluorosulphonic acid, the reaction taking place according to the equation



With sulphuric acid containing 60% of the anhydride, a practically quantitative yield of fluorosulphonic acid is obtained.

Full details are given for the best methods of preparing aqueous and 95% hydrofluoric acid, and fluorosulphonic acid. T. S. P.

**Fluorosulphonic Acid.** OTTO RUFF (*Ber.*, 1914, **47**, 656—660).—Sodium fluorosulphonate (compare Traube, A., 1913, ii, 947) is readily obtained by heating fluorosulphonic acid (50 grams) and sodium chloride (92.2 grams) in a platinum retort under reflux at 230° for half an hour. Extraction of the resulting product with boiling absolute alcohol gives a solution of sodium fluorosulphonate, from which the salt separates on cooling in the form of iridescent plates or needles.

Thorpe and Kirman (T., 1892, **61**, 924) claim to have prepared sulphuryl fluoride by boiling fluorosulphonic acid, reaction taking place according to the equation  $2\text{F}\cdot\text{SO}_2\cdot\text{OH} = \text{SO}_2\text{F}_2 + \text{H}_2\text{SO}_4$ . The author cannot confirm this observation, finding, on the contrary, that fluorosulphonic acid is stable even at 900°. On boiling with sulphur, however, reaction takes place according to the equation  $2\text{F}\cdot\text{SO}_2\cdot\text{OH} + \text{S} = 3\text{SO}_2 + 2\text{HF}$ .

Dumas and others claim to have obtained a chromium fluoride, either  $\text{CrO}_2\text{F}_2$  or  $\text{CrF}_6$ , by heating a mixture of potassium dichromate, calcium fluoride, and sulphuric acid. Repetition of their experiments gave a very small yield of a red product, gaseous at room temperatures; a better yield was obtained when fluorosulphonic acid was used instead of calcium fluoride and sulphuric acid, and a mixture of potassium dichromate and chromium trioxide instead of potassium dichromate. The product, however, was not of a definite composition, and all results published hitherto as to the composition of the red gas are untrustworthy.

On warming a mixture of potassium permanganate and fluoro-

sulphonic acid, a beautiful violet vapour is evolved, which decomposes on contact with the air. T. S. P.

**The Reaction Products of Sulphur Dioxide and Ammonia.** MASATAKA OGAWA and SHINICHI AOYAMA (*Sci. Reports Tôhoku Imp. Univ.*, 1913, **2**, 121—129).—The results of Ephraim and Piotrowski (A., 1911, ii, 274) not being in agreement with those obtained by Ogawa and Divers (T., 1900, **77**, 327), the authors have further investigated the reaction between sulphur dioxide and ammonia. All the reactions were carried out in ethereal solution.

When sulphur dioxide is in excess, the compound formed is amidosulphinic acid,  $\text{NH}_2 \cdot \text{SO}_2\text{H}$  (compare Schumann, A., 1900, ii, 271), a pale, yellow-coloured compound; when ammonia is in excess, the ammonium salt,  $\text{NH}_2 \cdot \text{SO}_2\text{NH}_4$ , of this acid is formed as a white substance. The authors do not agree with Ephraim and Piotrowski that the orange or red-coloured substance produced by the action of heat on these substances cannot be a decomposition product.

Further investigation of the compound  $\text{N}_4\text{H}_{12}\text{S}_5\text{O}_{10}$ , described by Divers and Ogawa (T., 1901, **79**, 1102), showed that it does not exist. The substance obtained was really impure ammonium trithionate. T. S. P.

**Colloidal Selenium.** A. GUTBIER and R. EMSLANDER (*Ber.*, 1914, **47**, 466—467).—The authors have used (compare Emslander, Diss., May 9th, 1913) the same method as that described by Meyer (A., 1913, ii, 1048) for preparing colloidal selenium, not only for making hydrosols, but also alcohol-sols of selenium. The method is not new, since Ephraim and Piotrowski (A., 1911, ii, 275) have used it for making colloidal solutions of sulphur, phosphorus, and arsenic. T. S. P.

**An Explosive Luminous Phenomenon in Rarefied Nitrogen.** J. DE KOWALSKI (*Compt. rend.*, 1914, **158**, 625—627).—The author has confirmed Strutt's observations on the transformation of nitrogen into an active form, and its appearance in this form (compare A., 1911, ii, 482, 678; 1912, ii, 153, 214, 447, 935), and has, in addition, observed a highly luminous phenomenon. Strutt's phenomenon was observed after interruption of the current, using a relatively weak electric field. If a very intense electric field is employed, almost immediately after the interruption of the current several small, luminous explosions are observed in the gas. The illumination of the gas in this phase is much more intense than during that of the phosphorescence of the nitrogen, and the gas is coloured an intense bluish-violet. Its spectrum is composed of the principal lines of mercury. W. G.

**The Oxidation of Nitrogen in the Electric Discharge. II. The Activation of Nitrogen and Oxygen in the Direct Current Arc.** A. KOENIG and E. ELÖD (*Ber.*, 1914, **47**, 516—522. Compare A., 1913, ii, 1049).—The authors point out that the after-glow

observed in Strutt's experiments and their own with active nitrogen does not prove the existence of active nitrogen, but is only an accompanying phenomenon (compare Tiede and Domcke, this vol., ii, 122). The formation of active nitrogen is proved by the reaction products resulting from the action of the nitrogen on other substances at room temperature, which reaction products in certain cases, for example, hydrogen cyanide and nitrides, cannot be explained by the presence of oxygen in the gas.

The objection might be raised that the gas submitted to the action of the so-called active nitrogen may have possibly been drawn into the zone of electric discharge, the resulting products being really due to actions taking place in that zone. To meet this objection, the authors have investigated the action of a direct-current arc on nitrogen, the electrode near to the pump being earthed; the apparatus was also so designed that the admixed gases could not possibly diffuse back to the arc, so that neither mixture of the gases in the discharge zone, nor a subsidiary discharge through them, could take place.

Purified nitrogen at 15 mm. pressure, when passed through the arc, emitted a bright, orange-yellow light; there was a very marked after-glow, which persisted the longer the lower the pressure. The optimum brightness of the after-glow was obtained between 2 and 8 mm. pressure.

The following effects were observed when various gases were mixed with the glowing nitrogen: nitrogen, hydrogen, water vapour, and oxygen merely acted as diluents; ozonised oxygen appeared to diminish the glow somewhat; with none of these gases could any reaction product be detected. Methane had no action, but ethylene and acetylene reacted vigorously; the after-glow disappeared, and where the two gases met a lilac flame, showing the cyanogen spectrum, was formed; hydrogen cyanide was also found among the products of reaction in a quantity corresponding with that found by Strutt in his experiments with the spark discharge. Pentane gave ammonia, amylene, and traces of hydrogen cyanide. Nitric oxide reacted, as described by Strutt; nitrogen peroxide also destroyed the glow immediately.

The fact that oxygen and ozone are passive towards active nitrogen appears not to be in accordance with the fact that nitrogen and oxygen react under the influence of the electric discharge, and to an extent which is greater than can be accounted for by assuming that the action is merely a thermal one (compare Haber, Koenig and Platou, A., 1910, ii, 1057). The authors now find that when pure, dry, ozone-free oxygen is treated in the same apparatus as that used for nitrogen, it gives a weak, bluish-green after-glow, which is not so persistent as that of nitrogen. If this glowing oxygen is mixed with glowing nitrogen from another apparatus, the glows are immediately extinguished, and oxides of nitrogen are formed in quantity. If the arc is extinguished in either apparatus, there is no further formation of nitric oxide. From these experiments the authors draw the conclusion that an active modification of oxygen is formed, which is different from ozone, and capable of existing for a short time only. T. S. P.

**The After-Glow of Nitrogen.** A. KOENIG and E. ELÖD (*Ber.*, 1914, **47**, 523—529).—Using nitrogen which has been purified from oxygen by the action of copper and potassium vapour, followed by low cooling and filtration from the last traces of oxygen, the authors have been able, in their apparatus (A., 1913, ii, 316), to observe a strong after-glow at pressures from 1—20 mm. of mercury. The nitrogen was so pure that the third group of the nitrogen band spectrum in the short ultra-violet had practically disappeared, this being the most delicate test there is for the presence of traces of oxygen or nitric oxide in nitrogen.

The active nitrogen so produced reacts with potassium or mercury, forming nitrides. If mercury vapour is mixed with the nitrogen before it is activated, the yellow after-glow (Strutt phenomenon) does not occur; the gas either does not glow at all, or only gives an after-glow in mercury light. That the vapours of alkali metals act in the same way has been previously shown by Mosengeil (A., 1906, ii, 714). It seemed therefore probable that the results obtained by Tiede and Domcke (this vol., ii., 122) were due to mercury vapour or vapours of potassium or barium (from decomposition of the potassium or barium azide used to furnish the nitrogen) present in their apparatus. Repetition of their experiments showed that this was the case. When the tube was exhausted with the mercury pump, the spark discharge showed the lines of the mercury spectrum, but there was no after-glow of the nitrogen; the mercury pump was then disconnected, and the mercury vapour in the apparatus condensed in a side-tube by means of liquid air; a weak after-glow was then obtained. If nitrogen was then evolved by heating potassium, barium, or calcium azoimide, the after-glow disappeared, but, at the same time, the spark discharge gave the spectral lines of the metal of the azoimide. Addition of oxygen again gave the after-glow, owing to the removal of the metal vapours by their oxidation; mercury vapours were similarly removed, with the formation of mercuric oxide.

The after-glow is brightest, and lasts longest, when mercury vapour is completely excluded, and is obtained with azoimide nitrogen when the metal vapour in the latter has been deposited either as nitride or oxide. The precautions taken by Tiede and Domcke for preventing the diffusion of metal vapours into their apparatus were insufficient. Also, the after-glow is seen the better the larger the apparatus, and it depends considerably on the gas-pressure and on the kind and strength of the discharge.

The results described by Tiede and Domcke in their last communication (this vol., ii, 196) can all be explained by the presence of mercury vapour in the apparatus. T. S. P.

**Hydrazine and its Inorganic Derivatives. II. The Monotropy of Hydrazine Nitrate.** FRITZ SOMMER (*Zeitsch. anorg. Chem.*, 1914, **86**, 71—87. Compare A., 1913, ii, 952).—A comparison between ammonium nitrate and hydrazine nitrate,  $\text{N}_2\text{H}_4\cdot\text{HNO}_3$ , has been made. The latter salt, which melts at  $70^\circ$ , may be heated to nearly  $300^\circ$  without decomposition. It is conveniently pre-

pared from hydrazine disulphate and barium nitrate, adding sodium carbonate to remove free nitric acid, and separating the sodium and hydrazine nitrates by crystallisation, fusion at  $70^{\circ}$ , and crystallisation from methyl alcohol. It is necessary to fuse for some time in a vacuum to remove the last traces of alcohol.

The m. p. is  $70.71^{\circ}$  (corr.). A transformation is not found by the thermal method, or by dilatometric measurements, and the curve of solubility in water is continuous from  $10^{\circ}$  to the melting point. By careful cooling from  $100^{\circ}$ , a labile modification is obtained at  $62^{\circ}$ , differing from the stable crystals, but this always changes into the stable modification before  $40^{\circ}$  is reached. The labile crystals have m. p.  $61.8^{\circ}$  (corr.). C. H. D.

**The Forms of Phosphorus. I. The Changes of Phosphorus Vapour in a Luminous Discharge.** V. KOHLSCHÜTTER and A. FRUMKIN (*Zeitsch. Elektrochem.*, 1914, **20**, 110—123).—The authors have investigated the action of a luminous discharge on yellow phosphorus. The yellow phosphorus was placed in a small side-tube, attached to a 100 c.c. vacuum-tube fitted with aluminium electrodes. A current of  $3 \times 10^{-4}$  amperes was used in the experiments; the voltage applied was at the commencement of each experiment 800 volts, but it had to be raised to about 5000 to maintain the current, owing to deposition of phosphorus on the electrodes. Experiments were also carried out in hydrogen, helium, argon, and nitrogen at pressures of 0.5 mm. In the experiments the phosphorus vapour is changed, and deposited in a finely dispersed condition on the walls of the vessel. The dispersity of the layers is also shown by the fact that the appearance and the other properties of the layers are changed in the presence of indifferent gases. The influence of the indifferent gases is shown in a loosening of the deposit, more so in the case of argon than in that of helium. On examination of the deposit after removal from the discharge-tube, it is seen that argon and phosphorus vapour are both simultaneously adsorbed, which points to the high dispersity of the deposit. Hydrogen and nitrogen react with phosphorus vapour in the discharge in the sense that solid compounds are formed. These solid products are deposited on the walls along with the changed phosphorus, without giving the deposit a non-homogeneous appearance under the microscope, when the pressure of the gas at the formation is low. If, however, the pressure is raised, then the deposit can be seen to be a mixture of several substances. On heating, the homogeneous deposit passes over into the ordinary red phosphorus, and all its peculiarities, such as colour, vanish. The author is of the opinion that the layer at first deposited is identical with the product obtained by suddenly cooling superheated phosphorus vapour, and therefore consists of finely divided Hittorf's phosphorus. On heating, this sinters and passes into the ordinary form of red phosphorus, and has the appearance of a homogeneous, dried tin oxide gel. J. F. S.

**The Constitution of the Carbon Molecule.** HANS MEYER (*Monatsh.*, 1914, **35**, 163—170).—The author discusses the various

suggestions hitherto made as to the structure of the carbon molecule. He regards each of the forms of carbon as an aggregation of particles of various sizes, so that in the absence of any uniformity the question of the structure of the carbon molecule loses considerably in importance.

Diamond resisted oxidation by wet processes, but graphite on oxidation failed to give any mellitic acid as a direct product of the oxidation, although it could be obtained by the oxidation of the primarily produced graphitic acid. Experiments on the oxidation of amorphous carbon gave widely differing quantities of mellitic acid, ranging from 0 to 40%; the yield varied with the origin of the charcoal and with the temperature at which it had been produced. Coal gave very little mellitic acid.

D. F. T.

**The Solubility of the Cubic and Octahedral Faces of Rock Salt.** M. LE BLANC and G. VON ELISSAFOV (*Chem. Zentr.*, 1914, i, 609—610; from *Ber. K. Sächs. Ges. Wiss.*, 1913, 65, 199—209).—The authors have revised Ritzel's results (A., 1911, ii, 488). They have taken large crystals of salt and coated all but the required faces with picein, and then suspended them in strongly agitated, almost saturated, solutions of salt. In general, the loss of weight was greater when the octahedral faces were exposed, but the difference was small, and it is not proved that the different speeds of solution are really due to different solubilities. The velocity of growth in a supersaturated solution showed no difference.

J. C. W.

**Another Form of the Ammonia-Soda Process.** P. P. FEDOTÉEV and J. KOLTUNOV (*Zeitsch. anorg. Chem.*, 1914, 85, 247—260. Compare Fedotéev, A., 1904, ii, 730).—The reaction  $\text{NaNO}_3 + \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{NaHCO}_3 + \text{NH}_4\text{NO}_3$  has been proposed for use in a modified ammonia-soda process. The nitrogen of the nitrate is recovered as calcium nitrate. An apparatus is described in which the experiments at 30° may be conducted without loss of carbon dioxide. Within the range 0—30°, the salt-pair  $\text{NaHCO}_3$ ,  $\text{NH}_4\text{NO}_3$ , is stable, and there are therefore two series of solutions saturated in respect to three salts. The practical conditions for the precipitation of sodium hydrogen carbonate are almost exactly the same as in the ordinary ammonia-soda process, but the precipitation is even more complete. By evaporation and further addition of sodium nitrate, it is possible to precipitate the whole of the sodium as sodium hydrogen carbonate, and to obtain 87.56% of the ammonia as nitrate, the remainder being distilled. Otherwise, by recovering all the ammonia by distillation, a product may be obtained containing 79.42%  $\text{Ca}(\text{NO}_3)_2$  and 20.58%  $\text{NaNO}_3$ .

C. H. D.

**Silver Fluoride and Subfluoride. II.** P. SACHS and L. VANINO (*Zeitsch. anal. Chem.*, 1914, 53, 154—160).—Contrary to Wöhler's conclusions (A., 1912, ii, 1169), the authors uphold their previous view (A., 1911, ii, 884) that the supposed subfluoride is merely a mixture of silver, silver fluoride, and silver oxide.

In addition to the hydrated silver fluorides with  $\text{H}_2\text{O}$  and  $2\text{H}_2\text{O}$ , the authors have now also obtained crystals containing  $4\text{H}_2\text{O}$  by cooling, in a platinum dish placed in ice, a concentrated aqueous solution of silver fluoride prepared according to Moissan from dry silver carbonate and hydrofluoric acid. This compound melts at the ordinary temperature, and when placed in a vacuum desiccator the dihydrated salt is deposited.

Anhydrous silver fluoride cannot be prepared in a pure condition by evaporating the aqueous solutions.

L. DE K.

**Reaction between Sulphur and Calcium Hydroxide in Aqueous Solution.** HERMAN V. TARTAR (*J. Amer. Chem. Soc.*, 1914, **36**, 495—498).—Experiments on the reaction between sulphur and calcium hydroxide in hot aqueous solution have shown that the primary reaction takes place in accordance with the equation  $3\text{Ca}(\text{OH})_2 + 10\text{S} = 2\text{CaS}_4 + \text{CaS}_2\text{O}_3 + 3\text{H}_2\text{O}$ . This reaction is analogous to that which occurs with potassium hydroxide and sulphur (A., 1913, ii, 1054), except that in the latter case the trisulphide,  $\text{K}_2\text{S}_3$ , is formed instead of the tetrasulphide. When an excess of sulphur is used, a secondary reaction takes place, in which the tetrasulphide is converted into the pentasulphide,  $\text{CaS}_5$ .

E. G.

**Fusion Experiments with Calcium and Magnesium Silicates.** VERA SCHUMOFF DELEANO (*Zeitsch. anorg. Chem.*, 1914, **84**, 401—430).—Mixtures corresponding with the composition of mixtures of bronzite ( $\text{MgSiO}_3 + 10\% \text{FeSiO}_3$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) have been examined. It is necessary to melt the components together, to grind to a fine powder after solidification, and to re-melt, in order to ensure homogeneity. The optical pyrometer method and the heating microscope method give slightly different values for the melting point, but the two curves are sensibly parallel. There is a eutectic point at 30 mol. % of anorthite. Bronzite then behaves towards anorthite like diopside.

Forsterite,  $\text{Mg}_2\text{SiO}_4$ , melts at about  $1600^\circ$ , and with  $\alpha$ -wollastonite gives an apparent eutectic at  $1300^\circ$ ; but the system is really a quaternary one, as periclase and some enstatite are formed.

Mixtures of forsterite with lime olivine,  $\text{Ca}_2\text{SiO}_4$ , give a eutectic at 80%  $\text{Mg}_2\text{SiO}_4$ , but this represents a complex mixture. Mixtures rich in calcium orthosilicate disintegrate on cooling. Enstatite is sometimes formed. Monticellite,  $\text{CaMgSiO}_4$ , is not obtained, and the volcanic products which contain this mineral must have contained mineralisers.

The disintegration of calcium orthosilicate also takes place in presence of enstatite up to 50%. A simple eutectic is formed. A mixture of 30 mol. % of forsterite and 70% enstatite is also a eutectic. Natural olivine, free from iron, melts above  $1550^\circ$ .

The results are collected in a triangular diagram, with lime, magnesia, and silica as components.

C. H. D.



**The Preparation of Eye-preserving Glass for Spectacles.** SIR WILLIAM CROOKES (*Phil. Trans.*, 1914, [A], 214, 1—25).—The primary object of the author's investigations was to find a glass that will cut off as much as possible of the heat radiation; the research was extended, however, to find glasses which are opaque to the ultra-violet; the transparency of the glasses was also a desideratum. Taking each of the desiderata by itself, the author has succeeded in preparing glasses which cut off more than 90% of the heat radiation, which are opaque to the invisible ultra-violet rays, and are sufficiently free from colour to be scarcely noticeable when used as spectacles. It has not been possible, however, to combine in one specimen of glass these three desiderata in the highest degree; the ideal glass which will transmit all the colours of the spectrum, cutting off the invisible rays at each end, has still to be discovered.

The following elements were found likely to give the best results, and experiments were made by combining them two, three, and four at a time in one glass, so as to enable the advantages of one to make up for the shortcomings of another: cerium, chromium, cobalt, copper, iron, lead, manganese, neodymium, nickel, praseodymium, and uranium. More than 300 different glasses were investigated, and the compositions of nineteen are given, which are useful from the point of view of one or more of the three desiderata given above.

The physical methods used in testing the glasses are described.

T. S. P.

**The Binary Systems Zinc-Tin and Zinc-Cadmium, and the Ternary System Zinc-Tin-Cadmium.** RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1914, 85, 435—436).—Reference is made to later publications by various authors dealing with these systems since 1910 (compare Lorenz and Plumbridge, A., 1913, ii, 1056).

C. H. D.

**Spectrographic Study of Spanish Blendes.** ANGEL DEL CAMPO Y Cerdán (*Anal. Fis. Quim.*, 1914, 12, 80—96).—Sixty-eight specimens of blende were examined. Of these, only 4 were completely free of germanium, gallium, and indium; 38 contained small proportions; 19 were notably, and 7 relatively, rich in these elements.

The relative frequency is gallium in 60, germanium in 50, and indium in 37 specimens. All three elements were found in 29 cases, germanium and gallium in 18, gallium and indium in 4, whilst germanium and indium only were found in none. Four examples showed gallium, three showed germanium, and one showed indium only. In twenty-three blendes it appears feasible to extract these elements.

G. D. L.

**The Cause of the Oxidation of Type Metal.** RICHARD MEYER and SIEGFRIED SCHUSTER (*Zeitsch. angew. Chem.*, 1914, 27, 121—127).—The authors have submitted ten different specimens of

type metal to chemical and micrographical examination, in order to ascertain the factors which cause the letters of the type to undergo, in some cases, considerable oxidation. The specimens varied in age up to seventy-five years; some were oxidised and some in good condition.

The results indicate that the oxidisability of the type depends, not on its chemical composition, but on the way in which it has been cast and on the method used for cleaning and storing it. A porous cast facilitates the absorption of moisture, with consequent oxidation. Oxidation is also facilitated by storing in a damp place. The type should not be cleaned with water or sodium hydroxide, but with turpentine oil, petroleum, etc.

Oxidisability has been ascribed to the presence of arsenic in the metal, but both good and bad types were found to contain arsenic, which, when present to the extent of a few tenths of a per cent., has no influence. Tin may possibly increase the permanency of the type, but some specimens which were sixty and seventy-five years old were in very good condition, although they were either free from or contained very little tin. T. S. P.

**The Equilibrium between Lead Chloride and Sodium Chloride in Aqueous Solution.** (Mme.) N. DEMASSIEUX (*Compt. rend.*, 1914, 158, 702—703).—A study of the equilibrium between lead chloride and sodium chloride in aqueous solution at 13°, 50°, and 100° shows that at none of these three temperatures do these chlorides form a double salt. The solubility of lead chloride in a solution of sodium chloride varies with the concentration of the latter in much the same way as its solubility in a solution of hydrogen chloride. The results are shown by curves. W. G.

**Alloys of Copper, Nickel, and Aluminium.** LÉON GUILLET (*Compt. rend.*, 1914, 158, 704—706).—An examination of the mechanical properties of alloys of copper, nickel, and aluminium, containing 60, 83, or 90% of copper with varying percentages of nickel and aluminium. The addition of a very small amount of aluminium considerably improves the quality of a copper-nickel alloy. The breaking-strain and the hardness increase very rapidly with the aluminium content to a maximum, and then decrease, the value of the maximum being higher the lower the percentage of copper. The maximum corresponds with a lower aluminium content the higher the percentage of copper. The structure of the alloys is the same as that of binary copper-aluminium alloys with the same percentage of aluminium, being either a heterogeneous or homogeneous solid solution. Annealing tends to make the solid solution uniform, but the process is very slow. Tempering is without action, except on alloys containing the  $\beta$ -constituent of aluminium bronzes. Hammering considerably modifies the mechanical properties, excepting the resilience. W. G.

**Place of Mercury in the Periodic System.** PRAFULLA CHANDRA RAY (*Chem. News*, 1914, 109, 85).—It is pointed out that

whilst silver and mercury have very slight relationship with gold, monad mercury is closely related to silver. It is therefore suggested that monad mercury should be placed at the bottom of group I, and gold in group VIII, immediately after platinum. Univalent mercury should be regarded as a distinct metal from bivalent mercury.

N. H. J. M.

**Application of the Laws of Transparency of Matter to X-Rays, to Fixing some Contested Atomic Weights: Case of Thorium and Cerium.** LOUIS BENOIST and HIPPOLYTE COPAUX (*Compt. rend.*, 1914, 158, 689—692. Compare A., 1901, ii, 308).—The authors have determined for cerium and thorium which multiple of their equivalents gives their atomic weights, by comparing their transparency to X-rays with that of other metals the atomic weights of which come near to various multiples of the equivalents of the two metals under examination. Cerium was compared with zirconium, molybdenum, barium, and lanthanum, and as a result the value 140.25 was fixed for its atomic weight. A similar comparison of thorium with lead gave for its atomic weight the value 232.

W. G.

**Galvano-Catalytic Explanation of the Destruction of Aluminium Apparatus by Copper.** PAUL PIKOS (*Zeitsch. angew. Chem.*, 1914, 27, 152).—Liquids such as glycerol, formaldehyde, methyl alcohol, allyl alcohol, ethyl alcohol, acetone, acetic acid, and tannin solutions which, in the pure condition, are incapable of attacking aluminium, even at an elevated temperature, completely alter in behaviour in the presence of small quantities of solutions of copper salts. Since the latter are almost invariably present as impurities in the technical, crude, and pure products, destruction of aluminium apparatus thereby is inevitable.

The assumption that the superficial layer of aluminium oxide is a sufficient protection is unwarranted. As soon as the solution is warmed, a galvanic process commences, whereby the copper is precipitated; from acid solution the deposit is purely metallic; from neutral solution it is a mixture of metal and oxide. Subsequently, a catalytic decomposition commences, whereby hydrogen is evolved from the solution, which causes the removal of the precipitate. The copper particles sink, again make a temporary contact, and are again removed by hydrogen. Formation of an aluminium-copper alloy has not been observed, the deposit of metal being invariably readily removed. The chemical action results in the formation of colloidal aluminium hydroxide, and frequently a precipitate of aluminium oxide. The destruction of the aluminium is irregular.

The destruction of aluminium vessels can only be prevented by complete removal of copper from the solutions which are to be used.

H. W.

**The Constitution of the Kaolinite Molecule. III.** J. W. MELLOR and A. D. HOLDCROFT (*Trans. Eng. Ceramic Soc.*, 1913-4, 13, 83—90. Compare A., 1913, ii, 232).—Polemical against the

views expressed by W. and D. ASCH in their book, "Die Silicate in chemischer u. technischer Beziehung."

W. ASCH and D. ASCH (*ibid.*, 90—112) reply to these criticisms.  
T. S. P.

**Bromination of Manganese in Ether.** F. DUCELLIEZ and A. RAYNAUD (*Compt. rend.*, 1914, 158, 576—578; *Bull. Soc. chim.*, 1914, [iv], 15, 273—275).—By addition of the calculated quantity of dry bromine to finely divided manganese under ether, and then warming the mixture on a water-bath, an orange-yellow, semi-fluid substance is obtained, which when left over sulphuric acid rapidly loses its excess of ether, leaving behind transparent needles of manganous bromide, having the composition  $\text{MnBr}_2 \cdot \text{Et}_2\text{O}$ . This substance fumes in air, is very deliquescent, and on heating loses its ether, leaving the anhydrous bromide as a white powder.

If in the above preparation an excess of bromine is used, the compound  $\text{MnBr}_2 \cdot \text{Et}_2\text{O}$  slowly dissolves, and the liquid separates into two layers, from the denser of which on warming the excess of ether is removed, and a solid substance, m. p. 65—70°, and having the composition  $\text{MnBr}_3 \cdot 3\text{Et}_2\text{O}$ , is obtained. This substance is soluble in water, and on heating decomposes at 100°, losing its ether and evolving fumes of hydrogen bromide.  
W. G.

**Higher Manganese Phosphides.** S. HILPERT and TH. DIECKMANN [with O. HANF] (*Ber.*, 1914, 47, 780—784).—A mixture of manganese (2 grams) and red phosphorus (2.4 grams) was heated in an exhausted, sealed Jena-glass tube, first at 400°, and finally at 600°, for a considerable length of time. Any phosphorus unacted on distilled into the drawn-out end of the tube. The grey contents of the tube, after triturating with benzene, washing with alcohol and ether, and drying over sulphuric acid in a vacuum, had a composition agreeing with the formula  $\text{MnP}_2$ . No alteration in weight took place on heating for thirteen hours in a current of hydrogen at 290°. When heated at 400°, however, phosphorus was gradually lost, giving, finally, a compound of the composition  $\text{MnP}$  (compare A., 1911, ii, 1090), and having  $D_4^{25}$  5.39.

Both phosphides are blackish-grey powders, not acted on by oxygen-free acids, and only slowly attacked by nitric acid. They are both ferromagnetic, the Curie-point for the compound  $\text{MnP}_2$  being approximately 38°, that for  $\text{MnP}$  about 28°. T. S. P.

**Theory of the Removal of Manganese from Drinking Water.** J. TILLMANS and O. HEUBLEIN (*Zeitsch. Nahr. Genussm.*, 1914, 27, 253—264).—The elimination of manganese salts from water contaminated with the same (compare A., 1907, ii, 888), by filtering the water through material containing manganese dioxide, depends on the formation of a mangano-manganite by the combination of the dioxide with the manganous salts present. The acid radicle of the manganous salt is at the same time set free. This free acid is always carbon dioxide, since all natural waters contain hydrogen carbonates in quantity more than sufficient to combine with any mineral acid which may be liberated.  
W. P. S.

**The Action of Concentrated Sulphuric Acid on Iron.**

CHARLES E. FAWSITT and CHARLES W. R. POWELL (*J. Soc. Chem. Ind.*, 1914, **33**, 234—237).—The effect of temperature, quality of iron, and quality of acid on the products and rate of reaction were investigated. The temperatures varied between 25° and 200°, and the kinds of iron used were steel plate, steel cut from a sulphuric-acid drum, steel wire, wrought iron, British pig iron, No. 1 foundry, British white cast iron, Lithgow (N.S.W.) cast iron, reduced iron. The analyses of the various kinds of iron are given.

Concentrated sulphuric acid acts at the ordinary temperature on steel and some kinds of cast iron, the products being ferrous sulphate and hydrogen, with a small quantity of sulphur dioxide. A rise in temperature of 10° trebles the reaction velocity; at 180° the gaseous products are sulphur dioxide, with occasional small quantities of hydrogen sulphide, but no hydrogen.

The rate of reaction depends on the concentration of the acid, but for the dilutions used (94·6—97·5%) the ratio of hydrogen to sulphur dioxide in the mixture of gases evolved remains almost unchanged.

The condition of the surface of the iron appears to be the most important factor governing the rate of reaction with any one sample; the rate also depends on the composition of the iron, pig iron, for example, giving sulphur dioxide at a lower temperature than steel wire.

Experiments on a large-scale with a steel drum containing concentrated sulphuric acid gave similar results to the laboratory experiments, at temperatures varying from 12—20°.

From the results of the above experiments, the authors draw the conclusion that the safety of the carriage of sulphuric acid in iron drums will depend on the quality of the acid, the size of the air space left when filling, the temperature, and the time that elapses before the pressure is released.

T. S. P.

**The Volume Changes of Steel during Quenching.**

M. OKNOV (*Ferrum*, 1913, **11**, 1—11).—Steel quenched from a temperature above A1 occupies a larger volume than when slowly cooled. The magnitude of the change is dependent on the proportion of carbon and other elements, and on the velocity of cooling, but is, within the limits 700—1000°, independent of the temperature of quenching. When the carbon is below 0·5%, quenching between 750° and 800° gives a smaller volume than quenching from 700°; this corresponds with the existence of  $\beta$ -iron.

Repeated quenching of hypereutectoid steels gives a progressive increase of volume, owing to liberation of temper carbon.

The maximum volume change is given by eutectoid steel, the change diminishing as the carbon content either rises or falls.

C. H. D.

**The System Iron-Copper.**

RUDOLF RUER and CARL FICK (*Ferrum*, 1913, **11**, 39—51. Compare Sahmen, A., 1908, ii, 187).—The freezing-point curve of the system iron-copper indicates the

formation of three series of solid solutions, one of which is restricted to a very small range of composition at the copper end. From 30 to 70% Cu the freezing-point curve is horizontal, and the diagram can only be interpreted on the assumption that two liquid phases are formed, but actual separation of the alloys into two layers is not observed. Separation into two layers occurs, however, as soon as carbon is added, even when the quantity is near to 0.02%. The action of carbon may be merely a deoxidising one, removing the films of oxide which hinder intermixture of the two emulsified liquids.

Copper retains iron in solid solution up to between 1 and 2%, whilst the iron-rich solid solution contains about 20% Cu at 1440°, and a much smaller percentage at lower temperatures. The magnetic change point is lowered to 760° by copper. C. H. D.

**The System Iron-Cobalt.** RUDOLF RUER and KIOSUKE KANEKO (*Ferrum*, 1913, 11, 33—39. Compare Guertler and Tammann, A., 1905, ii, 528).—Pure iron has a transformation point ( $\delta \rightarrow \gamma$ ) at 1420°, and this temperature is raised by addition of cobalt. The freezing-point curve of the system has two branches, one of which passes through a minimum at 1475° and 65% Co. The two branches, which correspond with the solidification of two series of solid solutions, intersect at 1493° and 15.5% Co.

The thermal changes at lower temperatures accord closely with the magnetic changes. The  $\gamma\beta$  and  $\beta\alpha$  transformations coincide from 15% Co onwards, the temperatures rising with increasing cobalt. The transformation curve passes through a maximum at 980° and 45% Co. The eutectoid point must lie between 70 and 75% Co.

All the alloys are homogeneous, and microscopical evidence of the transformations has not been obtained. C. H. D.

**The Preparation of Metallic Cobalt by Reduction of the Oxide.** HERBERT T. KALMUS (*J. Ind. Eng. Chem.*, 1914, 6, 107—115).—The reduction of cobalt oxide,  $\text{Co}_3\text{O}_4$ , by carbon, hydrogen, carbon monoxide, and aluminium, respectively, has been investigated at varying temperatures, using either an oil-fired or electric crucible type of furnace.

Using anthracite coal, rapid reduction does not take place until a temperature in the neighbourhood of 1200° is reached. Better reduction is obtained with charcoal, and complete reduction takes place at 900° if a 20—30% excess of charcoal is used; powdered lampblack gives similar results to charcoal. Briquetting the charge with an organic binder increases the rate of reduction at all temperatures, and a minimum temperature of 800° may then be used. When sufficient carbon is used for complete reduction, the final product need contain only 0.2% of carbon.

The reduction of cobalt oxide by hydrogen takes place very rapidly at all temperatures above 500°, and is complete at temperatures from 960° to 1100°; the greater part of the reduction takes place in the first few minutes. Very pure carbon-free cobalt is thus obtained; it is necessary to cool the cobalt in hydrogen.

Carbon monoxide rapidly reduces cobalt oxide at all temperatures above  $600^{\circ}$ , the reduction being complete in the neighbourhood of  $900^{\circ}$ ; the first stages of the reduction take place very quickly. Between  $350^{\circ}$  and  $450^{\circ}$  reduction takes place at first, but after a time the finely divided cobalt decomposes the carbon monoxide, carbon being deposited. Cobalt prepared by this method must be cooled in an atmosphere of carbon monoxide.

Reduction of cobalt with aluminium by the thermit process gives a metal which very frequently contains less than 0.1% of aluminium.

T. S. P.

**Cobalt Oxides.** HERBERT T. KALMUS (*J. Ind. Eng. Chem.*, 1914, 6, 115—116).—The composition of the various oxides of cobalt has been investigated by determining the loss in weight occurring when they are reduced with hydrogen or carbon monoxide, or with a mixture of these gases.

The ordinary black commercial cobalt oxide, prepared from the hydrate by calcining in the neighbourhood of  $750^{\circ}$ , is a mixture of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_6\text{O}_7$ , but largely of the former. Apparently the quite pure oxide  $\text{Co}_3\text{O}_4$  has not been obtained. The oxide  $\text{Co}_6\text{O}_7$  is not to be distinguished from  $\text{Co}_3\text{O}_4$ , either in appearance or in the method of preparation; it could not be obtained pure.

Above  $910^{\circ}$  the black oxide gives cobaltous oxide,  $\text{CoO}$ , which is readily obtained as a grey powder by calcination at about  $1000^{\circ}$ . It also exists in a yellowish-green allotropic form, which is obtained by heating the black oxide with 2—3% of its weight of carbon at temperatures in the neighbourhood of  $900^{\circ}$ .

All the above oxides are non-magnetic.

T. S. P.

**The Reduction of Nickalous Oxide and the Existence of a Sub-oxide of Nickel.** PAUL SABATIER and LÉO ESPIL (*Compt. rend.*, 1914, 158, 668—675. Compare von Glaser, A., 1903, ii, 646).—A study of the reduction of nickalous oxide by dry hydrogen under varying conditions, the course of the reduction being followed by absorbing and weighing the water vapour produced. The oxide used was obtained by calcining nickel nitrate at temperatures from  $550^{\circ}$  upwards, and warming the products for a few moments in hydrogen at a temperature below  $150^{\circ}$ . The velocity of reduction was found to vary with several factors. The higher the temperature at which the original oxide was calcined, the slower was the reduction. The velocity of the current of hydrogen controlled the reduction, the latter being roughly proportional to the former for slow currents of hydrogen. Elevation of the temperature enormously accelerated the reduction, but it was impossible to fix any definite lower limit below which reduction did not occur. In a given reduction by plotting the amount of oxide reduced after any given time against the time, a curve was obtained formed of two branches, each branch being approximately a straight line, similar results being obtained at different temperatures. By following the slight variations in the inclinations of these curves with rise in temperature, the authors find that the velocity of reduction is an exponential function of the temperature.

These results point to the formation of a sub-oxide, but the authors have been unable to find the conditions under which this would not be simultaneously reduced along with the protoxide. From a study of the reduction curves, they consider that there is formed an unstable sub-oxide having the formula  $\text{Ni}_2\text{O}$ , which, being reduced at the same temperatures as the protoxide, always results in the presence of some metallic nickel in the products of reduction. Moist hydrogen reduces nickelous oxide much more slowly than when it is dry.

W. G.

**Nickel and Cobalt Sulphides. I. Apparent Anomalies in the Behaviour of Nickel Sulphide towards Acids.** A. THIEL and H. GESSNER (*Zeitsch. anorg. Chem.*, 1914, 86, 1—57).—The experiments were conducted in an atmosphere of nitrogen, and filtration was effected by an inverted asbestos filter connected with a pump. All reagents were prepared with water free from dissolved oxygen.

The precipitates from a neutral solution of nickel chloride and soluble sulphides consist mainly of a modification which dissolves readily in acids. This result is not much altered by using an excess of either reagent, or by varying the rate of precipitation or the temperature, but the less soluble modification is formed by boiling with water or by long contact with a cold solution containing nickel, or with cold dilute acetic acid. All modifications of nickel sulphide have the same composition,  $\text{NiS}$ , and the most soluble is the most readily oxidised by air.

$\alpha$ -Nickel sulphide is soluble in strong mineral acids down to 0.01*N*, whilst  $\beta$ - $\text{NiS}$  is fairly rapidly dissolved by 2*N*-hydrochloric acid, and  $\gamma$ - $\text{NiS}$  is not appreciably dissolved except on addition of oxidising agents. When very dilute reagents are used, the precipitate is chiefly  $\beta$ - and  $\gamma$ - $\text{NiS}$ . The  $\beta$ -modification is converted into  $\gamma$  by boiling acetic acid. The latter modification is obtained in a pure, crystalline condition from hot, strongly acid solutions. Under ordinary analytical conditions, a variable mixture of the three modifications is obtained.

The differences of solubility are too great to be explained by colloidal conditions, and must be attributed to polymerisation.

When nickel sulphide is attacked by acids, apparently well-defined equilibria are reached; but it has not been found possible to approach these equilibria from the opposite side, from hydrogen sulphide and acid solutions of nickel, even when the corresponding solid sulphide is added to inhibit supersaturation. This fact has not been explained.

C. H. D.

**Solubility Relations of Nickel Sulphide.** A. THIEL [with H. GESSNER] (*Chem. Zentr.*, 1914, 1, 18—20; from *Sitzungsber. Med.-naturwiss. Ges. Münster*, 1913, reprint 7 pp.).—Experiments have been made which show that the anomalies observed in connexion with the precipitation of nickel sulphide and its solubility in acids are due to the existence of three different modifications. The sulphide which is precipitated under ordinary analytical conditions



consists of a mixture of the three forms, which may be separated more or less completely by means of 2*N*-hydrochloric acid. The  $\alpha$ -form dissolves very readily in cold 2*N*-hydrochloric acid saturated with hydrogen sulphide, whilst the  $\beta$ -form dissolves only to the extent of about 0.033 gram per litre, and the  $\gamma$ -form is practically insoluble. On the other hand, the  $\beta$ -form dissolves very readily in boiling 2*N*-hydrochloric acid, whilst the  $\gamma$ -form is only soluble to the extent of about 0.013 gram per litre.

The  $\alpha$ - and  $\beta$ -modifications cannot be obtained quite free from the  $\gamma$ -form. A sulphide containing 85% of the  $\alpha$ -form is obtained when dilute solutions of nickel salts are slowly mixed with dilute solutions of alkali metal sulphides at the ordinary temperature and in the absence of air. The  $\beta$ -sulphide, mixed with a little  $\gamma$ -sulphide, is obtained when a solution of nickel acetate, acidified with acetic acid, is precipitated by hydrogen sulphide, or by the precipitation of acetic acid solutions of nickel salts which contain large quantities of alkali metal tartrates. The  $\gamma$ -form is obtained by boiling the mixed sulphides with 2*N*-hydrochloric acid, or by the precipitation of a hot solution of a nickel salt acidified with mineral acid.

The  $\alpha$ -sulphide is stable in the absence of air if kept in contact with pure water. In contact with solutions which dissolve it to a slight extent, it is transformed into a mixture of the  $\beta$ - and  $\gamma$ -forms. This change is effected by 0.2*N*-acetic acid in the course of a few hours. The  $\beta$ -sulphide is similarly converted into the  $\gamma$ -form if subjected to the action of boiling 2*N*-acetic acid for several hours. In presence of sodium acetate, the action is appreciably retarded. In both cases the transformation of the soluble into the less soluble form depends on the action of a reagent which dissolves the one form and has no appreciable solvent action on the other.

The  $\gamma$ -sulphide is undoubtedly crystalline, and the  $\beta$ -form appears to be so, but no evidence has been obtained which would suggest that the  $\alpha$ -form is crystalline. The difference between the three forms is supposed to be due to differences in the molecular complexity (polymerisation).

The observations which have been made, indicate that the anomalous behaviour of nickel sulphide towards acids is only apparent. Freshly precipitated nickel sulphide is not insoluble in dilute mineral acids, but in consequence of the presence of the  $\alpha$ -form, it dissolves to a considerable extent. Nickel sulphide may be precipitated by hydrogen sulphide from acid solutions, although this reaction is comparatively slow. The precipitated sulphide which is obtained under these conditions is identical with that which remains behind when freshly precipitated nickel sulphide is subjected to the action of acids of the same concentration.

H. M. D.

**Some Double Chromates.** M. BARRE (*Compt. rend.*, 1914, 158, 495—497. Compare Gröger, A., 1907, ii, 624).—An examination of the double chromates of calcium, strontium, barium, and lead with potassium. The author confirms Gröger's results and has, in

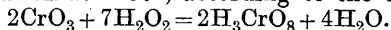
addition, obtained certain new double salts. By the direct action of calcium chromate on solutions of potassium chromate at temperatures below  $45^{\circ}$ , large orthorhombic prisms of the salt  $K_2CrO_4, CaCrO_4, 2H_2O$  are obtained. These, in contact with a solution of potassium chromate at  $60^{\circ}$ , slowly disappear, and small, hexagonal prisms of the anhydrous salt,  $K_2CrO_4, CaCrO_4$ , are formed. Both these salts are decomposed by water. Strontium chromate yields one double salt,  $K_2CrO_4, SrCrO_4$ , decomposable by water. Barium chromate gives the double salt,  $K_2CrO_4, BaCrO_4$ , lead chromate the salt  $K_2CrO_4, PbCrO_4$ . The conditions of temperature and solution concentration for the formation of all these salts are given. W. G.

**Higher Oxidation Products of Chromium. VI. Preparation of the Blue Perchromic Acid.** E. H. RIESENFELD and W. MAU (*Ber.*, 1914, 47, 548—553).—Hitherto it has not been possible to isolate perchromic acid, but evidence has been obtained (Riesenfeld, A., 1908, ii, 951) that it has the composition  $H_3CrO_8$ , corresponding with the red perchromates, although it is blue in colour.

When the red potassium or sodium perchromate is suspended in well-cooled ether and either anhydrous hydrogen chloride or fluoride gas led into, or else anhydrous sulphuric, phosphoric, or acetic added to, the suspension, no reaction takes place. If the temperature is slowly raised, the perchromates decompose to chromic salts without the formation of a trace of blue colour, although perchromic acid is readily soluble in ether. If, however, a few drops of water are added to the ethereal suspension before the decomposition of the perchromate takes place, the blue colour is always formed. Experiments showed that in the presence of water the power of liberating the blue perchromic acid when equivalent quantities of other acids were added depended on the strength of the acid. Acids down to a strength corresponding with the dissociation-constant  $8.2 \times 10^{-4}$  (citric acid) liberated the blue acid, whereas weaker acids, such as mandelic, benzoic, succinic, and acetic acids, had to be used in large excess to obtain the same result. Very weak acids did not liberate the perchromic acid. These results indicate that perchromic acid is of about the same strength as acetic acid.

Attempts to prepare perchromic acid by the interaction of silver perchromate and hydrochloric acid, or of barium perchromate and sulphuric acid, were not successful, decomposition taking place rapidly at  $-20^{\circ}$  to  $-40^{\circ}$ . Better results, although not quite satisfactory, were obtained by the interaction of chromyl chloride and 98% hydrogen peroxide at  $-30^{\circ}$ , the reaction occurring according to the equation  $2CrO_2Cl_2 + 7H_2O_2 = 2H_3CrO_8 + 2H_2O + 4HCl$ .

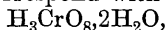
Pure perchromic acid,  $H_3CrO_8, 2H_2O$ , was finally obtained by the interaction of chromium trioxide and 97% hydrogen peroxide in methyl ether solution at  $-30^{\circ}$ , according to the equation



After the reaction was complete, the blue solution was poured off

from the excess of either chromium trioxide or hydrogen peroxide, dried with phosphoric oxide, and then evaporated in a vacuum at  $-30^{\circ}$ . A dark blue, crystalline mass remained, which gave analytical results corresponding with the ratio  $O_2:Cr:H_2O=3.50:1:3.50$ , no matter whether hydrogen peroxide was used in large excess or not. The crystals decompose at a few degrees above  $-30^{\circ}$ .

The analytical results correspond with the formula



the water being water of constitution, since the blue colour only results when perchromates, free acid, and water are brought together. The red perchromates must therefore be considered as anhydro-salts of the blue perchromic acid, their constitution being  $O \gg Cr(O \cdot OM)_3$ , whilst that of the acid is  $(HO)_4Cr(O \cdot OH)_3$ .

T. S. P.

**Preparation of the Metaphosphate of Molybdenum Sesquioxide.** A. COLANI (*Compt. rend.*, 1914, 158, 499—501).—By reduction of molybdic acid, dissolved in metaphosphoric acid at a red heat either by hydrogen or by molybdenum sulphide in a current of carbon dioxide, the author has obtained a yellow, crystalline powder having the composition  $Mo(PO_3)_3$ . The same product is obtained by heating anhydrous molybdenum sulphide in a current of carbon dioxide with orthophosphoric acid. This substance, however prepared, has  $D_4^{20} 3.28$ . It is stable in dry air, and on heating only oxidises superficially. When heated with water in a sealed tube, it is attacked at  $250-300^{\circ}$ , with the formation of phosphoric acid. At  $100^{\circ}$  hydrochloric, nitric, and sulphuric acids, concentrated or dilute, are without action on it. It is slowly soluble in warm aqua regia. Concentrated solutions of alkalis attack it at  $100^{\circ}$ , giving a black substance, and on fusion with alkali phosphates it yields double phosphates. Tungsten under similar treatment only gives compounds soluble in water. W. G.

**Investigations at High Temperatures. III. Tungsten and Carbon.** OTTO RUFF and RUDOLF WUNSCH (*Zeitsch. anorg. Chem.*, 1914, 85, 292—328).—When solid tungsten is heated in a carbon electric furnace, carbon is absorbed, and a relatively infusible outer layer is formed, which may contain more carbon than is capable of being retained in liquid solution.

The carbide,  $CW_3$ , melts above  $2700^{\circ}$ , and solidifies as a homogeneous substance. It does not form solid solutions with tungsten to any considerable extent, as a separate constituent may be detected when the carbon reaches 0.12%. As much as 6.17% of carbon has been dissolved in the liquid metal, and on rapid cooling from  $2800^{\circ}$  the whole of this may be obtained as a carbide,  $CW$ . On cooling slowly, much of this carbide is decomposed, yielding graphite. The carbide does not melt without decomposition, but forms lower carbides and graphite, but at higher temperatures it is probably again stable in the liquid.

A third carbide,  $CW_2$ , probably exists, as a micrographic constituent has been detected between the mono- and tri-tungsten carbides, although its composition has not been definitely determined.

The melting points have been determined by means of a Wanner pyrometer. Three eutectics have been observed, with 1.4, 2.4, and 3.5% C respectively, melting at about  $2690^\circ$ ,  $2660^\circ$ , and  $2580^\circ$  respectively.

The carbide,  $CW$ , may be isolated by chemical treatment. The finely powdered alloys are treated with a mixture of nitric and hydrofluoric acids, washed, and separated from graphite by means of acetylene tetrabromide. The carbides,  $CW_3$  and  $CW_2$ , are not obtained in a pure state by this treatment. It is not possible to obtain homogeneous alloys by sintering compressed rods of tungsten and carbon.

The tungsten-carbon system is in some respects similar to the alloys of iron, nickel, and manganese with carbon. All contain carbides of the type  $CM_3$ , and in all cases the solubility of carbon in the molten metal passes through a maximum at a definite temperature.

C. H. D.

**Improvement in the Preparation of Some Pure Metals.** MAURICE BILLY (*Compt. rend.*, 1914, 158, 578—580. Compare Hunter, A., 1910, ii, 302).—The author has prepared pure titanium by passing the vapours of pure titanium chloride over sodium hydride at about  $400^\circ$ . The whole operation is conducted in a special glass apparatus, the sodium hydride being prepared *in situ* by passing hydrogen over sodium heated to  $400^\circ$ , prior to the passage of the titanium chloride. The titanium so prepared is entirely free from any trace of iron, and analyses show it to be extremely pure.

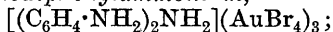
The same method has been applied to the preparation of pure vanadium from its chloride, but in this case the metal must be dried in a current of carbon dioxide at  $100^\circ$ , after extraction of the sodium chloride by acid and water.

W. G.

**Gold.** A. GUTBIER and J. HUBER (*Zeitsch. anorg. Chem.*, 1914, 85, 353—400).—The bromine compounds of gold have been very little investigated. Organic auribromides readily undergo decomposition, with reduction to metallic gold, especially when aromatic groups are present. By keeping the temperature low and removing the film of gold from the surface as it forms, many of these may be isolated, but alcoholic solutions must generally be avoided. The melting points and crystalline characters are less well defined than with the corresponding chlorine compounds. The bromoauric acid is prepared by dissolving gold chloride in hydrobromic acid.

*Ammonium auribromide*,  $NH_4AuBr_4$ , forms large, bluish-black prisms. The potassium, rubidium, and caesium salts have been previously prepared. Only the potassium salt contains  $2H_2O$ ; the others are anhydrous. The following auribromides have also been obtained, and are all anhydrous:

*Mono-, di-, tri- and tetra-methylammonium, mono-, di-, tri- and tetra-ethylammonium, n- and iso-propylammonium, di- and tri-propylammonium, n-butylammonium, mono-, di- and tri-isobutylammonium, allylammonium, mono-, di- and tri-isoamylammonium, guanidinium, aminoguanidinium, triphenylguanidinium, anilinium, mono- and di-methylanilinium, nitrosomethylanilinium, mono- and di-ethylanilinium, isoamylanilinium, benzylianilinium, benzylidene-anilinium, o-, m- and p-chloroanilinium, 2:4-dichloroanilinium, o-, m- and p-bromoanilinium, m- and p-nitroanilinium, 2:4-dinitroanilinium, p-diaminodiphenylammonium,*



*o-, m- and p-toluidinium, dimethyl-o- and -p-toluidinium, 2:4- and 3:4-xylidinium,  $\psi$ -cumidinium, mono- and di-benzylammonium, benzylmethylammonium, benzylethylammonium, benzylidenemethylammonium, benzylidene-ethylammonium, o- and p-anisidinium, dianisidinium, o- and p-phenetidinium, pyridinium, 2- and 3-methylpyridinium, lutidinium, collidinium, piperidinium, quinolinium, isoquinolinium,  $\beta$ -naphthylammonium, o-, m- and p-phenylenediammonium,  $[C_6H_4(NH_2)_2](AuBr_4)_2$ ; 2:4- and 3:4-tolylenediammonium auribromides are also described, and the crystalline form is described in many cases.*

C. H. D.

### Mineralogical Chemistry.

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**Cobaltnickelpyrite, a New Mineral of the Pyrites Group from Müsen, Siegen Westphalia.** M. HENGLEIN (*Centr. Min.*, 1914, 129—134).—This mineral occurs as confused aggregates of small cubic crystals, together with quartz, chalybite, pyrites, and copper-pyrites, in the Victoria Mine at Müsen. The crystals show the forms of the cube, octahedron, and a pentagonal-dodecahedron {320}; there is a fairly distinct cleavage parallel to faces of the cube. The colour is steel-grey with a metallic lustre, and the streak is greyish-black.  $D^{19-20} 4.716 \pm 0.028$ ,  $H 5-5\frac{1}{2}$ . The mineral is decomposed by nitric acid, and when heated it gives off sulphur. Analyses lead to the formula  $(Fe, Ni, Co)S_2$ . In other partial analyses the iron ranges from 16 to 27.15%:

Fe.	Ni.	Co.	S.	Insol.	Total.
21.15	17.50	[6.61]	53.70	1.04	100.00
22.8	11.7	10.6	53.9	0.7	99.7

L. J. S.

**Laterite and its Consideration in the Light of Colloid Chemistry.** A. LUZ (*Kolloid. Zeitsch.*, 1914, 14, 81—90).—A summary is given of the views which have been put forward by different observers in regard to the nature and origin of laterite.

Specimens of laterite from Brazil and German East Africa have been examined microscopically, by means of their behaviour towards dyes, and also by determining the loss of water at different temperatures. From these observations, in combination with earlier data, it is suggested that laterite is the result of a series of changes, in which aluminium silicates containing sodium, potassium, calcium, iron and magnesium give rise in succession to (1) colloidal aluminium silicate, (2) colloidal aluminium hydroxide and silica, (3) crystalline hydrargillite, (4) crystalline diaspore. By a collateral series of changes, crystalline limonite is supposed to be formed from colloidal ferric hydroxide.

H. M. D.

**Wilkeite, a New Mineral of the Apatite Group from California.** ARTHUR S. EAKLE and AUSTIN F. ROGERS (*Amer. J. Sci.*, 1914, [iv], **37**, 262—267).—This mineral occurs as pale rose-red crystals in blue, crystalline limestone near a granodiorite contact at Crestmore, in Riverside Co., California. The crystals are hexagonal, with a prismatic habit and angles near to those of apatite ( $a:c=1:0.730$  about); they are optically uniaxial and negative.  $D^{20} 3.234$ ,  $H 5$ . The mineral is readily soluble in dilute acids with the separation of flocculent silica; and it is remarkable in containing four acid radicles. Analysis gave:

CaO.	MnO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.
54.44	0.77	20.85	12.28	9.62	2.10	trace	100.06

The formula  $20CaO, 3P_2O_5, 3SiO_2, 3SO_3, CO_2$ , when written in the form  $3Ca_3(PO_4)_2, CaCO_3 + 3Ca_3[(SiO_4)(SO_4)], CaO$ , shows a relation to the apatite formula. The wilkeite is often altered to a white, opaque mineral with a pearly lustre and fibrous structure, which was identified as okenite (hydrated calcium silicate).

L. J. S.

**Chemical Composition of Aluminous Augites: an Application of Quaternary Graphical Representations.** H. E. BOEKE (*Zeitsch. Kryst. Min.*, 1914, **53**, 445—462).—Many (163) published analyses of aluminous augites are reduced to molecular percentages of  $SiO_2 + TiO_2$ ,  $CaO$ ,  $(Al, Fe''', Cr)_2O_3$ , and  $(Mg, Fe'', Mn)O$ , and these components are plotted along four of the sides of a regular tetrahedron. A point inside the tetrahedron thus expresses the composition given by each analysis. The whole series of points is inscribed within a solid, the form of which is shown more clearly by projections on three planes at right angles.

L. J. S.

**The Melting Points of Some Japanese Minerals.** YASUTARO YAMASHITA and MASAICHI MAJIMA (*Sci. Reports Tôhoku Imp. Univ.*, 1913, **2**, 175—178).—The melting points of the following Japanese minerals were determined by the heating-curve method; temperatures up to  $1500^\circ$  were measured with a platinum-rhodium thermocouple, and above that temperature with an optical pyrometer. The localities are given in brackets: Anorthite (Miyakojima),  $1528^\circ$ , (Tarumae),  $1533^\circ$ ; bronzite (Anijima, Ogasawara),  $1459^\circ$ ; andesine (Thioda, Shinano),  $1333^\circ$ ; oligoclase andesine (Yûôshima),  $1232^\circ$ ,

1257°; augite (Otomezaka, Echigo), 1074°; orthoclase-albite, 1250°, 1228°; granite, 1446°, 1478°, 1509°. T. S. P.

**Ferri-allophane from the Neighbourhood of Moscow.** F. A. NIKOLAEVSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 147—150).—The secondary dolomites immediately below the shallow band of clay adjacent to the carboniferous limestone in the neighbourhood of Moscow contain, besides colloidal crusts of allophanoids, a mineral which in its most typical and pure form possesses the form of a colloidal substance with a vitreous lustre and an irregular conchoidal fracture. At the edges it transmits a dense, dark brown light, and its hardness is 3·5, its specific gravity 2·14, and its streak yellow-ochre. It is difficult to obtain quite free from admixtures of calcium carbonate, and, allowing for this, its mean percentage composition is:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.
20·18	23·77	25·05	31·00	100·00

As is the case in the argillaceous allophanes, the relations between the oxides vary within somewhat wide limits approximating in the mean to the simple ratio: SiO<sub>2</sub>:R<sub>2</sub>O<sub>3</sub>:H<sub>2</sub>O=1:1:5. Such variations are often encountered in substances of colloidal structure, but these substances generally approximate to simple formulæ, since the colloidal nature of the compound does not exclude the possibility of perfectly definite, stoicheiometrical relations (compare Cornu, A., 1909, ii, 222; Gans, this vol., ii, 55).

The author suggests the name *ferri-allophane* for the mineral described above. T. H. P.

**Chemical Investigation of Certain Minerals from Ceylon Gravel.** VI. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 103—114. Compare this vol., ii, 211).—Fine concentrates from the Sabaragamuwa Province were found to contain rounded crystals quite black on the crystal faces, but greyish-black on the rounded surfaces. Their fracture is not characteristic, but is somewhat of an imperfectly conchoidal form, and the fresh fracture shows an intense glassy lustre. No cleavage is exhibited, and the streak is dark brownish-grey. The hardness is slightly inferior to that of orthoclase, and the specific gravity 4·83, and thin sections transmit a faint reddish-brown light. Concentrated mineral acids, even when boiling, are almost entirely without action on it. The percentage composition is as follows:

FeO.	CaO.	MgO.	ThO <sub>2</sub> .	U <sub>3</sub> O <sub>8</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	Ce <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	WO <sub>3</sub> .
7·55	10·51	0·94	7·43	0·08	0·12	1·52	17·03	0·22	trace

SiO <sub>2</sub> .	TiO <sub>2</sub> .	ZrO <sub>2</sub> .	Loss on ignition	Total.
0·16	20·77	32·17	0·47	99·02

This composition is expressed approximately by the formula:  
 4FeO, 8CaO, ThO<sub>2</sub>, Na<sub>2</sub>O, 2Ce<sub>2</sub>O<sub>3</sub>, 10ZrO<sub>2</sub>, 10TiO<sub>2</sub>, aq., or  
 ThO<sub>2</sub>(TiO<sub>2</sub>)<sub>2</sub> + 2[Ce<sub>2</sub>O<sub>3</sub>(TiO<sub>2</sub>)<sub>3</sub> + 4CaO, ZrO<sub>2</sub> +  
 (FeO)<sub>2</sub>TiO<sub>2</sub>] + Na<sub>2</sub>O(ZrO<sub>2</sub>)<sub>2</sub> + aq.



The physical and chemical properties of the mineral characterise it as a modification of zirkelite, which has been found previously in Ceylon (compare Hussak and Prior, A., 1895, ii, 508; Prior, A., 1897, ii, 411).

The methods of analysis are described in detail. T. H. P.

**Recognition and Determination of Combustible Gases in Mineral Waters.** ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1913, 11, 515; 1914, 12, 61—78; *Compt. rend.*, 1914, 158, 634—637).—Methane is present in the dissolved gases of some spring waters. In the water of Zaldívar the quantity is less than 0.03 c.c. per litre.

G. D. L.

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## Analytical Chemistry.

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**Quantitative Sublimation.** II. E. PHILIPPE (*Chem. Zentr.*, 1914, i, 576; from *Mitt. Lebensmitt. Hyg.*, 1913, 4, 351—365. Compare A., 1912, ii, 932).—A further account of the applications of an apparatus for quantitative sublimation. It is recommended that the extraction of fat from coffee preparations should be carried out with the acidified material in order to fix the caffeine completely. The acid solution may then be treated with ammonia, extracted with chloroform, and the residue from the extract sublimed.

J. C. W.

**Employment of the Interferometer in Agricultural Chemical Investigations.** H. KAPPEN (*Landw. Versuchs.-Stat.*, 1914, 83, 385—400).—The results of experiments made with Zeiss' new form of interferometer indicated that the instrument may be of considerable value in a variety of ways. In the examination of a number of river waters it was found that the results corresponded well with estimations of dry matter. Preliminary experiments are also described in connexion with the estimation of potassium and sodium, and the examination of milk serum. Promising results were obtained with soil extracts, especially in connexion with the amounts of soluble colloids present.

N. H. J. M.

**The Properties of the Phthaleins as Indicators, and the Application of the "Acid Step" Method to Clinical Purposes.** A. THIEL (*Chem. Zentr.*, 1914, i, 423—424; from *Sitzungsber. Med.-naturwiss. Ges., Münster i/W.*, 1913, pp. 27).—The author discusses the theory of indicators (compare A., 1913, ii, 425), and introduces the conception of the "characteristic" of an indicator, which is a curve connecting the hydrogen-ion concentration with the "heterochromic" part of the indicator. The latter is represented by the fraction  $I_2/I_1 + I_2$ , where  $I_1$  and  $I_2$  are the colour-bearing forms of the indicator.

In the original, a simple method, based on the study of the "characteristics," is described, by which the actual hydrogen-ion concentration of a colourless or moderately coloured solution may be colorimetrically determined.

J. C. W.

**A New Weighing Bottle.** FRITZ FRIEDRICHS (*Zeitsch. anal. Chem.*, 1914, 53, 177—178).—The apparatus consists of a small, oval-shaped glass bulb drawn out at the lower end to a very narrow tube. The top part is fitted with a glass stopper, and into this is fused a platinum or nickel wire, which reaches to the lower end of the tube, and closes it. After introducing a suitable quantity of the fine powder and weighing the whole, the stopper is lifted, and by moving the wire upwards and downwards the powder is made to fall into the desired receptacle, and the bottle is then re-weighed.

L. DE K.

**A Double-walled Crucible for Ignition Purposes.** A. C. VOURNASOS (*Zeitsch. anal. Chem.*, 1914, 53, 175—177).—A porcelain crucible is suspended by means of a bent rim within a second crucible made of any suitable material. The empty space between the crucibles occupies about 1 cm., and may be filled with sand, asbestos, etc., but this is generally unnecessary. The inner crucible when in use is covered with a lid having a depth of 6 mm., and fitted with a hollow T-handle. Many advantages are claimed for this double-walled crucible.

L. DE K.

**Detection and Estimation of Small Quantities of Iodine in Oils.** G. FENDLER and W. STÜBER (*Zeitsch. physiol. Chem.*, 1914, 89, 123—132).—The amounts of iodine stated to be present in certain oils vary very greatly, probably owing to unsatisfactory modes of estimation. By selecting a suitable mode of incineration, a suitable oxidising agent and a suitable solvent for the extraction of the iodine, accurate estimations can be made, judging from the results obtained with oils containing iodine in amounts previously controlled gravimetrically. The oil (25 grams) is saponified in a platinum dish with 50 c.c. of aqueous-alcoholic potassium hydroxide (potassium hydroxide 14 grams, alcohol 70 c.c., water to 100 c.c.). After removing the alcohol, the residue is cautiously incinerated, and then completely extracted with water. The filtered aqueous solution is treated with 50 c.c. of sulphuric acid (containing 24 grams of sulphuric acid in 100 c.c.) and 20 c.c. of 10% potassium dichromate solution, and the liquid is extracted with small quantities of carbon tetrachloride. The united carbon tetrachloride extracts are titrated with 0.01*N*-thiosulphate until colourless, no indicator being used.

R. V. S.

**Detection of Fluorine in Wine.** CHARLES BLAREZ (*Ann. Falsif.*, 1914, 7, 65—67).—Referring to a method described by Gautier (A., 1912, ii, 681) and to a more recent note by the same writer, the author points out that this method of concentrating the fluorine in the barium sulphate precipitate was described previously by himself (*Bull. trav. Soc. Pharm. Bordeaux*, 1904, 321). W. P. S.

**Estimation and Distinction of Ozone, Nitrogen Peroxide, and Hydrogen Peroxide at High Dilutions.** J. N. PRING (*Chem. News*, 1914, 109, 73—75).—A 50% potassium iodide solution may be employed as a reagent for the detection of these gases in air. In the reaction between ozone and potassium iodide, the ratio of iodate (+periodate) to free iodine (+hypoiodite) formed increases with the concentration of the gas and the total amount which is passed through the solution; at some point between 6 and 160 parts of ozone per million of air no iodate is formed, but only free iodine and hypoiodite. This relation does not hold at temperatures below  $-24^{\circ}$ , the freezing point of the reagent. With nitrogen peroxide the reaction results mainly in the formation of iodate, whatever the dilution of the gas. Even minute quantities of nitrogen peroxide act catalytically when present in an acidified potassium iodide solution, and iodine is liberated continuously; this reaction is characteristic of the gas. Hydrogen peroxide behaves in a similar manner to ozone towards potassium iodide, but may be distinguished by means of titanous acid. A solution of titanium sulphate in sulphuric acid becomes yellow in the presence of small quantities of hydrogen peroxide, but is not affected by ozone.

W. P. S.

**Estimation of Sulphur in Iron Pyrites.** ERNEST MARTIN (*Mon. Sci.*, 1913. [v], 3, ii, 686—688).—0.5 Gram of the dry and powdered sample is placed in a 150 c.c. flask and 25 c.c. of aqua regia are added (equal parts of nitric and hydrochloric acid). After standing overnight, the whole is evaporated on a sand-bath to near dryness, best with addition of 1 gram of sodium chloride. The residue is treated with 2 c.c. of hydrochloric acid and 2 c.c. of water, 50 c.c. of boiling water are added, and then little by little 4 grams of sodium carbonate; the iron is thus precipitated, and is collected and thoroughly washed with boiling water. After removing the carbon dioxide by boiling, the liquid, when cold, is carefully neutralised with dilute hydrochloric acid, using methyl-orange as indicator.

To the warmed liquid are then added 60 c.c. of barium hydroxide solution (45 grams per litre). A drop of phenolphthalein is added, and enough carbon dioxide is passed to decolorise the solution. The precipitate is then collected and washed with warm water, and the filtrate when cold is titrated with  $N/2$ -hydrochloric acid. The result represents sulphuric acid (sulphur).

When applying the process to the assay of burnt pyrites, from 2 to 5 grams are operated on. Before adding the baryta solution the liquid should be well boiled.

L. DE K.

**Estimation of Sulphur in Caoutchouc.** HENRY P. STEVENS (*Analyst*, 1914, 39, 74—78).—Loss of sulphur occurs to a greater or less extent when caoutchouc and its products are oxidised with nitric acid, owing to the formation of volatile sulphur compounds. Such volatile compounds may be retained, for estimation as barium sulphate, by passing the evolved gases through potassium hydroxide

solution, nitric acid, or even water, if this is treated subsequently with nitric acid. The loss may also be prevented by carrying out the oxidation in a flask attached to an efficient reflux apparatus.

W. P. S.

**A Method for the Determination of the Injuries of Cultivated Plants Caused by Sulphur Dioxide.** GIUSEPPE DI STEFANO (*Chem. Zentr.*, 1914, i, 415—416; from *Staz. speriment. agrar. ital.*, 1913, **46**, 780—782).—The injured material is cut into very small fragments, and digested with cold water for two days in the shade, when the extract is treated with iodic acid and shaken with chloroform. Small traces of sulphur dioxide may be detected by the violet colour imparted to the chloroform.

J. C. W.

**Physico-chemical Estimation of Sulphates.** ANDRÉ KLING and A. LASSIEUR (*Compt. rend.*, 1914, **158**, 487—489.\* Compare Bruno and Turquand d'Auzay, A., 1912, ii, 600).—Dutoit's method for estimating sulphates by conductivity measurements gives false results in estimating sulphates in wines, owing to various external factors. The error arises from the presence of organic acids, from variation in the sulphate concentration and that of the reagent, from variations in the temperature, and the presence of alcohol. The error varies with the metal in the sulphate, being, in the case of the alkalis, at its maximum with potassium and rubidium, and at its minimum with lithium and caesium. A further source of error is the carrying down of soluble sulphate with the barium sulphate, this being controlled in its turn by numerous factors which are given in detail. The presence of alkali checks it, but at the same time some of the alkali is carried down.

W. G.

**Detection of Carbon Disulphide in Extracted Oils.** URZ (*Chem. Zentr.*, 1914, i, 578; from *Farbenzeit.*, 1913, **19**, 698—700).—Two methods are recommended for this purpose, namely, precipitation with thalloacetylacetone (Kurowski, A., 1910, i, 361) and conversion of the carbon disulphide into cuprous xanthate. In the former case, the oil is diluted with alcohol, and then the first 5—10 c.c. of the distillate are treated with the reagent, when the characteristic orange precipitate is gradually formed. The presence of 1% of carbon disulphide can be detected with certainty.

J. C. W.

**Gravimetric Estimation of Selenium.** JULIUS MEYER (*Zeitsch. anal. Chem.*, 1914, **53**, 145—153).—The author states that when evaporating selenious acid solutions on the water-bath a marked loss of selenium is noticed, which becomes very serious when hydrochloric acid is present; addition of potassium or sodium chloride, which has been recommended, does not prevent this loss. The reduction to selenium is best effected by boiling with hydrazine hydrate. As the spray formed by the escaping nitrogen carries off a certain amount of finely-divided selenium, a special apparatus should be used in which the spray is condensed, and flows back into the reduction flask.

L. DE K.

\* and *Anal. Falsif.* 1914, **7**, 145—151.

**Estimation of [Total] Organic Nitrogen.** LAURENT SLIZEWICZ (*Ann. Chim. anal.*, 1914, 19, 54—56).—The result of the "Kjeldahl destruction" is neutralised with sodium hydroxide with phenolphthalein as indicator, and after adding neutralised formaldehyde the acidity liberated is titrated with standard alkali; the result represents the nitrogen. On account of the phenolphthalein titration, a correction of  $1/30$  of the nitrogen should be made.

When, as in the case of alkaloids, it is necessary to complete the destruction by means of mercuric oxide or copper sulphate, these metals should be eliminated before proceeding to the formalin titration. This may be effected by adding 150 c.c. of water and boiling with some 5 grams of sodium hypophosphite. When cold, the whole is made up to 200 c.c. and an aliquot part taken and treated as directed.

L. DE K.

**Source of Error in the Analysis of Waste Acids obtained in the Manufacture of Nitrocelluloses.** TH. CHANDELON (*Bull. Soc. chim. Belg.*, 1914, 28, 58—62).—The dissolved nitrocellulose remaining in the mixture of acids used in the manufacture of this substance causes the formation of a small quantity of oxalic acid, and the latter reduces an equivalent amount of permanganate in the estimation of the nitrous acid present in the acid mixture. The error thus introduced is, however, small, amounting to about 0.0846% of  $N_2O_3$ , but it increases as the acid mixture is used for nitrating successive charges of cellulose.

W. P. S.

**Modifications of Grandval and Lajoux's Method of Determining Nitrates.** ANGEL SABATINI and LUCIANO P. PALET (*Anal. Soc. Quim. Argentina*, 1913, 1, 336—338).—Before proceeding to the estimation of nitrate in water, it is desirable to remove chlorides by means of dry silver oxide, a blank experiment being made to determine nitrate (if any) in the oxide. If this is not done, considerable loss of nitrate ensues.

G. D. L.

**Use of Sodium Citrate for the Estimation of Reverted Phosphoric Acid.** ALFRED W. BOSWORTH (*J. Ind. Eng. Chem.*, 1914, 6, 227—228).—Owing to the care required in preparing neutral ammonium citrate solution for the estimation of reverted phosphoric acid in phosphates, to the fact that ammonium citrate dissolves appreciable quantities of tribasic calcium phosphate, and to the dissociation of ammonium citrate (with loss of ammonia) when its solution is heated, the author proposes the use of sodium citrate solution for the purpose of the estimation. Results of preliminary experiments with sodium citrate solution indicate that its employment would be an advantage.

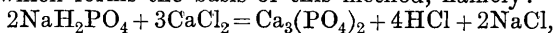
W. P. S.

**Simple and Rapid Method of Estimating Phosphoric Acid in Bakery Materials and Similar Products.** L. SOBEL (*Chem. Zentr.*, 1914, i, 73; from *Schweiz-Woch. Chem. Pharm.*, 1913, 51, 677—679).—Twenty-five grams of the well-dried and finely powdered sample are thoroughly ground with three portions each of

100 c.c. alcohol (96%), the filtrates united, and made up to 300 c.c. with washings from the residue. An aliquot portion of the solution is evaporated to dryness in a platinum crucible with 2—3 grams of magnesium chloride and 3 grams of potassium nitrate, and the residue cautiously incinerated in the covered crucible. Liquids are directly evaporated with magnesium chloride and potassium nitrate, the residue being dried and incinerated. The ash contains magnesium hydrogen phosphate, magnesium pyrophosphate, and carbonate in addition to complex compounds. Phosphoric acid is extracted with dilute aqueous hydrochloric acid, and estimated in the extract after addition of ammonia. A series of comparative analyses shows that the method has the advantage of great accuracy combined with rapidity.

H. W.

**Volumetric Estimation of Phosphates in the Ashes of Foodstuffs.** B. PFYL (*Arb. Kais. Gesund. Amt.*, 1914, **47**, 1—44).—The method which has been proposed for the volumetric estimation of phosphates in the ashes of foodstuffs (compare Doherty, *Analyst*, 1908, **33**, 273; Fiehe and Stegmüller, *Arb. Kais. Gesund. Arnt.*, 1912, **15**, 305), and depends on the use of two indicators, is not altogether satisfactory, since even solutions of pure phosphates do not give accurate results. The method consists in heating the ashes with a slight excess of acid to remove carbon dioxide, titrating the solution with alkali, using methyl-orange as indicator, and then, after the addition of 5 c.c. of a 20% solution of calcium chloride, using phenolphthalein as indicator. From the number of c.c. used in the second titration the percentage of phosphoric acid can be calculated. Experiments showed that the reaction which forms the basis of this method, namely:



is only complete when the solubility of the tricalcium phosphate, as also the formation of acid calcium phosphate and of basic polycalcium phosphates, is completely suppressed by the addition of sufficient calcium chloride, by using appropriate temperatures, and by waiting for a sufficiently long time.

With pure phosphate solutions the following method is generally sufficiently accurate. The volume of the solution should be 20—30 c.c., and it should not contain more than 70 mg. of  $\text{PO}_4$ , corresponding with about 15 c.c. of 0.1*N*-sodium hydroxide. After the addition of 1 drop of methyl-orange solution (1 gram per litre) the solution, contained in a Jena-glass flask, is titrated with 0.1*N*-hydrochloric acid to a red colour; then with 0.1*N*-sodium hydroxide to a yellow colour, using an equal volume of water containing 1 drop of methyl-orange and 1 drop of 0.1*N*-alkali as the comparison solution. To the solution are then added 30 c.c. of a 40% neutral solution of calcium chloride; the whole is then heated to boiling, and cooled to about 14°. Two drops of phenolphthalein solution (1 gram in 100 c.c. of 96% alcohol) are then added, and the solution titrated with 0.1*N*-sodium hydroxide free from carbonate to a distinctly red colour. The flask is then closed with a rubber stopper, kept for two hours at 14°, when the contents generally

become colourless, and again titrated to a red colour. From the results the percentage of phosphate can be calculated.

If the solution contains more than 70 mg.  $\text{PO}_4$  and the results are to be accurate, not more than 20—25 c.c. of the solution, containing at the most 119 mg.  $\text{PO}_4$ , should be taken; it should be cooled to  $4^\circ$  before titration against phenolphthalein, and then kept in an ice-chest overnight before the final titration.

A blank test should be carried out with a solution of 0.1*N*-hydrochloric acid equivalent to the number of c.c. of sodium hydroxide used, and to which calcium chloride has been added.

An extended series of experiments was made to ascertain the influence of other substances on the phosphate estimation in the ashes of foodstuffs. Pyro- and meta-phosphates must be prevented from forming by adding alkali to the foodstuff before it is ashed; this precaution is always necessary when boric acid is present.

The disturbing effect of aluminium and iron salts is obviated by precipitating them as tertiary phosphates by incomplete neutralisation of the acid solution towards methyl-orange; the collected phosphates are then dissolved in neutral sodium citrate solution and titrated.

When boric acid is not present, silicic acid and manganese compounds of higher valency are removed by evaporation of the ash with concentrated hydrochloric acid; pyro- and meta-phosphates are thereby converted into orthophosphates.

When boric acid is present, iron and aluminium phosphates are removed as before, the solution is made neutral to methyl-orange, neutral sodium citrate solution added, together with hydrogen peroxide, and the titration carried out as before, except that the addition of calcium chloride is not necessary. The errors due to borates, silicates, and small quantities of the manganese compounds of higher valency are thus obviated. Also, after the addition of mannitol, the boric acid can be estimated.

When the ash contains no phosphate or only small quantities of the same, together with iron, aluminium, or manganese salts, it is necessary to add a known quantity of a phosphate solution, in order to prevent being misled by these salts.

T. S. P.

**Iodometric Estimation of Arsenic in Iron and Iron Ores after Precipitation with Hypophosphorous Acid.** LANCELOT ANDREWS (*Chem. Zeit.*, 1914, 38, 295).—A reply to Brandt (this vol., ii, 68). The author thinks his method of reducing with stannous chloride is preferable to the hypophosphite process, which yields an arsenic deposit contaminated with phosphorus. A volatilisation of arsenic as chloride is also to be feared in Brandt's process.

L. DE K.

**Iodometric Estimation of Arsenic in Iron and Iron Ores after Precipitation with Hypophosphorous Acid.** L. BRANDT (*Chem. Zeit.*, 1914, 38, 295—296).—A reply to Andrews (preceding abstract). The objections to the hypophosphite process are not justified, and the use of stannous chloride presents no advantages.

L. DE K.



**Iodometry of Arsenic, Copper, and Iron.** G. D. LANDER and J. J. GEAKE (*Analyst*, 1914, **39**, 116—121).—The accuracy of the process given by Avery and Beans (*A.*, 1901, ii, 623) for the iodometric estimation of arsenic in Paris-green and similar cupriferrous mixtures is confirmed.

Arsenates are reduced by means of sulphur dioxide, and any volatile acids should be expelled by evaporation with sulphuric acid.

The method is also suitable for the estimation of arsenites in the presence of ferric iron, but not in mixtures containing ferrous iron, chromium, nickel, cobalt, bismuth, and zinc salts. The best procedure is to add Rochelle salts first, and then slight excess of sodium hydrogen carbonate to the solution before titrating.

As regards the iodometric titration of cuprous chloride, the authors find that the reaction is a reversible one, and the process is therefore best carried out by adding excess of iodide and titrating with thiosulphate. Titration of ferrous salts has been attempted with but indifferent results.

Attention is also called to the slight absorption of iodine by acid carbonate.

L. DE K.

**Solubility of Silica in Hydrochloric Acid, Nitric Acid and Sulphuric Acid, and its Recovery.** MAX WUNDER and A. SULEIMANN (*Ann. Chim. anal.*, 1914, **19**, 45—49).—From the authors' experiments it is evident that silica cannot be completely recovered by a single evaporation and subsequent drying at 110° in the presence of the above acids, but the acid filtrate should be again examined for silica. After digesting gelatinous silica with dilute hydrochloric acid (1:2) for two hours on the water-bath, the liquid contained 0.12 gram of silica per litre; after twelve hours at 18°, 0.03 gram was found. With acid (1:1) the result was 0.14 and 0.03 gram per litre respectively, and with acid (2:1) 0.331 and 0.05 gram.

When substituting nitric for hydrochloric acid, the results were 0.10, 0.08, and 0.04 gram per litre (water-bath), and 0.02, 0.03, and 0.03 gram at 18°.

With dilute sulphuric acid (1:2) the result was 0.02 gram per litre (water-bath), and 0.04 gram at 18°.

L. DE K.

**Analysis of Silicol and other Silicon Compounds Used in Generating Hydrogen.** GEORGE F. JAUBERT (*Chem. Zentr.*, 1914, **85**, 73—74; from *Rev. gen. Chim. pure. appl.*, 1913, **16**, 341—347).—The apparatus consists of a two-litre round-bottomed flask connected with a series of three wash-bottles, the first containing water to condense steam, the second bromine water and an excess of bromine to retain phosphine compounds, and the third 10% sodium hydroxide; the latter is connected with a gasometer for measuring the volume of gas evolved, and is provided with a thermometer, the bulb of which does not dip into the solution.

In an experiment, 500 c.c. of 40% sodium hydroxide are heated to about 80° in the flask. Fifty grams of the material under investi-

gation are accurately weighed, and enclosed in portions of 10 grams in cartridges of smooth paper, one end of which is securely fastened, the other loosely wrapped together. A cartridge is introduced into the flask, which is then securely corked. A steady evolution of gas occurs, during which the paper cartridge functions in much the same manner as a Kipp's apparatus. When the evolution of gas ceases, a second cartridge is introduced, and so on. The temperature of the gas leaving the last wash-bottle is observed, and the volume corrected to 0° and 760 mm. For the determination of phosphorus compounds the contents of the second wash-bottle are boiled to expel the excess of bromine, and, after cooling, precipitated with magnesium solution after addition of ammonia and ammonium chloride.

*Gravimetric Analysis of Silicol.*—For the determination of silicon, 0.5 gram of the finely-powdered material is cautiously heated in a nickel dish of 8 cm. diameter with a mixture of 5 grams of dried sodium carbonate and 10 grams of sodium peroxide, and, finally, with continuous agitation, melted to a clear fluid. After cooling, the product is dissolved in water, acidified with hydrochloric acid, and the solution evaporated to dryness. The residue is treated with 10 c.c. of hydrochloric acid and 100 c.c. of water and filtered, the process being repeated with the filtrate. The combined precipitates are dried, ignited, and weighed, and the silica found from the loss incurred on treatment with hydrofluoric and sulphuric acids.

Titanium is determined by melting the residue in the crucible with potassium hydrogen sulphate (1 gram), dissolving the fused mass in much hot water, and uniting the solution with the two filtrates obtained in estimating the silicon. The mixed solutions are neutralised with ammonia, acidified with 1—2 drops of sulphuric acid, and treated with 60 c.c. of aqueous sulphurous acid. After boiling for an hour, the titanium dioxide is filtered, ignited, and weighed.

For the estimation of iron, the filtrate is made up to 500 c.c., of which 250 c.c. are titrated with potassium permanganate. Aluminium is determined in the remaining 250 c.c. After exact neutralisation with ammonia, hydrochloric acid (4 c.c.) is added, followed by solutions of tribasic ammonium phosphate (2 grams), sodium thio-sulphate (10 grams), and acetic acid (15 c.c.). After boiling for fifteen minutes, the precipitate is filtered, ignited, and weighed as aluminium phosphate. A commercial specimen of silicol examined according to the above method had the composition: Si, 70.35%; Fe, 11.90%; Ti, 3.55%; Al, 14.05%. For the evaluation of silicon compounds which are intended for the preparation of hydrogen, the author recommends the determination of the volume of hydrogen evolved by the action of sodium hydroxide in the above manner. Fifty grams of silicol yield 70—75 litres of hydrogen. H. W.

**Estimation of Free Alkali Hydroxide in Soaps.** P. HEERMANN (*Zeitsch. angew. Chem.*, 1914, 27, 135—136).—Polemical against Bosshard and Huggenberg (this vol., ii, 218), the author emphasising the fact that solid soaps are far from homogeneous, so

that great care is necessary in sampling them; 20, 50, or 100 kilos. of the soap should be dissolved in water or other solvent, and the solution thus obtained should be sampled. T. S. P.

**Estimation of Free Alkali in Commercial Sodas and Soaps by the Barium Chloride Method.** ANDRÉ KLING, VICTOR GENIN and D. FLORENTIN (*Bull. Soc. chim.*, 1914, [iv], 15, 200—205; *Ann. Falsif.*, 1914, 7, 81—85)—The authors have made a series of experiments on the method of estimating free alkali in the presence of alkali carbonates, etc., by use of barium chloride in the cases of pure sodium carbonate, stearate, oleate, silicate, and borate. Slight residual alkalinity is found with the first three substances; with the last two, the alkalinity of the filtrate is considerable, and in the case of borax varies with the volume of barium chloride solution used. In the case of sodium silicate, it is found (1) that the residual alkalinity is proportional to the volume of the solution, and is unaffected by the length of time during which the precipitate remains in contact with the solution; (2) that the residual alkalinity is independent of fluctuations in temperature during the time the precipitate and solution are in contact, provided always that it is determined in the filtrate after cooling to the initial temperature; and (3) that the ratio  $\text{SiO}_2 : \text{BaO}$  in the filtrate is unity. Residual alkalinity is therefore caused by dissolved barium silicate.

The following are the general conclusions:

(1) The barium chloride method of determining free alkali in soda does not give exact results when the latter contains such salts as sodium silicate or borax, which can give rise to appreciably soluble barium salts, that behave towards indicators in the same manner as barium hydroxide. On the other hand, the results are perfectly trustworthy if the soda is dissolved in water, a slight excess of barium chloride solution (10%) added, and the mixture treated with an equal volume of alcohol (95%); after remaining for some time, the precipitate is filtered, and the alkalinity of the filtrate estimated in the usual manner by  $N/20$ -sulphuric acid in boiling solution, litmus being used as indicator.

(2) The method is equally applicable to soaps which contain borates or silicates. On the other hand, the method has no advantage for soaps which only contain fatty esters, and, above all, oleates, since the solubility of barium oleate in 50% alcohol is considerable, exceeding even its solubility in water. H. W.

**Estimation of Hardness in Natural Waters.** CLARENCE BAHLMANN (*J. Ind. Eng. Chem.*, 1914, 6, 209—211)—A summary is given of the results obtained in an investigation dealing with the accuracy of certain volumetric methods for the estimation of calcium-, magnesium-, and total-hardness in waters. In the case of water of medium hardness, the total hardness may be estimated in the usual way by means of standardised sodium carbonate and sulphuric acid solutions, and the calcium hardness by titrating the precipitated calcium oxalate with permanganate solution, the magnesium hardness being found by difference. With very hard

waters containing only small quantities of magnesia, it is necessary to estimate the latter gravimetrically.

W. P. S.

**Valuation of Fluorspar.** E. BIDTEL (*J. Ind. Eng. Chem.*, 1914, 6, 265).—The following modifications are made in the method described previously by the author (A., 1912, ii, 997). The acetic acid solution is evaporated to dryness, the residue is dissolved in water, and the solution is boiled in order to precipitate the iron as basic acetate. After the silica has been volatilised and the residue weighed, the latter is again evaporated with hydrofluoric acid, in order to ensure that all nitrates have been converted into fluorides.

W. P. S.

**New Method of Separating and Estimating Glucinum.** ANDRÉ KLING and E. GELIN (*Bull. Soc. chim.*, 1914, [iv], 15, 205—210).—It has been shown by Urbain and Lacombe (A., 1902, i, 132) that the basic acetate of glucinum,  $\text{Gl}_2\text{O}(\text{OAc})_2$ , is readily soluble in chloroform, and can be distilled without decomposition at the ordinary pressure. The first of these properties has been utilised by Haber and Van Oordt (A., 1904, ii, 659) for the preparation of glucinum oxide free from alumina. The authors have attempted to apply it to the quantitative separation of glucinum from aluminium, but find that it is impossible to obtain a complete extraction of the basic glucinum acetate, owing to the difficulty with which the chloroform penetrates the particles of the latter. In the presence of iron the results are still less favourable, since iron salts pass into the organic solvent.

The following method is advocated, which depends on the fact that basic glucinum acetate is readily sublimed at  $160\text{--}170^\circ/19\text{ mm.}$ , whilst the basic acetates of iron and aluminium are non-volatile in these circumstances.

The solution of the chlorides of glucinum, aluminium, and iron is precipitated at the boiling point with a slight excess of ammonia in the presence of ammonium chloride. After removal of the precipitate, the filtrate is evaporated to dryness, the residue dissolved in warm water, and precipitated with ammonia. The combined precipitates are dissolved in dilute nitric acid, and the solution evaporated to dryness on the water-bath. The residue is cautiously ignited until a porous mass is obtained; complete decomposition of the nitrates is not essential. The product so obtained is repeatedly evaporated with acetic acid. The vessel containing the basic acetates is placed in a long glass tube, which is connected with a small manometer (the limb of which next to the tube is filled with glacial acetic acid) and a water-pump, so that sublimation occurs in an atmosphere of acetic acid. After exhaustion, the tube is gently heated at  $160\text{--}170^\circ$  until sublimation commences, and after four hours the temperature is gradually raised to about  $250^\circ$ . The sublimate of basic acetate of glucinum is dissolved in fuming nitric acid, the solution cautiously evaporated, the residue dried at  $110^\circ$ , and subsequently calcined until constant in weight. A second sublimation of the basic acetates of iron and aluminium is advisable.

Iron and aluminium are estimated in the residue by treatment with fuming nitric acid and subsequent calcination.

Test analyses show that the method is less accurate in the presence of preponderating amounts of alumina, and, in general, is best suited to those cases in which oxide of glucinum is present to the extent of at least 50%. If this is not the case, it is advisable to treat the mixture of oxides with a concentrated solution of ammonium carbonate, which dissolves the whole of the glucinum oxide, and only small quantities of iron and aluminium oxides. The analysis is effected on the residue obtained by evaporating the ammonium carbonate solution. H. W.

**Rapid Estimation of Zinc in its Ores. Direct Application of Frary's Method to the Analysis of Ores.** SILVIO ZUBLENA (*Atti R. Accad. Sci. Torino*, 1913-1914, 49, 178-194. Compare Frary, A., 1908, ii, 68).—The ore (2-5 grams) is moistened with sulphuric acid and treated with hydrofluoric acid. Sulphuric acid (D 1.8; 30 c.c.) is added in small portions, and the whole is cautiously warmed until dense fuming occurs. After cooling and treating with a little water, the precipitate of sulphates is filtered off and washed with water containing sulphuric acid. The filtrate is treated at 70° with hydrogen sulphide, then cooled, and diluted to 200 c.c. Of this solution, 150 c.c. are filtered through a dry filter-paper, and the hydrogen sulphide is removed from this portion by boiling. After cooling, the iron present is oxidised with a few drops of hydrogen peroxide. The free acid is then neutralised with sodium carbonate until a precipitate is formed, which redissolves with difficulty, and after boiling for some minutes the liquid is poured into the requisite quantity of sodium hydroxide (compare Frary, *loc. cit.*). The turbid liquid is boiled for five minutes, cooled, made up to 500 c.c., and filtered through an alundum filter. A portion of the filtrate (100 c.c.) is then electrolysed as described by Frary. In the operations described, care must be taken to use glass vessels which do not contain zinc. Some kinds of glass, including Jena glass, are found to yield appreciable quantities of zinc to boiling, concentrated alkalis. R. V. S.

**Effect of Tungsten on the Ammonium Molybdate Assay for Lead.** HERBERT LAVERS (*Chem. News*, 1914, 109, 97).—Lead cannot be estimated directly, by titration with ammonium molybdate solution, in such minerals as wolfram and scheelite, because the tungstic acid combines with the lead during the preparation of the sample for titration, and the molybdate titration yields a negative result. Trustworthy results are obtained, however, if the tungstic acid is separated previously. For this purpose, the mineral is digested with hydrochloric acid, nitric acid is added, the mixture is evaporated to a small volume, then diluted with water, boiled, and the tungstic acid, silica, etc., are separated by filtration. The lead in the filtrate is precipitated as sulphate; this is dissolved in ammonium acetate solution, and the titration is carried out in the usual way. The tungsten may be estimated by dissolving the

separated tungstic acid in ammonia, adding a known quantity of standard lead acetate solution, and titrating the excess of lead with ammonium molybdate solution. The reaction between lead acetate and ammonium tungstate is shown by the equation  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + (\text{NH}_4)_2\text{WO}_4 = \text{PbWO}_4 + 2\text{NH}_4\cdot\text{C}_2\text{H}_3\text{O}_2$ . W. P. S.

**Electrolytic Estimation of Copper.** H. CLOUKEY (*J. Ind. Eng. Chem.*, 1914, 6, 265—266).—In cases where copper is not deposited properly from its nitric acid solution, the addition of sodium acetate to the electrolyte is recommended. W. P. S.

**Method for the Electrolytic Estimation of Mercury in Urine.** HERMAN PALME (*Zeitsch. physiol. Chem.*, 1914, 89, 345—348).—The method, which is described in detail in the original, consists in treating the urine with hydrogen sulphide, some copper sulphate having been previously added. The organic matter present must first be oxidised with sulphuric acid and potassium permanganate, any precipitated manganese compounds being removed by means of hydrogen peroxide. The mixture of copper sulphide and mercury sulphide is dissolved in bromine water, and after removal of the excess of bromine by means of carbon dioxide, the copper and mercury are deposited on a platinum cathode. The mercury is then driven off by heating the cathode in a current of carbon dioxide, and the difference in weight gives the amount of mercury present. R. V. S.

**Volumetric Estimation of Mercuric Chloride.** W. STÜWE (*Chem. Zeit.*, 1914, 38, 320).—The process is based on the reduction of mercuric chloride to metal by hydrazine sulphate, and titration of the excess of the reagent added. Into a 100 c.c. flask are introduced 10 c.c. of the solution of mercuric chloride (of about 2% strength) and 10—15 c.c. of 1% hydrazine sulphate solution (accurately measured). A pinch of sodium hydrogen carbonate is added, and the flask is placed in luke-warm water. The reduction is complete in a quarter of an hour. When cold, the liquid is made up to the mark and well shaken. After filtering, 50 c.c. are diluted up to 300 c.c., and acidified with acetic acid, a small spoonful of sodium acetate is added, and then a definite volume of *N*/10-iodine solution. After fifteen minutes, the excess of iodine is titrated with *N*/10-thiosulphate, with starch solution as indicator. The calculation is as follows. From the number of c.c. of iodine required for the oxidation of the total quantity of hydrazine sulphate added is deducted the number of c.c. of iodine used in the experiment, remembering that only 50 c.c. have been taken for the titration. Each c.c. of iodine thus found, when multiplied by 0.013576, represents the mercuric chloride present. L. DE K.

**The Assay of Iron Pyrites.** ERNEST MARTIN (*Mon. Sci.*, 1913, [v], 3, ii, 688—689).—*Estimation of Lead, Copper and Zinc.*—Three grams of the powdered sample are mixed in a porcelain crucible with 2 grams of sulphur and 8 grams of potassium-sodium carbonate for

fifteen minutes. The crucible is placed in a dish containing 300—400 c.c. of hot water, and 20 c.c. of hydrochloric acid are then added. After introducing 25 grams of sodium acetate, the precipitate is collected and washed with water acidified with acetic acid and containing hydrogen sulphide, and the zinc is then removed by treatment with dilute hydrochloric acid. It generally contains a trace of iron, from which it is separated in the usual manner (bromine and ammonia); it is then reprecipitated as sulphide, and burnt to oxide.

The insoluble portion is dried and heated in a porcelain crucible, and is then re-dissolved in nitric acid, and the lead is separated from the copper as follows. One to two c.c. of sulphuric acid are added, and the nitric acid expelled by evaporation. On adding water, the lead sulphate remains insoluble, and after washing with water containing a little sulphuric acid it is dissolved in ammonium acetate and precipitated as chromate. The copper is reprecipitated as sulphide, and then burnt to oxide, or the nitric acid solution of the lead and copper may be submitted to the usual electrolysis.

L. DE K.

**Detection of Nickel in Fats.** ROBERT H. KERR (*J. Ind. Eng. Chem.*, 1914, 6, 207).—In testing hydrogenised cottonseed oil for the presence of nickel, it sometimes happens that a fugitive red coloration is obtained on the addition of the dimethylglyoxime reagent and ammonia. This coloration fades rapidly, and is not likely to be mistaken for that given by nickel, but, in order to avoid confusion, it is recommended that the hydrochloric acid extract of the fat should be evaporated to dryness, and the residue again evaporated with nitric acid in order to destroy all organic matter before the test is applied.

W. P. S.

**Colorimetric Estimation of Nickel.** V. LINDT (*Zeitsch. anal. Chim.*, 1914, 53, 165—175).—To 20 c.c. of the ammoniacal solution of nickel (containing 0.1—0.02 mg. per c.c.) is added 0.5 c.c. of a freshly prepared 4% solution of potassium thiocarbonate, and the reddish coloration produced is compared immediately with that of a standard solution of nickel in the well-known manner.

The process is recommended for the rapid estimation of nickel in steels, the iron being eliminated by means of bromine and excess of ammonia. The ammoniacal liquid is made up to a definite bulk, and 20 c.c. of the filtrate are tested as described.

L. DE K.

**Estimation of Titanium as Phosphate.** GEORGE S. JAMIESON and RICHARD WRENSHALL (*J. Ind. Eng. Chem.*, 1914, 6, 203—205).—The authors have investigated a method proposed by Ericson (*Iron Age*, 1903, August 27th, 4), which depends on the precipitation of titanium by treating its boiling solution with ammonium phosphate after any iron present has been reduced by means of ammonium hydrogen sulphide or sulphur dioxide. The method was found to be trustworthy, except when very small quantities of titanium were present. Even in this case but slight loss occurs if

excess of sulphuric acid in the solution is neutralised before the titanium is precipitated as phosphate. Titanium may also be precipitated as phosphate from its hydrochloric acid solution in the presence of tartaric acid and ferrous salts, and also of aluminium salts, provided that sufficient hydrochloric acid is present to prevent the precipitation of aluminium phosphate. For the precipitation of titanium in the presence of relatively large amounts of iron, the solution should measure about 100 c.c., and contain 15 c.c. of dilute hydrochloric acid (1:1).  
W. P. S.

**Use of Ammonium Nitrosophenylhydroxylamine ("Cupferron") in the Quantitative Separation of Titanium from Iron.** WILLIAM M. THORNTON, jun. (*Amer. J. Sci.*, 1914, [iv], 37, 173—178. Compare A., 1913, ii, 250).—It is shown that titanium may be precipitated quantitatively by means of "cupferron" from a solution containing tartaric acid, for instance, from such a solution as is obtained when any iron present has been separated previously as its sulphide in the presence of tartaric acid. In the case of a solution containing both iron and titanium, a quantity of tartaric acid equal to three times the weight of the ferric oxide and titanous oxide is added, the solution is neutralised with ammonia, 2 c.c. of dilute sulphuric acid (1:1) are added, and hydrogen sulphide is passed through the solution until the iron has been reduced; the solution is then rendered ammoniacal, a further quantity of hydrogen sulphide is introduced, and the ferrous sulphide is separated by filtration. The filtrate is acidified with dilute sulphuric acid, boiled to expel hydrogen sulphide, then neutralised partly with ammonia (leaving about 2.5 c.c. of sulphuric acid, 1:1, for every 100 c.c. of the solution), and the titanium is precipitated with "cupferron."  
W. P. S.

**Analysis of Ferrozirconium.** LUDWIG WEISS and WALDEMAR TRAUTMANN (*Zeitsch. anal. Chem.*, 1914, 53, 114—115).—A controversy with Wunder and Jeanneret (A., 1913, ii, 249), who state that zirconium oxide, after fusion with alkali, is insoluble in hydrochloric acid.

The authors state that zirconium oxide, after fusion with sodium hydroxide, is soluble in hydrochloric acid, which fact was, moreover, well known.  
L. DE K.

**Volumetric Estimation of Vanadium.** GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 1914, 53, 81—99).—The estimation of vanadium by titrating with permanganate after previous reduction with sulphur dioxide is accurate within 0.2% when operating on 0.3—0.4 gram of the vanadium compound. An addition of manganous sulphate is useful should chlorine be present.

The reduction by means of hydrochloric acid and alcohol also leads to good results, provided the evaporation with alcohol is once more repeated. Iron in the ferric state does not interfere, but large quantities of sulphuric acid should not be present.



The iodometric estimation of vanadium can also be recommended in all cases where no interfering substances are present.

Pure vanadium pentoxide, useful in checking the standard solutions, may be conveniently prepared by boiling vanadium oxychloride with water and fusing the precipitate after previous moistening with nitric acid. A less pure article may be obtained by igniting ammonium vanadate. L. DE K.

**Rapid Estimation of Antimony and Arsenic in Antimonial Leads and Anti-friction Alloys.** L. BERTIAUX (*Ann. Chim. anal.*, 1914, 19, 49—51).—Five grams of the alloy are heated with 40 c.c. of sulphuric acid in a distillation flask until dissolved. When cold, an equal volume of water is added, the whole heated to boiling and then at once titrated with standard permanganate. This gives the joint arsenic and antimony.

The arsenic is then estimated by adding 15 grams of ferrous sulphate and 150 c.c. of fuming hydrochloric acid, and distilling the liquid. The distillate is titrated by means of standard iodine as usual.

Iron, if present in appreciable quantities, should be estimated separately, say, colorimetrically, and allowed for when recording the antimony. One part of iron=1.0714 parts of antimony. L. DE K.

**The Examination of Antimony Pentasulphide.** W. SCHMITZ (*Chem. Zentr.*, 1914, i, 495—496; from *Gummi-Zeit.*, 1913, 28, 453—455).—Antimony may be estimated in the pentasulphide by a volumetric method based on the following reactions: (1)  $\text{Sb}_2\text{S}_5 + 6\text{HCl} = 3\text{H}_2\text{S} + 2\text{S} + 2\text{SbCl}_3$ , (2)  $2\text{KBrO}_3 + 2\text{HCl} + 3\text{Sb}_2\text{O}_3 = 2\text{KCl} + 2\text{HBr} + 3\text{Sb}_2\text{O}_5$ . A standard solution of pure dry potassium bromate, containing 2.7850 grams, is very stable, and 1 c.c. corresponds with 6 mg. of antimony. The pentasulphide is boiled with hydrochloric acid until the hydrogen sulphide is expelled, and the solution is treated with tartaric acid, filtered, and titrated with the above solution, using methyl-orange in the cold, or indigo in the hot, liquid.

Extraction with carbon disulphide is a sufficiently accurate method for the estimation of free sulphur in the pentasulphide.

Small quantities of lead in presence of much antimony may be estimated in caoutchouc wares by precipitating as sulphide, dissolving in dilute nitric acid with sufficient tartaric acid, and converting the lead into the sulphate. J. C. W.

**Some Physical Properties and the Analysis of Ternary Mixtures of Toluene, Carbon Tetrachloride, and Ethylene Dibromide.** JOHN F. W. SCHULZE (*J. Amer. Chem. Soc.*, 1914, 36, 498—513).—A graphical method is described for determining the composition of certain ternary mixtures which is based on the principle that measurements of two physical properties are necessary and sufficient for the purpose. After the two physical properties have been sufficiently determined for known mixtures of the

three given substances, the analysis of unknown mixtures can be rapidly effected. A complete set of preliminary measurements has been made for mixtures of toluene, carbon tetrachloride, and ethylene dibromide, three constants being determined, namely, the specific volumes, boiling points, and refractive indices. E. G.

**Estimation of the Hydrocarbon Content of Concentrated Oil of Lemon.** E. BÖCKER (*J. pr. Chem.*, 1914, [ii], 89, 199—207).—The method of estimation consists in removing the citral with sodium hydrogen sulphite, and shaking the residue with ice-cold dilute alcohol (51% by vol.), in which the hydrocarbons are practically insoluble. Full experimental details are given. F. B.

**Further Comparative Investigations of Crude Caoutchouc and Caoutchouc by Bromination.** W. VAUBEL and E. WIENERTH (*Chem. Zentr.*, 1914, i, 82; from *Gummi Zeit.*, 1913, 28, 92. Compare A., 1913, ii, 630).—The authors have investigated Para-caoutchouc and soft rubber prepared from it, together with various samples of crude caoutchouc (South Cameroon, Black Balata, Guayule, pale Madagascar, Don de Mazambique, Negro head), according to the Budde-Axelrod (A., 1911, ii, 545) and Vaubel methods. Concordant results were obtained with Para-caoutchouc. On the other hand, further experiments are necessary to render the method applicable to vulcanised rubber and crude caoutchouc. H. W.

**Direct Estimation of Pure Caoutchouc in Crude Caoutchouc.** PONTIO (*Ann. Chim. anal.*, 1914, 19, 60—62).—Boiling with the higher homologues of benzene (toluene, xylene, cymene) is recommended. The solution, which is filtered while hot, is evaporated to a syrupy consistence (if necessary under reduced pressure), and then poured into an excess of absolute alcohol or acetone, which completely precipitates the pure caoutchouc. L. DE K.

**Physiochemical Wine Analyses.** W. I. BARAGIOLA and CH. GODET (*Zeitsch. anal. Chem.*, 1914, 53, 100—114).—In order to get a good insight into the constitution of a wine a very exhaustive analysis should be made, coupled with physical tests, such as conductivity, refraction, etc. A full analysis of the ash is also desirable.

L. DE K.

**Estimation of Extract in Wines.** VLADIMIR NJEGOVAN (*Zeitsch. anal. Chem.*, 1914, 53, 160—165).—Into a weighing-glass of 60 mm. diameter and 30 mm. in height are placed approximately 5 grams of anhydrous sodium sulphate, and the whole is carefully weighed. Five c.c. of the wine (at 15°) are then carefully added so as to moisten the mass completely, and the open glass is placed in a vacuum desiccator, in which is inserted 15 c.c. of sulphuric acid. After one or two hours the pressure is reduced to 10—15 mm., and after another twelve to fourteen hours a current of dry air is passed. The glass is then closed and again weighed, the increase representing the amount of extract in the 5 grams of wine. As the

sodium sulphate obstinately retains traces of water, a correction must be applied, which is determined practically by a blank experiment with water. L. DE K.

**Accurate Estimation of [Solid] Extract in Wines and Fermented Liquids.** PH. MALVEZIN (*Ann. Chim. anal.*, 1914, 19, 62—65).—The liquid is evaporated (in two portions of 25 c.c.) in a little flask at 75—80° under reduced pressure. The contents are then boiled for one hour in a current of steam, the object being to eliminate the glycerol completely. A convenient apparatus is described.

The residue is now completely dried by heating for ten minutes in a vacuum at the temperature of boiling water. L. DE K.

**Estimation of Alkyl Groups Attached to Nitrogen** HANS MEYER and KARL STEINER (*Monatsh.*, 1914, 35, 159—161).—The method of Herzig and Meyer for the estimation of alkyl groups attached to nitrogen, by treating with hydriodic acid, fails in some cases to give accurate results. This is found to occur where the substance under examination easily undergoes scission of methylamine, for example, with benzomethylamide and phthalomethylimide. Even after several repetitions of the treatment with hydriodic acid, the amount of silver iodide obtained may fall considerably short of the theoretical, this being due to the volatility of methylamine hydriodide.

The best method of treatment for such substances is hydrolysis with potassium hydroxide, the liberated methylamine being absorbed in standard acid. D. F. T.

**Estimation of Phenol in the Presence of Hexamethylenetetramine and Formaldehyde.** L. V. REDMAN, A. J. WEITH, and F. P. BROCK (*J. Ind. Eng. Chem.*, 1914, 6, 205—206).—Phenol in the presence of hexamethylenetetramine may be estimated by a method described previously by the authors (A., 1913, ii, 632, 988). Formaldehyde interferes with the volumetric estimation of phenol with bromine, and must be converted into hexamethylenetetramine by the addition of ammonia before the estimation is commenced.

W. P. S.

**Estimation of Cholesterol and Oxycholesterol by Autenrieth and Funk's Method.** E. SCHREIBER (*Chem. Zentr.*, 1914, i, 78; from *Münch. med. Woch.*, 1913, 60, 2001—2002).—In a three months' old, greatly decomposed sample of blood, Autenrieth and Funk have found a substance which still gives the Liebermann colour reaction, but does not yield a precipitate with digitonin. This is a property of oxycholesterol. With the aid of Autenrieth-Funk's method, the latter may be estimated in the following manner: In one portion of the solution the total cholesterol is estimated colorimetrically, whilst in a second portion the cholesterol is precipitated with digitonin. The filtrate is evaporated, and the residue treated with a little ether. The latter is placed on ice for

a short time, and the excess of digitonin removed. The ether is evaporated, the residue dissolved in chloroform, and again colorimetrically estimated. From the results obtained, the amount of each substance is readily calculated. In the investigation of blood, portions of 10 c.c. must be taken, since the quantity of oxysterol is very small. In any case, the presence of cholesterol in the residual chloroform solution should be determined by use of the glacial acetic-sulphuric acid reaction or by the spectrum.

H. W.

**Table for Calculating Dextrose, Invert Sugar, Lactose and Maltose from the Weighed Cuprous Oxide.** TH. VON FELLEBERG (*Chem. Zentr.*, 1914, i, 575; from *Mitt. Lebensmitt. Hyg.*, 1913, 4, 369—374).—The author has elaborated Kelhofer's table of invert sugar values (A., 1906, ii, 311) by introducing the values for other sugars which correspond with weights of cuprous oxide or copper from 10 to 520 mg.

J. C. W.

**Influence of Ammonium Sulphate on the Specific Rotation of Milk Sugar.** R. ROSEMAN (*Zeitsch. physiol. Chem.*, 1914, 89, 133—140).—Although the specific rotation of lactose is not affected by dilution with water, it is decreased by dilution with ammonium sulphate solution, the diminution amounting to nearly 4% when the solution is saturated with the salt. This is in agreement with the results of Jahnson-Blohm (A., 1913, ii, 351), so that the correction recommended by him in Salkowski's method for the estimation of milk-sugar is justifiable on this ground. According to Kretschmer, however (A., 1913, ii, 635), Salkowski's method gives rather high results, so that perhaps it is preferable not to apply the correction.

R. V. S.

**Behaviour of Refined Sugar towards Fehling's Solution under the Conditions of Herzfeld's Method for Estimating Invert Sugar.** F. STROHMER (*Bied. Zentr.*, 1914, 43, 113; from *Oesterr.-Ung. Zeitsch. Zuckerind. Landw.*, 42, Heft. 3).—Under the conditions of Herzfeld's method, pure sucrose undergoes inversion, and considerably more cuprous oxide is produced than when the Fehling's solution is heated with water alone. Experiments with refined sugar, free from colouring matters, showed that the reducing power is influenced by the nature, as well as the amount, of the non-sugar present.

N. H. J. M.

**Estimation of Glycogen in Yeast.** F. SCHÖNFELD and E. KÜNZEL (*Chem. Zentr.*, 1914, i, 578—579; from *Woch. Brauerei*, 1913, 31, 9—12).—The glycogen was estimated by a modification of Pflüger's method.

S. B. S.

**Detection of Small Quantities of Formaldehyde and Formaldehyde Compounds by means of Magenta-Sulphurous Acid containing Hydrochloric Acid.** HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1914, 27, 246—253).—In the presence of an excess of hydrochloric acid, formaldehyde yields a characteristic color-

tion with a magenta-sulphurous acid solution. The reagent is prepared by dissolving 1 gram of rosaniline hydrochloride in 500 c.c. of water, adding 25 grams of sodium sulphite and 15 c.c. of hydrochloric acid (D 1.124), and diluting the mixture with water to 1 litre. Ten c.c. of the liquid to be tested are treated with 2 c.c. of hydrochloric acid (D 1.124) and 1 c.c. of the reagent; if formaldehyde is present, a violet-red coloration develops within a period varying from a few minutes to twelve hours. Other aldehydes do not yield a coloration under these conditions. The test will detect formaldehyde in a dilution of 1 in 500,000. Where possible, the test should be applied directly to the liquid under examination; dark-coloured liquids may be treated previously with animal charcoal and hydrochloric acid. Formaldehyde combines with certain organic substances, and is not liberated by treatment with hydrochloric acid; this is particularly noticed in the cases of rhubarb leaves. Milk combines with formaldehyde to a certain extent, but the aldehyde is set free on the addition of a mineral acid, although a portion disappears when the milk is kept for some time. The test may be employed for the detection of hexamethylenetetramine after this has been decomposed by heating with hydrochloric acid, but formaldehyde combined previously with sulphurous acid cannot be detected by means of the reagent.

W. P. S.

**Estimation of  $\beta$ -Hydroxybutyric Acid.** E. L. KENNAWAY (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, 47, xxvii—xxix).—In Shaffer's method, the acid is oxidised by potassium dichromate and sulphuric acid to acetone, which is distilled off and estimated by iodine and thiosulphate. It is preferable to use Scott-Wilson's method with mercuric cyanide for the estimation of the acetone. W. D. H.

**Determination of the Freezing Point of Milk.** A. LAM (*Chem. Weekblad*, 1911, 11, 198—200; M. C. DEKHUYZEN (*ibid.*, 201—204); N. SCHOORL (*ibid.*, 204); J. D. FILIPPO (*ibid.*, 204—206); VAN RAALTE (*ibid.*, 206—207); M. G. HUMMELINCK (*ibid.*, 207—209); P. A. MEERBURG (*ibid.*, 209—211)).—A polemical discussion, partly on the work of Dekhuyzen (this vol., ii, 169), and partly on the method recommended in the Dutch *Codex Alimentarius* for the determination of the freezing point of milk.

A. J. W.

**Analysis of Decomposed Milks.** A. GASCARD (*Ann. Chim. anal.*, 1914, 19, 57—62).—To the weighed and also measured sample is added an equal bulk of sulphuric acid with rotatory shaking, and when cold the whole is shaken with 100 c.c. of pure benzene in a stoppered and graduated tube. Ten c.c. of the benzene are then taken, and on evaporation yields the fat.

An aliquot part of the acid liquid is then treated for nitrogen proteins by the Kjeldahl process. The density, for calculation purposes, may be taken as 1.033.

L. DE K.

**Glycerides of Fats and Oils. VIII. Application of the "Melting-point Difference" Number in Fat Analysis.** A. BÖMER, R. KRÖNIG, R. LEY, and H. MERTEN (*Zeitsch. Nahr. Genussm.*, 1914, **27**, 153—172. Compare A., 1913, ii, 444).—Further investigation of a method described recently by the authors for the detection of beef fat in lard shows that the results obtained are not influenced by the presence of cocoanut oil, earthenut oil, sesame oil, and cottonseed oil. Mixtures of lard and hydrogenised (hardened) oils behave, however, like mixtures of lard and beef fat, but in this case the presence of a vegetable fat may be ascertained by means of the phytosteryl acetate test. Lard obtained from pigs fed on maize, cocoanut, cottonseed, and sesame meals or cakes yields the same figures as does ordinary lard. Results of preliminary experiments indicate that the method will be of use in the detection of lard in butter fat.

W. P. S.

**Composition of Palm-Kernel Oil.** G. D. ELSDON (*Analyst*, 1914, **39**, 78—80. Compare A., 1913, i, 159).—From the weights of the different fractions obtained on distilling the esters produced by submitting palm-kernel oil to alcoholysis, the composition of the fatty acids of the oil was found to be as follows: hexoic acid, 2%; octoic acid, 5%; decaoic acid, 6%; lauric acid, 55%; myristic acid, 12%; palmitic acid, 12%; stearic acid, 7%; oleic acid, 4%. These figures do not differ from those found for cocoanut oil (*loc. cit.*) to such a degree as to afford a means of detecting the two oils in a mixture of the same.

W. P. S.

**Phosphomolybdic Acid as a Reagent for Chemical and Microchemical Tests for Adulterations in Saffron.** A. VERDA (*Chem. Zeit.*, 1914, **38**, 325—327).—The colouring matter of saffron gives a pronounced green colour with phosphomolybdic acid; other vegetable adulterants do not give this colour, which may therefore be used as a test. When there is considerable adulteration, the chemical test is sufficient, but when the quantity of adulterant does not exceed 5%, it is necessary to make a microchemical test. The behaviour, chemical and microchemical, of the various likely adulterants, when submitted to the action of the reagent, is described in detail.

The phosphomolybdic acid is made by dissolving 25 grams of sodium phosphomolybdate in 90 c.c. of water and 20 c.c. of concentrated nitric acid; the solution is filtered after keeping for eight days, and is then ready for use. Instead of this solution, a solution made by mixing 40 c.c. of a 10% solution of sodium phosphomolybdate with 60 c.c. of concentrated sulphuric acid may be used; it gives a blue colour with saffron, which remains unchanged for a day or longer; adulterants give other colours, which are described.

The colour reaction given by the saffron is to be ascribed to the crocin present, which possesses a glucosidic structure.

T. S. P.

**Nitrogen Metabolism. New Methods for the Estimation of Urea, Ammonia, and Amino-acids.** L. LEMATTE (*Chem. Zentr.*, 1914, i, 500; from *Bull. Sci. Pharmacol.*, 1913, **20**, 577—584, 647—659).—A method is described for the estimation of urea,

ammonia, and amino-acids in two portions of urine. In one, ammonia is precipitated by phosphotungstic acid and magnesium chloride, and the filtrate is divided, urea being estimated in one part by sodium hypobromite, and the amino-acids in the other by titration in presence of formaldehyde. In the other portion, urea and ammonia are returned as nitrogen by means of sodium hypobromite, after precipitation with lead acetate. J. C. W.

**The Estimation of Urea, and Indirectly of Allantoin, in Urine by means of Urease.** ROBERT HENRY ADERS PLIMMER and RUTH FILBY SKELTON (*Biochem. J.*, 1914, 8, 70—73).—The estimation of urea in urine is quickly and accurately made by decomposing it with urease at 35—40° for one hour. The ammonia evolved is estimated by Folin's air-current method; anhydrous sodium carbonate is then added, and the air current continued for another hour. Liquid paraffin is convenient to lessen frothing. Urease does not decompose allantoin, and since allantoin and urea are both quantitatively decomposed by Folin's magnesium chloride method, the amount of the former is readily estimated by difference. W. D. H.

**Ureometer for Use with Water.** D. E. TSAKALOTOS (*J. Pharm. Chim.*, 1914, [vii], 9, 287—288).—A compact form of ureometer, which can also be employed for the determination of urea in blood, is described. The advantages claimed are that the size of the apparatus is such that it can conveniently be immersed in a vessel of water, and that exact measurement of the volume of hypobromite solution is unnecessary.

The apparatus consists of a tube 9—10 cm. long and 1.5 cm. in diameter, at the bottom of which are placed a number of glass beads; this tube communicates by means of a stop-cock with a similar, but shorter, tube, which can be closed by a rubber stopper. Each of these tubes is separately connected with the upper portion of the measuring vessel. The urine (1 c.c.) is introduced into the lower tube. The stop-cock is shut, the hypobromite solution placed in the upper tube, and the whole apparatus immersed in a beaker of water. The level of the water is adjusted to zero in the measuring vessel, and the upper tube securely stoppered. The hypobromite solution is added to the urine, the apparatus vigorously shaken, and the volume of nitrogen read off after twenty minutes. H. W.

**Purification of Alcoholic Extracts of Putrifying Viscera and Other Organic Substances.** JORGE MAGNIN and ENRIQUE V. ZAPPI (*Anal. Soc. Quim. Argentina*, 1913, 1, 327—336).—Treatment of alcoholic extracts in toxicological analysis by aluminium sulphate and potassium hydroxide is superior as a means of purification to the treatment with aluminium amalgam recommended by Kohn-Abrest (*A.*, 1913, ii, 81), and does not demand so much attention during the process. As regards ptomaines, the addition of either aluminium reagent to the final aqueous extracts effects a notable

increase in purity as compared with the original Dragendorff method.

Other reducing agents, such as stannous chloride, sodium amalgam, and zinc dust, do not appear to be of much value as purifying agents.

G. D. L.

**Estimation of Strychnine in the Presence of Quinine**  
CHARLES SIMMONDS (*Analyst*, 1914, 39, 81—83).—In the process described, the strychnine is separated as its ferrocyanide from an acid solution of the mixed alkaloids; the quinine is estimated by difference, or weighed separately. The mixed alkaloids, obtained in the usual way (say, from 50 c.c. of such a preparation as Easton's syrup), are weighed, dissolved in 50 c.c. of 10% sulphuric acid, and 5 c.c. of a 4% potassium ferrocyanide solution are added drop by drop. After a few hours, the precipitate is collected on a small filter, washed three times with 5% sulphuric acid, using 3 c.c. each time, then dissolved in dilute ammonia, and the solution extracted with chloroform. The chloroform solution is shaken with successive quantities of 20% sulphuric acid, the strychnine is reprecipitated from the acid solution as ferrocyanide, and again obtained in chloroform solution; this solution is evaporated, and the residue dried at 100° and weighed.

W. P. S.

**Estimation of Alkaloids. Application to Nux vomica Preparations.** A. AZADIAN (*Chem. Zentr.*, 1914, i, 431—432; from *Schwetz. Woch. Chem. Pharm.*, 1913, 51, 761—765).—The alkalimetric estimation of strychnos alkaloids is untrustworthy, but a useful method, which may be applied to all strychnine preparations, depends on the precipitation with silicotungstic acid. The powdered drug is macerated with ammonia and a mixture of chloroform and ether; the extract is then shaken with nitric acid, and the concentrated acid solution is precipitated with a 5% solution of silicotungstic acid. The precipitate is ignited, and the weight of the residue,  $\text{WO}_3 \cdot \text{SiO}_2$ , multiplied by 0.4980, gives the number of grams of alkaloid.

J. C. W.

**Estimation of Strophanthine in the Seeds and Tincture of Strophanthus.** J. B. LAMPART and A. MÜLLER (*Arch. Pharm.*, 1913, 251, 609—632).—The methods of Fraser, Fromme (1897), Fromme (1900), Thoms, Mann, and Dohme, and the W.K. method for the estimation of strophanthine in the seeds, and those of Dowzard and Barclay for the tincture, are found to give unsatisfactory results. The authors recommend Fromme's method (1910) both for the seeds and the tincture. The method is as follows. Seven grams of the crushed seeds and 70 grams of absolute alcohol are weighed in a flask, and boiled for one hour. After cooling, the mixture is made up to the original weight with alcohol and filtered. The residue obtained by evaporating 50.5 grams of the filtrate (corresponding with 5 grams of the seeds) is treated with petroleum and filtered. The insoluble portion is boiled with 5—8 grams of water, treated with five drops of lead acetate and about 0.2 gram of kieselguhr, well mixed, and filtered into a 100 c.c. flask, the dish



and filter being well washed with small quantities of boiling water. The filtrate is treated with five drops of hydrochloric acid and boiled gently for about two hours until its weight is about 10 grams. After the addition of about 10 grams of water and cooling, the liquid is extracted twice with 10 c.c. of chloroform, the extracts being filtered into a tared 100 c.c. flask. The aqueous liquid is again boiled for thirty minutes, cooled, and extracted thrice with 10 c.c. of chloroform, the operations being repeated if the aqueous liquid still tastes bitter. The combined extracts are freed from chloroform, and the residue of strophanthidine is dried in a desiccator and weighed. The weight multiplied by 2.187 and by 20 gives the percentage of strophanthine in the seeds.

The method, as applied to tincture of strophanthus, is as follows. The tincture, 51.0 grams (corresponding with 5 grams of seeds), is freed from alcohol on the water-bath, and the residue is treated with about 20 grams of hot water, fifteen drops of lead acetate, and 0.2 gram of kieselsuhr. The subsequent treatment is like that described above.

The method gives higher percentages than any of the others; Rydén claims that they are too high. C. S.

**Estimation of the Salt-Soluble Proteins in Wheat Flour.** GEO. A. OLSON (*J. Ind. Eng. Chem.*, 1914, 6, 211—214).—Edestin, leucosin, and gliadin are extracted from flour when this is treated with a 1% sodium chloride solution, the quantity of gliadin thus extracted amounting to about 29% of the total proteins; when 10% sodium chloride solution is employed, the quantity of gliadin obtained in solution is only about 5% of the total proteins. In the estimation of edestin and leucosin, a correction may be made for gliadin, since the sum of the quantities of amido-, globulin-, and albumin-nitrogen subtracted from the total salt-soluble nitrogen gives the amount of gliadin-nitrogen soluble in 1% sodium chloride solution. The amount of nitrogenous substances extracted by sodium chloride solutions, and directly coagulated by heat, varies with the concentration of the solvent, the 10% concentration giving higher results than the 1% solution. These substances are partly or wholly soluble in dilute alcohol, the solubility varying with the concentration of the sodium chloride solution employed.

W. P. S.

**Estimation of Protein in Urine.** PFEIFFER (*Chem. Zentr.*, 1914, i, 431; from *Zeitsch. Allg. Österr. Apoth. Ver.*, 1913, 51, 420—421).—To 10 c.c. of the urine are added 10 c.c. of a reagent made by dissolving 1 gram of phosphotungstic acid and 5 c.c. of concentrated hydrochloric acid in 100 grams of 96% alcohol. The reaction is carried out in specially made graduated tubes, and the volume of the precipitate is measured. From the height of the precipitate in these tubes after twenty-four hours or forty-eight hours at 15°, or after one hour at 30°, the percentage of protein can be ascertained by reference to tables prepared by the author. Under certain conditions specified, it is necessary to dilute the urine.

S. B. S.

**Pfeiffer's Method for Estimating Protein in Urine.** GEORG GREGOR (*Chem. Zentr.*, 1914, i, 431; from *Zeitsch. Allg. Österr. Apoth. Ver.*, 1913, 51, 669—670).—Pfeiffer's method gives results agreeing fairly well with those obtained by Esbach's method, but is to be preferred when a rapid estimation is not necessary. S. B. S.

**Estimation of Albumin in Urine.** FRANK M. ELDRED and C. M. PENCE (*Lilly Sci. Bull.*, 1914, 1, 121—122).—Into a graduated 5 c.c. test-tube of 9 mm. diameter, 1 c.c. of the urine is introduced. About 0.04 gram of monosodium hydrogen phosphate is added, and then a mixture of 98 vol. % of acetone and 2 vol. of glacial acetic acid. This mixture is added until the 4 c.c. mark is reached. After closing the tube and shaking, the albumin separates, and the volume of the precipitate is ascertained after half an hour. The amount of albumin can then be found by reference to a table constructed from a series of experiments made to ascertain the volume of the precipitate obtained from solutions with varying albumin content. S. B. S.

**Analysis of Urine. Possibility of Mistaking Hexamethylenetetramine for Albumin when Using Esbach's Method.** EDUARD SCHMIZ (*Chem. Zentr.*, 1914, i, 81; from *Apoth. Zeit.*, 1913, 28, 937).—The author finds that picric acid solution reacts with hexamethylenetetramine to yield a yellow precipitate of trinitrophenol-hexamethylenetetramine,  $C_6H_2(NO_2)_3 \cdot OH, C_6H_{12}N_4$ , which dissolves sparingly in water, readily in alcohol, and gives the general formaldehyde and ammonia reactions. When warmed with an excess of potassium hydroxide, it gives an intense red coloration, the reaction being hastened by previous addition of ammonia. The author also shows that hexamethylenetetramine appears in the urine shortly after administration, so that Esbach's method of estimating albumin may easily lead to false results. The precipitate should therefore be examined as described above, and the albumin determined, if necessary, by other methods. H. W.

**A Rapid Method for Estimating the Percentage of Casein in Milk.** W. O. WALKER (*J. Ind. Eng. Chem.*, 1914, 6, 131—133).

The method used by the author depends on the fact that when formaldehyde is added to proteins, the neutral character of the molecule disappears, with the result that the acidic property predominates strongly. The acidic groups may then be titrated with standard alkali, and if the value of the alkali in terms of protein is known, the percentage of protein present may be estimated.

To 10 c.c. of milk is added 1 c.c. of a 1% solution of phenolphthalein, and *N*/9-sodium hydroxide run in until a fairly pink colour develops. About 2 c.c. of a neutral solution of formaldehyde (40%) are then added, and the milk again titrated to the same pink colour. The number of c.c. used in the second titration, multiplied by the factor 1.63, gives the percentage of casein.

The results agree with those obtained by other methods.

T. S. P.

**New Methods of Obtaining Teichmann's Crystals.** ENRICO BARALDI (*J. Pharm. Chim.*, 1914, [vii], 9, 284—286).—The author has been able to obtain good results by the substitution of different haloids of sodium and potassium for the sodium chloride usually employed in obtaining these crystals. The following are the solutions recommended, and the results obtained with blood of varying origin: (a) sodium chloride, sodium bromide, sodium iodide, water, acetic acid; reddish-brown crystals: (b) a drop of a solution of sodium and potassium carbonates, acetic acid and water mixed with a drop of an alcoholic solution of hydrochloric, nitric, sulphuric and acetic acids, and a drop of acetic acid; small brown crystals: (c) an aqueous solution of sodium chloride and potassium bromide, or of the latter and hydrochloric acid, mixed with acetic acid; well-defined crystals grouped in crosses or rosettes: (d) an aqueous solution of potassium iodide and hydrochloric acid; strongly-coloured crystals: (e) a solution of potassium chloride, bromide and iodide, water, and acetic acid; individual, brown crystals: (f) an intimate mixture of sodium chloride and potassium bromide; yellowish-orange or reddish-brown crystals: (g) a mixture of the chloride, bromide and iodide of potassium with sodium chloride; results similar to those with (f): (h) a mixture of potassium iodide with sodium chloride and bromide; large crystals.

The size of the crystals is found to vary with the species of animal from which the blood is obtained. H. W.

**Method of Estimating the Value of Disinfectants.** C. A. DUYSER and W. K. LEWIS (*J. Ind. Eng. Chem.*, 1914, 6, 198—200).—The following is an outline of the method recommended. The disinfectant to be examined as to its relative bactericidal power is diluted with water to three or four definite concentrations, the extent of the dilution depending on its strength; pure, synthetic phenol is diluted similarly. Equal volumes of a bacteria culture are placed in a series of these solutions of phenol and of the disinfectant under examination, and, after an exact number of minutes, an aliquot portion of each mixture is plated out on nutrient agar and incubated until the colonies representing the surviving bacteria can be counted. At the same time, plates of equal dilutions of the culture, but without the disinfectant, are incubated. The ratio of the surviving organisms to the number present on the corresponding undisinfected plates is then plotted against the dilution, and two curves, one for the standard phenol and one for the disinfectant, are obtained. The relative strengths of the disinfectant and the phenol may be read off at any desired point on the curves, and the coefficient may be calculated either for total "killing" or for any definite percentage of "killing."

W. P. S.

**A Comparison of Various Preservatives of Urine.** WILLIAM M. DEHN and FRANK A. HARTMAN (*J. Amer. Chem. Soc.*, 1914, 36, 409—417).—From an examination of the effects produced by various preservatives for urine, the conclusion is drawn that the

most suitable preservatives are salicylic acid, strychnine sulphate, sodium arsenite, and possibly sandalwood oil. Chloroform, toluene, ether, and thymol are less satisfactory, whilst formaldehyde, hydrogen peroxide, phenol, boric acid, sodium borate, hydrochloric and sulphuric acids, etc., are considered poor.

The ideal preservative must be soluble, non-volatile, and neutral or slightly acid, but as no one preservative is effective in all directions, different preservatives must be employed for different purposes.

D. F. T.

**A Preliminary Study of the Changes Occurring in Meats During the Process of Drying by Heat and in a Vacuum.** L. H. DAVIS and A. D. EMMETT (*J. Amer. Chem. Soc.*, 1914, **36**, 444—453).—In determining the percentage of dry material in fresh or desiccated beef, the result is higher with vacuum drying than with heating at 100—105°, the discrepancy amounting to about 1·9% of the dry material. The percentage of fat is the same for products dried by either method; the percentage of nitrogen, however, calculated on the dried material, is slightly lower for the vacuum-dried samples, but no loss of nitrogen was observable in drying in a vacuum or at 100—105°.

The average percentage fat-content of the samples, calculated on dry material, was not altered during desiccation. The percentage of total nitrogen in the desiccated meats was slightly higher than in the fresh samples; it is found that the proportion of soluble nitrogen is distinctly lower in desiccated meat, and that the amount of coagulable nitrogen is decreased during desiccation by approximately the same amount; there was, however, a distinct increase of water-soluble proteose nitrogen in the desiccated meats. D. F. T.

**The Estimation of Peptic Value.** OTTO FREY (*Chem. Zentr.*, 1914, i, 430; from *Zeitsch. Allg. Österr. Apoth. Ver.*, 1913, **51**, 593—595, 611—612, 623—624, 635—638, 649—652).—An account is given of a method for evaluation of pepsin in commercial preparations, the principle of which depends on the digestion of 100 c.c. of a 1% egg-white solution with 10 c.c. *N*-hydrochloric acid for two hours at 55°, coagulating after this interval by heat in the presence of sodium chloride, and weighing the coagulum. A certain standard is suggested for a normal pepsin preparation, and tables and curves are prepared to show the amount of lactose which may be added to an active pepsin preparation to reduce it to the standard for the amount of undigested coagulum produced under the conditions suggested for the test.

S. B. S.

**Determination of the Diastatic Power of Malt.** A. MONNIER (*Ann. Chim. anal.*, 1914, **19**, 51—54).—In Liutner's original process ten test-tubes are taken, into which are placed 10 c.c. of a 2% solution of soluble starch. To each tube is then added, respectively, 0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7, 0·8, 0·9 l c.c. of a 5% infusion of malt, and the whole kept for one hour at the temperature of the room. To each of the tubes is then added 5 c.c. of Fehling solu-

tion, and they are then heated on the boiling water-bath for five minutes. If now, say, tube 5 is just decolorised, the diastatic power will be 100/5, etc.

The author now works exactly at 18°, and makes a correction for the decolorisation caused by sugar pre-existing in the malt infusion. He also, in the calculation, replaces the figure 100 by 77·8, thus obtaining a figure representing the number of grams of maltose formed by 10 grams of the extract. L. DE K.

**Estimation of the Surface of Soils.** J. A. HANLEY (*J. Agric. Sci.*, 1914, 6, 58—62).—Estimations of the amounts of dye (methyl-violet) absorbed by three soils from solutions of different strengths (König, Hasenbäumer and Hassler, *Landw. Versuchs-Stat.*, 1911, 75, 377). The results indicate that the solution employed should contain between 0·0375 and 0·1125% of the dye. N. H. J. M.

**Estimation of Humus in Heavy Clay Soils.** WILLIAM BEAM (*Cairo Sci. J.*, 1913, 7, 219—224).—The soil (7·5 grams) is mixed with twice its weight of powdered quartz (which will pass through a 60, but not a 120, mesh sieve), transferred to a 10 cm. Büchner funnel, covered with a layer (2·5 mm.) of ground quartz, and extracted with 0·5% hydrochloric acid as long as calcium can be detected in the filtrate. It is then washed with 0·02% hydrochloric acid. The acid extraction is made without using a pump, and takes about three hours. The humus is then extracted with 4% ammonia under very slight pressure (3 to 5 cm. of water). The filtrate is generally colourless after 200 c.c. or 300 c.c. has been collected. It should always be treated with a little ammonium carbonate (0·5 gram per 100 c.c.) to precipitate the clay, which is not always visible.

As regards the effect of the strength of the ammonia employed, it was found that in the case of the Nile soils examined variations in strength from 2% to 16% were without effect, provided that the soil was in a properly flocculated condition. When the soil is not properly flocculated, the more dilute ammonia fails to extract all the humus.

Satisfactory results were also obtained colorimetrically. The best results are obtained with extracts prepared as described. In the case of soils of approximately the same composition, as regards clay and humus, the soil (5 grams) may be boiled for five minutes with 400 c.c. of water to disintegrate it, after which 20 c.c. of hot 12·5% sodium carbonate solution are added, and the boiling continued for one minute. The liquid is quickly cooled, diluted to 500 c.c., and left overnight. The comparison is made with a similar extract of a soil of known humus content. N. H. J. M.

## General and Physical Chemistry.

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**Dispersion of Aqueous Salt Solutions in the Ultra-violet.** KARL LÜBBEN (*Ber. Deut. physikal. Ges.*, 1914, **16**, 180—190, 314).—Measurements have been made of the refractive index of solutions of lithium chloride, sodium chloride, caesium chloride, lithium bromide, rubidium bromide, sodium iodide, ammonium fluoride, thallous fluoride, sodium chlorate, and sodium perchlorate for ultra-violet light of wave-length ranging from  $\lambda$  214 to  $\lambda$  460. Each of the salts was examined in 0.5, 1, 2, and 4*N*-solution.

The results obtained are in good agreement with the Ketteler-Helmholtz dispersion formula, and indicate that the dispersion is due to the characteristic frequency of the anion. In agreement with this, it is found that solutions which contain the same anion give the same spectrum. The characteristic wave-lengths for the anions are Cl' 165  $\mu\mu$ , Br' 186, I' 207, F' 100, ClO<sub>3</sub>' 175. In the case of the chlorine, bromine, and iodine ions, the relationship between the wave-length and the atomic weight is given by  $\lambda^2 = 170A + 21150$ .

The characteristic wave-length of the free anion is somewhat greater than that of the undissociated anion, whereas the reverse would be expected according to the theory of quanta. The discrepancy is attributed to the inexactness of the dispersion formula. It is shown that the theory of quanta may be applied in the calculation of the change in the characteristic frequency which occurs when a solid salt is dissolved in water. H. M. D.

**Ultra-red Dispersion of Diatomic Crystalline [Substances].** W. DEHLINGER (*Physikal. Zeitsch.*, 1914, **15**, 276—283).—The theory of diatomic substances is discussed in reference to the formulæ of Einstein and Debye (compare A., 1912, ii, 1134), and it is shown that there is only one frequency for the residual rays which are characteristic of diatomic substances. The experimental data for sodium chloride, potassium chloride, and calcium fluoride are shown to be in fair agreement with the requirements of the dispersion formula which the author has deduced. H. M. D.

**The Atomic Weight of Nebulium and the Temperature of the Nebula of Orion.** H. BOURGET, CH. FABRY, and H. BUISSON (*Compt. rend.*, 1914, **158**, 1017—1019. Compare *Astrophysical J.*, 1911, **33**, 406).—The authors have studied by interference the different monochromatic radiations emitted by the nebula of Orion. In addition to measurements for H $\gamma$ , they find a strong double line in the ultra-violet  $\lambda$  3726—3729, which must be attributed to an unknown gas, named by them nebulium. From their interference measurements they determine its atomic weight to be approximately 3. There is also a strong green ray,  $\lambda$  5006, belonging to an unknown gas, but as the measurements for this

ray are not yet precise, the atomic weight of the gas cannot be given, although it probably lies between 1 and 3. The maximum temperature of the nebula, as calculated from the limit of interference of the hydrogen ray, is  $15,000^{\circ}$ . W. G.

**Differences in the Pole Spectra of Various Elements in the Geissler Tube.** BERNHARD REISMANN (*Zritsch. wiss. Photochem.*, 1914, **13**, 269—312).—A method is described for the production of highly luminous spectra by means of direct-current discharge through Geissler tubes. This has been employed in the examination of the spectra emitted from different regions of the discharge tube by chlorine, bromine, iodine, oxygen, hydrogen, nitrogen, and the vapours of bismuth, antimony, cadmium, zinc, mercury, and silver.

The halogens exhibit the line spectrum at the cathode, whereas the positive column and anode are characterised by the emission of the continuous spectrum. In the case of bromine, it has been found that the cathode luminosity consists of the spark spectrum. It is probable that this is also true for chlorine. From observations made with tubes containing hydrogen chloride, stannic chloride, and carbon tetrachloride it would appear that the polar differences are due to differences in the relative intensities of two spectra, both of which are observable at the anode and cathode.

Oxygen shows the series, the elementary line, and the banded spectrum at the cathode, but only the series spectrum in the positive column.

Hydrogen shows both its spectra at the cathode and anode, but there is a marked difference in the relative intensities at the two poles. In both hydrogen and oxygen the carbon monoxide bands tend to concentrate at the cathode end of the positive column.

Nitrogen gives a special negative band spectrum at the cathode. The regional colour differences shown by the nitrogen spectrum are due to variations in the relative intensities of the red and yellow bands.

The metallic vapours give a band spectrum in which the arc lines of the respective elements are readily observable. The regional influence on these lines is scarcely appreciable. At the cathode, lines characteristic of the spark spectra are also emitted.

The observations seem to show that a particular luminous emission cannot be definitely identified with a particular spectral region, but that much depends on the conditions of the discharge. The spectrum attributable to cathode rays may, for instance, be exhibited at quite different points. In the case of bromine, chlorine, oxygen, cadmium, antimony, bismuth, and lead this spectrum is identical with the spark spectrum. H. M. D.

**The Effect of the Electric Field on Spectral Lines. II. Longitudinal Effect.** J. STARK and G. WENDT (*Ann. Physik*, 1914, [iv], **43**, 983—990).—In a previous paper (this vol., ii, 2) the transverse effect of an electric field on the series lines of hydrogen and helium was examined, and the present paper affords an account

of the longitudinal effect. The results indicate that the components into which the hydrogen lines  $H\beta$  and  $H\gamma$ , and the helium lines  $\lambda 4922$ ,  $\lambda 4388$ , and  $\lambda 4472$ , are resolved, are in all cases unpolarised. The effect of the electric field is therefore in marked contrast to the Zeeman effect, for in this case the components are circularly polarised.

From the absence of polarisation in the component lines, the author concludes that the electrons which give rise to the spectral lines are free to rotate in either direction parallel to the axis of the electrical field.

H. M. D.

**The Effect of the Electric Field on Spectral Lines. III. Dependence on the Strength of the Field.** J. STARK and H. KIRSCHBAUM (*Ann. Physik*, 1914, [iv], **43**, 991—1016. Compare preceding abstract).—Further experiments have been made in relation to the transverse effect of the electric field on hydrogen and helium lines. From observations with different field strengths, it has been found that the distance between the extreme components is proportional to the strength of the applied field. This relationship holds for the  $H\beta$  and  $H\gamma$  lines, and also for the helium lines  $\lambda 4026$  and  $\lambda 4772$ , and is equally valid for vibrations parallel and perpendicular to the direction of the field.

In the case of the helium line  $\lambda 4472$ , and the  $\beta$  and  $\gamma$  hydrogen lines, all of which exhibit asymmetric resolution, it is found that the long-waved component is more intense than the corresponding component of shorter wave-length when the applied field is less than about 10,000 volts per cm., but that the intensities become more nearly equal for electric fields of greater strength.

Other observations have reference to the ratio of the intensities of the vibrations parallel and perpendicular to the electric field, and the intensity ratio of the components into which the hydrogen lines are resolved in its dependence on the direction of the electric field. The results are discussed in terms of the authors' theory of the origin of the spectral lines.

H. M. D.

**The Effect of the Electric Field on Spectral Lines. IV. Types of Lines and Broadening.** J. STARK and H. KIRSCHBAUM (*Ann. Physik*, 1914, [iv], **43**, 1017—1047. Compare preceding abstracts).—The effect of a strong electric field on the lines characteristic of various elements has been investigated. The recorded data show the dependence of the effect on the wave-length of lines which belong to one and the same series, and also the nature of the resolution which is brought about in the corresponding lines of different elements. The data refer to the series lines of hydrogen, helium, lithium, sodium, magnesium, calcium, aluminium, thallium, and mercury, and show the magnitude of the displacement both for the components which vibrate parallel and those which have vibrations perpendicular to the electric field. The relative intensities of the components are also indicated.

For lines which belong to the same series, the magnitude of the displacement increases with the number which, in accordance with



Rydberg's method of formulation, expresses the position of the line in the series. By comparing the displacements of corresponding lines, it is found that these are much larger for the diffuse subordinate series than for the sharp (principal and subordinate) series, both in the case of hydrogen and of lithium. Although a comparison of the effect of the field on corresponding lines of different elements has not as yet led to any definite quantitative result, it would seem that these lines are not always resolved in the same manner.

Observations have also been made in reference to the influence of the electric field on the broadening of lines which is brought about by increase in the vapour pressure or the current density.

H. M. D.

**Measurements in the Arc and Spark Spectrum of Strontium in Terms of the International Normals.** HEINRICH HAMPE (*Zeitsch. wiss. Photochem.*, 1914, **13**, 348—368).—The wave-length data are compared with those of previous observers, and the nature of the spectral series is discussed.

H. M. D.

**The Different Spectra of Mercury, Cadmium, and Zinc.** J. DE KOWALSKI (*Compt. rend.*, 1914, **158**, 788—789).—A description of a method by means of which it is possible to observe all the known spectra of mercury, cadmium, and zinc. A transparent quartz bulb is sealed to a small tube containing a few grams of the pure metal under examination. The bulb is maintained at a fairly high temperature, and then, by varying the temperature of the tube, the metallic vapour is obtained in the bulb under different pressures. The quartz bulb is circled by several turns of a copper spiral, through which a high-frequency current passes. The phenomena observed are of the same type for all three metals. At pressures above 10 mm., isolated discharges in the form of very fine bands are produced in the vapour from time to time, green in colour with mercury, bluish-green with zinc, and deep blue with cadmium. On lowering the pressure there is a glow of the same colour and an annular discharge, the spectra of which show in a brilliant manner the ultimate lines of the metal. The various lines appear in turn as the pressure gets less, not being present altogether. On lowering the temperature of the bulb, the annular discharge becomes steadily brighter, until suddenly, in addition to the principal rays of the metal, a magnificent band spectrum appears, only being maintained between narrow pressure limits. On further lowering the pressure, the luminous discharge becomes less bright, and finally completely disappears. The vapours of these three metals exhibit similar coloured luminescence at a relatively high pressure under the action of X-rays.

W. G.

**Series in the Spectra of Indium and Gallium.** F. PASCHEN and K. MEISSNER (*Ann. Physik*, 1914, [iv], **43**, 1223—1226).—The wave-lengths of lines in the spectra of indium and gallium have been measured, and it is shown that these may be represented by Paschen's series formulæ.

H. M. D.

**The Spark Spectra of Nickel and Cobalt in the Extreme Ultra-violet.** LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1914, 158, 784—787).—A comparison of the spark spectra of nickel and cobalt with those of iron and copper between  $\lambda$  1850 and  $\lambda$  2100. Photographs are given of the spectra and tables of intensities for the various wave-lengths. W. G.

**Arc and Spark Spectrum of Tin in I.Å.** RUDOLF ARNOLDS (*Zeitsch. wiss. Photochem.*, 1914, 13, 313—331).—Wave-length measurements have been made in the arc and spark spectra of tin between  $\lambda$  7800 and  $\lambda$  2069. The recorded data are expressed in terms of the international normals, and compared with the results obtained by previous observers. The existence of three groups of lines, characterised by a constant difference between the frequencies of corresponding members (Kayser and Runge, *Ann. Physik*, 1894, 52, 93), is confirmed by the author's measurements. On the other hand, the data afford no satisfactory evidence of the occurrence of spectral series of the type suggested by van Lohuizen (A., 1912, ii, 711). H. M. D.

**Flame Reactions. I.** WILDER D. BANCROFT and HARRY B. WEISER (*J. Physical Chem.*, 1914 18, 213—263).—A long critical review of the work done on the spectra of flames is given from the time of Bunsen up to the present day. The reactions and changes taking place in the substances introduced into the flames are specially considered. The observation of Smithells (*Phil. Mag.*, 1895, 39, 127), that metallic copper is deposited on cold porcelain from a Bunsen flame in which cupric chloride is being heated, has been repeated by the authors, and similar experiments have been carried out with a number of other substances. A large Bunsen burner was used for the more volatile substances, and a oxyhydrogen flame for the less volatile substances. The deposits were obtained by introducing a water-cooled porcelain tube. The substances introduced into the flame were cupric chloride, cadmium chloride, stannous chloride, mercuric chloride, silver nitrate, lead nitrate, bismuth nitrate, zinc chloride, arsenious oxide, antimony trichloride, molybdenum oxide, tungstic oxide, phosphorus trichloride, sodium chloride, potassium chloride, and sulphur. By precipitation from a Bunsen flame in the manner described, bright, metallic mirrors of copper, cadmium, tin, lead, silver, bismuth, zinc, arsenic, and antimony were obtained, together with various oxides at the edge of mirror. Mercury was obtained in metallic globules. By precipitation from the oxyhydrogen flame, metallic mirrors of molybdenum and tungsten were obtained. These results point conclusively to the fact that many salts are dissociated when heated in a Bunsen flame, and that at higher temperatures still more are dissociated. Sulphur can be precipitated from a hydrogen-free flame which contains sulphur dioxide; it can also be precipitated contaminated with carbonaceous matter from a Bunsen flame containing sulphur dioxide. Red phosphorus can be precipitated from a hydrogen air flame which is fed by phosphorus trichloride; it is

shown here that the flame of phosphorus burning in a very limited supply of air is green, and that the usual very bright, white flame is only obtained in the presence of excess of air. It is shown to be extremely probable that sodium and potassium are precipitated from an oxyhydrogen flame containing sodium chloride and potassium chloride respectively, although the evidence is not conclusive, owing to the ease with which the metals oxidise. The principle underlying the experimental results is that all exothermic compounds must decompose if sufficiently heated. The reducing action of the flame gases is not essential to the reaction, although it may at times increase the decomposition. In the hydrogen-chlorine flame the dissociation of the chlorides is driven back, in accordance with the law of mass action.

J. F. S.

**Light Absorption and Fluorescence.** E. C. C. BALY (*Phil. Mag.*, 1914, [vi], **27**, 632—643. Compare T., 1912, **101**, 1469, 1475; 1913, **103**, 91, 2086).—From an examination of a considerable number of compounds which exhibit two maxima in the absorption or fluorescence spectrum, it has been found that these correspond with frequency differences which are equal to, or a multiple of,  $1/\lambda = 400$ . This fact is shown to be in accord with the theory of quanta.

The existence of these maxima affords a means of determining the frequency of the characteristic band in the infra-red. If  $\nu_{\mu}$  is the frequency of this infra-red band, and  $\nu$  is the frequency of the light for which the refractivity is  $\mu - 1$ , then Sellmeyer's formula may be written in the form  $\mu - 1 = N / \{ (n\nu_{\mu})^2 - \nu^2 \}$ , in which  $N$  is a constant and  $n$  is an integer. This affords an accurate means of calculating the refractivities, for it is only necessary to find which value of  $n$  affords the best values of the constant  $N$  by making use of the observed refractivities. This calculation has been made for chlorine, hydrogen chloride, water vapour, ammonia, nitric oxide, and nitrous oxide, and it is shown that the calculated values are in good agreement with the observed refractivities in all six cases. The close agreement indicates that the application of the theory of quanta is completely justified.

H. M. D.

**The Selective Absorption of Ketones.** G. G. HENDERSON, J. A. R. HENDERSON, and I. M. HEILBRON (*Ber.*, 1914, **47**, 876—887).—An abstract of this paper has already been published in the Proceedings (1913, **29**, 354).

D. F. T.

**Tautomerism. Absorption of Ultra-violet Rays by Derivatives of Acetoacetic Acid.** JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1914, **158**, 866—869).—A quantitative examination of the absorption spectra in the ultra-violet of ethyl and methyl acetoacetates, and ethyl ethylacetoacetate and diethylacetoacetate, and substances having allied structures, namely, ethyl crotonate, mesityl oxide, pyruvic acid, ethyl pyruvate, and ethyl lævulate. Ethyl acetoacetate has an absorption band the maximum of which is at  $\lambda$  2430 in alcohol, ether, and hexane, and at  $\lambda$  2549 in water.

For values of  $\lambda$  above 2800, the absorption of this ester varies but little with the solvent, but below this value there is considerable variation. At  $\lambda$  2430 the molecular coefficient of absorption varies from 80 in water to 11,000 in hexane, this being due to variations in the proportions of the tautomeric forms present. Substances having an ethenoid linking in a conjugate position to a carboxyl group, such as ethyl crotonate, have no absorption band above  $\lambda$  2144. Substances having an ethenoid linking in a conjugate position to a carbonyl group, such as mesityl oxide, have an absorption band at  $\lambda$  2400, the molecular coefficient of absorption being 11,290 in water and 14,000 in alcohol and hexane. The tautomeric form of ethyl acetoacetate must therefore have this structure, and the proportions of this form present in the various solvents, deduced from the molecular coefficients of absorption, will be 0.7% in water, 14% in alcohol, and 70% in hexane (compare Meyer and Kappelmeier, A., 1911, i, 832).

W. G.

**Tautomerism. Absorption of Ultra-violet Rays by Aliphatic Diketones.** JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1914, **158**, 1022—1025. Compare this vol., ii, 230, and preceding abstract).—The authors have determined the molecular coefficients of absorption between  $\lambda$  2144 and 3329 of acetone, diacetyl, ethyl diketobutyrate, acetylacetone, methylacetylacetone, and acetonylacetone in solution in water, alcohol, dilute acid or alkali, and hexane, and for comparison mesityl oxide, methylheptenone, and allylacetone, and from their results have drawn the following conclusions. Acetone occurs in a very small amount in its enolic form,  $\text{CH}_3\cdot\text{C}(\text{OH})\text{:CH}_2$ , in alkaline solution, the absorption being slightly greater in this medium. The presence in a molecule of two carbonyl groups in conjugate positions provokes a displacement towards the red of the band characteristic of the carbonyl group, thus giving a hypsochrome effect. If the two groups are remote, as in acetonylacetone, there is an increase in the absorption, but no displacement, that is, a hyperchrome effect. The absorption spectrum of a  $\beta$ -diketone varies with the reaction of the medium and the nature of the solvent, the behaviour of these substances being explained if they are considered as a mixture of two forms, the proportions of which vary with the solvent. The relative amounts of these two forms can be calculated for the various solvents. The formula admitted for the tautomeric form of acetylacetone, namely,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\text{:C}(\text{OH})\cdot\text{CH}_3$ , is not in agreement with the absorption spectra, and should rather be  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\text{:CH}_2$ . Methylacetylacetone contains a much smaller proportion of the keto-ethenoid form than acetylacetone.

W. G.

**Secondary Colours.** E. HAVAS (*Ber.*, 1914, **47**, 994—995).—Kehrmann and Cordone (A., 1913, i, 1244) expressed the opinion that the greenish-yellow colour of 1-aminophenylnaphthaphenazonium chloride, in accordance with Piccard's conclusion (A., 1913, i, 895), is to be regarded as a secondary yellow yellow of the

second order). A spectroscopic examination of this compound confirms the opinion of the above authors. Replacement of the benzene nucleus in the green 1-aminophenylphenazonium chloride by the naphthalene nucleus leads to a normal deepening of colour, and the apparently paler colour is due to the fact that the band  $700\text{ }\mu\mu$  is shifted out of the visible part of the spectrum. J. C. C.

**Photometry of Luminescence Phenomena.** F. VON HAUER and J. VON KOWALSKI (*Physikal. Zeitsch.*, 1914, 15, 322—327).—An arrangement of apparatus is described which has been found suitable for the examination of the phenomena of luminescence. It consists of a monochromatic ultra-violet illuminator and a spectrophotometer adapted to the measurement of the intensity of comparatively faint luminescent radiation.

Various observations made with this apparatus are described. It is shown that the momentary and progressive phosphorescence of phenanthrene can be readily distinguished, and that the progressive bands are only excited by light which falls within the region of selective absorption of the phenanthrene.

From experiments with lithium platinocyanide, it is found that the intensity of the fluorescent light reaches a maximum when the wave-length of the exciting light is  $\lambda = 390\text{ }\mu\mu$ .

The data obtained with rubidium platinocyanide seem to show the existence of a maximum fluorescence, the position of which depends on the wave-length of the excitation.

From observations on the phosphorescence of calcium sulphide containing samarium as "active impurity" at different temperatures, it has been found that the rate of decay of the phosphorescence increases with the temperature, but this temperature effect varies from one band to another, and thus gives rise to change in colour of the phosphorescent light during the process of decay. For different bands the phosphorescence attains a maximum at about the same temperature, but since the influence of temperature on the intensity varies from one band to another, change of temperature produces a change in the colour of the phosphorescent light.

H. M. D.

**Dependence of Fluorescence on the Concentration.** WERNER MECKLENBURG and SIEGFRIED VALENTINER (*Physikal. Zeitsch.*, 1914, 15, 267—274).—Experiments have been made to determine the connexion between the intensity of the fluorescent light emitted by aqueous solutions of fluorescein and the concentration of the substance in solution. Since the exciting light is absorbed to a very considerable extent by the fluorescein solution, it was necessary to carry out a series of observations in which the exciting light was made to pass through layers of solution of different thickness, and by extrapolation of the data obtained in this way it was possible to eliminate the effect of absorption. By comparison, the fluorescent light is only absorbed to a negligibly small extent.

If pure aqueous (colloidal) solutions of fluorescein are examined, the intensity of the fluorescent light varies considerably, even when

the concentration remains constant. On addition of alkali to such a solution, the intensity increases with the amount of alkali added, but ultimately a maximum value is reached. This limiting value was found to be the same when either sodium carbonate, ammonium carbonate, potassium hydroxide, or ammonia was added to a given solution of fluorescein.

The experimental data for such alkaline solutions of fluorescein indicate that the intensity of the fluorescent light is approximately proportional to the concentration of the fluorescein in the solutions.

Attention is drawn to the fact that the absorption of the exciting light by the fluorescing solution is appreciably greater than would be expected according to the magnitude of the absorption coefficient (compare Nichols, *Jahrb. Radioakt. Elektronik.*, 1905, **2**, 149).

H. M. D.

**The Influence of Ultra-violet Light on Alkaline Salts of Acids Containing Halogen and Oxygen.** W. OERTEL (*Biochem. Zeitsch.*, 1914, **60**, 480—490).—Under the action of ultra-violet light, the alkali salts of chlorates, bromates, iodates, and periodates in aqueous solution decompose into oxygen and the halogenide, and the reaction is quantitative with a sufficiently long period of illumination. Only a very small decomposition could be observed in the case of the perchlorates. The rate of decomposition in the case of the bromates was greater than that of the iodates, and of the latter greater than that of chlorates. The amount of reaction products formed in a given time increased with increasing concentration of the solution, and the nature of the cation was without influence on the rate of decomposition. The solid substances also undergo decomposition when exposed to light, the chlorates decomposing readily, the bromates less so, the iodates being changed but very slightly.

S. B. S.

**Organic Syntheses by means of Light. IX. Action of Ammonia and Behaviour of Nitrogenous Compounds.** E. PATERNO [with G. CHIEFFI and G. PERRET] (*Gazzetta*, 1914, **44**, i, 237—257. Compare this vol., ii, 234).—Further results are as follows. Saligenin and alcoholic ammonia give a small proportion of a yellow, friable, resinous compound, m. p. 154—156°, containing 5.58% N. Benzoylacetone and alcoholic ammonia give benzoyl-isopropylideneimine,  $\text{CH}_2\text{Bz}\cdot\text{CMe}\cdot\text{NH}$ .

Benzil and alcoholic ammonia give, in addition to the products observed by Laurent (*J. pr. Chem.*, 1843, [i], **27**, 312; 1845, [i], **35**, 463) and by Henius (A., 1885, 1067), a white powder infusible at 300°. Dimethylpyrone and alcoholic ammonia undergo no change.

*photo*-Acetophenine (compare Paternò and Maselli, A., 1912, i, 295), which forms a *picrate*,  $\text{C}_{18}\text{H}_{22}\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , m. p. 266—267°, is not produced by the interaction of acetophenone and methyl alcoholic ammonia in the light. Acetophenone and methylamine in alcoholic solution yield a *compound*, m. p. 197—198°, whilst acetophenone and alcoholic ethylamine give acetophenonepinacone

(?) and a *compound*,  $C_{18}H_{22}N_2$ , which is isomeric with *photo* acetophenine, and forms a *picrate*,  $C_{18}H_{22}N_2 \cdot C_6H_3O_7N_3$ , m. p. 200—201°.

Parabanic acid and alcoholic ammonia give a crystalline compound, which does not melt at 280°. With barbituric acid, alcohol does not react, and alcoholic ammonia gives merely the ammonium salt.

No reaction occurs with aniline and benzophenone, *p*-toluidine and acetophenone, or methylaniline and amylene.

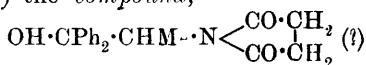
Methylaniline and acetophenone yield acetopinacone and an unstable additive *compound*,  $C_6H_4 \cdot NHMe + Ph \cdot COMe$ , which rapidly resinifies and gives a *platinichloride*. Methylaniline and benzophenone give benzopinacone and a base, the *platinichloride* of which closely resembles that of methylaniline in composition. This base forms unstable salts, and is similar in properties to those obtained by Willstätter and Kalb (A., 1904, i, 1050) from tetramethyl- and dimethyl-benzidines; its hydrochloride absorbs hydrogen in presence of palladium black in the ratio of two atoms per 1 mol. of methylaniline, and yields a green product on oxidation.

Benzamide does not react with decane, *p*-xylene, benzyl alcohol, or acetophenone, even after exposure to light for eight months.

Quinaldine does not react with benzophenone, but with acetophenone it yields diquinaldine (?) (compare Hinz, A., 1888, 300).

Benzylamine and benzophenone give ammonia and the basic *compound*,  $OH \cdot CHPh_2 \cdot CHPh \cdot NH_2$ , m. p. 148—150°, which forms a hydrochloride, and exhibits normal cryoscopic behaviour in benzene and in acetic acid.

Ethylsuccinimide and benzophenone yield (1) a compound (C 88.6, H 4.4%), m. p. 191—195°, which is possibly impure benzopinacone, and (2) the *compound*,



m. p. 158—162°.

2-Methylindole and salicylaldehyde give (1) a white *compound*, m. p. 223—225°, and (2) a red *compound*, which was not obtained pure, and is possibly an additive product of the two reacting substances.

Only resinous products were obtained from 2-methylindole and acetophenone, or benzophenone, and from *p*-aminoacetophenone and alcohol, *p*-toluonitrile, or benzyl alcohol.

Lutidine does not react with acetophenone, but with benzophenone it yields a small proportion of benzopinacone.

Collidine (trimethylpyridine) and benzophenone give a crystalline additive *compound*,  $C_8H_{11}N \cdot C_{13}H_{10}O$ , m. p. 205—207°, which has basic properties, and with sulphuric acid forms a reddish-yellow coloration, subsequently changing to green; its *platinichloride*,  $(C_{24}H_{21}ON, HCl)_2PtCl_4$ , was prepared.

*p*-Toluonitrile and acetophenone yield (1) a small proportion of liquid, b. p. 235—240°, and (2) a crystalline, nitrogen-free *compound* (C 80.07, H 6.00%), m. p. 140—142°.

*p*-Toluenitrile and benzophenone give a *compound*, m. p. 165—185°, which could not be obtained pure, but seems to be of the structure  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ . *m*-Toluenitrile and benzophenone yield a similar *compound*, m. p. 156—157°, but *o*-toluenitrile and benzophenone give only benzopinacone.

Phenylacetoneitrile and benzophenone give (1) benzopinacone; (2) *s*-diphenylsuccinonitrile; and (3) a compound, m. p. 158—167°, which gives an intense coloration with potassium hydroxide, and evidently contains an additive product (compare Hantzsch and Glover, A., 1907, i, 538).

Amylene, which combines with aldehydes and ketones under the influence of sunlight, does not do so with either pyridine or acetonitrile or benzonitrile.

T. H. P.

**Tables of Radioactive Constants.** LÉON KOLOWRAT (*Le Radium*, 1914, 11, 1—6).—This annual set of tables of radioactive constants has been brought up to date, and a list of references added as regards the origin of each constant. The first table gives the radioactive constants, the periods of half-transformation, the valency, the nature of the radiation, and the range in air of the  $\alpha$ -rays or the absorption coefficients of the  $\beta$ - and  $\gamma$ -rays of the known radioelements. The second table gives the atomic weights of the radioelements and their products as directly determined, the rate of disengagement of heat by radium and its products, the rate of production of helium by radium, the volume and condensation constants of the radium emanation. The third table deals with the value of the atomic charge, the number of molecules in a c.c. or mole of gas, the constants of the  $\alpha$ -particles, the constants of the  $\beta$ -particles, with a detailed list of their various velocities, and the number of ions produced by the three types of rays. The last table gives useful information with reference to the standards of radio-active measurements, the  $\alpha$ -ray ionisation current of a uranium oxide surface, the saturation currents per gram of uranium and radium, the equilibrium ratio of radium to uranium, the rate of production of emanation by radium, radium chloride, etc., in curies and Mache units, and the saturation current due to radium emanation under a variety of conditions.

F. S.

**The Structure of the Atom.** SIR ERNEST RUTHERFORD (*Phil. Mag.*, 1914, [vi], 27, 488—498).—The “nucleus” theory of the atom supposes that the atom consists of a positively charged nucleus of small dimensions, in which practically all the mass of the atom is concentrated, surrounded by a distribution of electrons sufficient to make the atom electrically neutral, and extending to distances from the nucleus comparable with the ordinary accepted radius of the atom. Experimental results on the scattering of  $\alpha$ -particles indicate the essential correctness of the hypothesis, for in this case the deflections resulting from the electronic distribution outside the nucleus are probably negligible. Experiments are in progress to test the scattering of swift  $\beta$ -particles, which should experience large-angle scattering from the nucleus in addition to relatively



rare large deflections in passing close to electrons. In passing through hydrogen, the theory indicates that a small number of the  $\alpha$ -particles should acquire, by collision, a velocity 1.6 times that of the  $\alpha$ -particle, and should have a range nearly four times as great as the  $\alpha$ -particle which sets them in motion. Experiments, by E. MARSDEN, with a sealed tube of 100 milli-curies of emanation, thin enough to allow the  $\alpha$ -particles to penetrate the walls, show that in hydrogen, whilst the great part of the scintillations on a zinc sulphide screen disappear at 20 cm. from the source, a few of less intensity persisted up to a distance of 90 cm. The number of such scintillations is of the correct order of magnitude supposing that the hydrogen and helium nuclei behave like point charges for distances up to  $10^{-13}$  cm. Darwin (see next abstract) has calculated that the centres of the hydrogen and helium nuclei must approach within  $1.7 \times 10^{-13}$  cm. The diameter of the nuclei must therefore be smaller than that ordinarily accepted for the electron,  $2 \times 10^{-13}$  cm., and it is not improbable that it may be so much smaller,  $1/1830$  times as great in the case of hydrogen, that its mass may be explained in the same way as that of the electron, as being entirely electromagnetic in origin. That is, the hydrogen nucleus may be the positive electron.

An examination with H. ROBINSON to see whether radio-active substances expel any other charged atoms except helium atoms has shown that if such particles are expelled, their number must be less than 1 in 10,000 of the helium atoms. The mass of the atom must depend, in the event of very close packing of the constituent charges, not only on their number, but on the way their external fields interact, and this may explain why the mass of the helium atom is not exactly four times that of hydrogen. Recent generalisations connecting the sequence of radio-active changes with the periodic law, and by Moseley (this vol., ii, 14) on the wavelengths of the characteristic X-rays emitted by various elements, have borne out the suggestion that the value of the charge on the nucleus, and consequently the number of the external electrons in an atom, is equal to the number of the element in the sequence of the elements when arranged in order of increasing atomic weight. This number determines the chemical and physical properties of the atoms, except those connected with gravitation and radio-activity. Atoms may differ in atomic weight and have the same nuclear charge and general properties. If the nucleus is considered to be made up of a mixture of hydrogen nuclei with one charge, and of helium nuclei with two charges, it is a priori conceivable that a number of atoms with the same nuclear charge, but of different atomic masses, may exist. F. S.

**Collision of  $\alpha$ -Particles with Light Atoms.** C. G. DARWIN (*Phil. Mag.*, 1914, [vi], 27, 499–506) —The simple treatment, due to Rutherford, of the case of the collision of  $\alpha$ -particles with heavy atoms, is modified to include the case where the nucleus of the atom struck is light enough to be set in motion by the collision. When the atom struck is greater in mass than the  $\alpha$ -particle, the

full expression differs from that used by Rutherford only by 1% in the case of the carbon atom, and still less for heavier atoms. The maximum velocity attainable by the carbon nucleus is one-half of that of the  $\alpha$ -particle. In helium, where the mass of the atom equals that of the  $\alpha$ -particle, no  $\alpha$ -particle can be deflected greater than a right angle, and the recoiling particles in this case would be quite indistinguishable from true  $\alpha$ -particles. In hydrogen, the greatest angle of deflection is  $14^{\circ}29'$ , but two types of  $\alpha$ -particles have to be distinguished. For example, among those not at all deflected are some that have not been in collision and others which have struck a hydrogen atom perfectly straight, and then followed on. In addition, there will be the recoiling hydrogen atoms with velocities very much greater than the  $\alpha$ -particles. On Bohr's reasoning, and Geiger's empirical formula connecting range and velocity, the behaviour of these hydrogen atoms may be deduced. In the most favourable type of collision possible, when an  $\alpha$ -particle at its highest velocity strikes a hydrogen nucleus straight on, the initial velocity of the hydrogen atom will be 1.6 times that of the  $\alpha$ -particle, and its range in hydrogen 117 cm., or perhaps even more than this. They should be scattered twice as much as  $\alpha$ -particles by their atomic encounters, for the angle of most probable scattering depends on the value of  $e/m$ .

The question whether any other than the law of force, the inverse square of the distance law, assumed by Rutherford, would give the same results in the scattering of  $\alpha$ -particles, is answered in the negative. Widely different results are got if an inverse cube law is assumed. The upper limit of the diameter of the nucleus for the case of a gold atom is calculated as  $3.5 \times 10^{-12}$  cm. In the case of a hydrogen atom struck by an  $\alpha$ -particle, the centres of the two nuclei approach to within  $1.7 \times 10^{-13}$  cm. in a straight-on collision.

F. S.

**The High frequency Spectra of the Elements and the Structure of the Atom.** J. W. NICHOLSON (*Phil. Mag.*, 1914, [vi], 27, 541—564).—A theoretical paper, in which the author discusses the question of atomic structure, with special reference to Bohr's theory (A., 1913, ii, 689, 943, 1045) and the nature of the high-frequency spectra (compare Moseley, this vol., ii, 14).

According to Moseley, the principal line in the X-ray spectra of the elements from calcium to zinc can be accounted for by Bohr's theory if his formula for spectra is applied to the steady states of an inner ring of four electrons rotating round a nucleus the charge of which corresponds with the so-called "atomic number" of the element; but the author considers that this application of the theory cannot be made without conflict with recent experimental results, which seem to show that the "atomic number" is about half the atomic weight.

The view that the position of an element in the periodic table is determined by its "atomic number" rather than by its atomic weight (van den Broek, A., 1913, ii, 90), involves the supposition that the atomic numbers of lithium, glucinum, and boron are three,

four, and five respectively, and it is shown that, on Bohr's theory, this cannot be reconciled with theoretical considerations. If Bohr's theory of such complex atoms is to be retained, it is necessary to abandon van den Broek's hypothesis in its present form, and replace it by a modified hypothesis.

From a mathematical consideration of the properties of various configurations of rotating electrons, it is shown that coplanar rings are impossible in a permanent atom constructed on the basis of ordinary electrodynamics, and that if the more complex atoms have the number of electrons, which seem to be necessary according to the results of experiments on scattering, these electrons must either form a single ring or rings in parallel planes.

In regard to the connexion between the high-frequency spectra and atomic structure, the author shows that Moseley's observations (*loc. cit.*) do not admit of the interpretation given to them on the basis of Bohr's theory. The conclusion to be drawn from these observations is that the frequencies of the principal X-rays of the elements are proportional to the squares of natural numbers. This relationship must inevitably lead to a further knowledge of atomic structure.

H. M. D.

**High-frequency Spectra of the Elements.** II. H. G. J. MOSELEY (*Phil. Mag.*, 1914, [vi], 27, 703—713).—The method of photographing X-ray spectra described in a previous paper (this vol., ii, 14) has been applied to some thirty other elements, and simple relations have been found to exist which make it possible to predict the position of the principal lines in the spectrum of any element from aluminium to gold.

The spectra of radiations belonging to Barkla's *K* series contain two lines, whilst the spectra of the *L* series contain five lines, which decrease in intensity with diminishing wave-length. If the square root of the frequency of the strongest ( $\alpha$ ) line is plotted against a series of integral numbers which are characteristic of the different elements, two approximately straight lines are obtained, one for the *K* and the other for the *L* spectra. The order in which the elements are arranged is that of the atomic weights, except in the case of argon, cobalt, and tellurium. The series begins with aluminium, to which the number 13 is assigned, and, with three or four exceptions, the integers assigned to the successive elements increase in perfectly regular order. Vacant spaces are left for an element between molybdenum and ruthenium ( $N=43$ ), between neodymium and samarium ( $N=61$ ), and between tungsten and osmium ( $N=75$ ). With this arrangement, perfect regularity is found in the X-ray spectra.

The integer  $N$ , or "atomic number," is supposed to represent the number of positive units of electricity contained in the atomic nucleus. This number determines the X-ray spectra of every element between aluminium and gold.

From the approximate linear relation between  $\nu^{1/2}$  and  $N$ , the general equation  $\nu = A(N - b)^2$  is obtained, in which  $\nu$  is the frequency and  $A$  and  $b$  are constants characteristic of each line in

the X-ray spectra. For the  $\alpha$ -line in the  $K$  series,  $A = 1/1^2 - 1/2^2)v_0$  and  $b = 1$ , and for the  $\alpha$ -line in the  $L$  series,  $A = (1/2^2 - 1/3^2)v_0$  and  $b = 7/4$ , where  $v_0$  is the fundamental Rydberg frequency.

The fact that the X-ray spectrum is determined by a characteristic integer is supposed to afford strong support for van den Broek's hypothesis, according to which the charge carried by the positive nucleus is in all cases an integral multiple of the charge on the hydrogen nucleus.

H. M. D.

**Nuclear Electrons.** A. VAN DEN BROEK (*Phil. Mag.*, 1914, [vi], 27, 455—457).—The number of the place an element occupies,  $M$ , when the elements are arranged in order of increasing atomic weight, is equal to the intra-atomic charge, because the scattering of  $\alpha$ -particles per atom divided by the square of this number is constant, and hence, on Rutherford's theory, the number must be equal to the charge. As the nuclear charge difference between uranium and lead is 10, and between thorium and bismuth is 7, as derived from the numbers of these elements in the sequence of elements, and as in these cases 16 and 12 positive charges, respectively, are expelled in the radioactive transformations, it follows that the  $\beta$ -particles, 6 from uranium and 5 from thorium, must come from the nucleus. This conclusion is independently arrived at in another way. Calling  $P$  the periodic number of the place an element occupies in a strictly periodic sequence, starting with lithium as unity, and assigning only one place to each triad of group VIII and to all the elements between cerium and tantalum,  $P = \{(A - 2M)/2c\}^{\frac{1}{2}}$ , where  $A$  is the atomic weight and  $c$  is 0.00468. If the total number of electrons in the atom is equal to half the atomic weight, and if  $M$  is the number surrounding the nucleus, then, since  $N - M = cP^2$ ,  $cP^2$  must be the number of electrons in the nucleus. A table is given in which  $A$  is calculated on these assumptions from the relation  $A = 2(M + cP^2)$  for a number of elements, and shown to agree with the experimental values. The values for  $cP^2$ , the number of nuclear electrons, is 17 for lead and bismuth, 22 for thorium, and 23 for uranium, in agreement with the figures previously given for the differences. These considerations indicate that the number of nuclear electrons in all the rare-earth elements is the same.

F. S.

**Thermal Emission of Electrons and the Photoelectric Effect of Potassium.** KARL FREDENHAGEN (*Ber. Deut. physikal. Ges.*, 1914, 16, 201—219. Compare Wiedmann and Hallwachs, this vol., ii, 162).—Experiments are described in which the author has investigated the thermal emission of electrons by potassium at temperatures between  $280^\circ$  and  $400^\circ$ , with the object of determining the factors on which the phenomenon depends. The results suggest that the emission of electrons is not a fundamental property of the metal, but is conditioned by the presence of some active agent (probably gaseous), which can be removed or rendered inactive by various methods of procedure. This can be accomplished, for instance, by the repeated distillation of the metal in

a highly exhausted apparatus, by long-continued electronic discharge in a reflux form of apparatus, or by the employment of an electric discharge from an induction coil. In presence of foreign gases, the removal of the active agent is found to be more difficult.

Other experiments show that there is some connexion between the thermal emission of electrons and the photoelectric effect, for those operations which bring about a diminution in the thermal emissivity are found to have a similar influence on the photoelectric activity.

It is suggested that the active agent on which the two phenomena in question are dependent is hydrogen, although no direct evidence of this has been obtained. The experiments show, however, that helium, argon, and nitrogen are inactive. H. M. D.

**Acid and Base as Expressions of the Intensity of Electrons.** E. CRATO (*Ber. Deut. Pharm. Ges.*, 1914, **24**, 172—184. Compare A., 1913, ii, 665).—Polemical. A reply to the criticism of Thiel (this vol., ii, 66). H. M. D.

[**Acid and Base as Expressions of the Intensity of Electrons.**] A. THIEL (*Ber. Deut. Pharm. Ges.*, 1914, **24**, 184—188).—Polemical in reply to Crato (compare preceding abstract). H. M. D.

**Recombination of Ions in Gases.** G. RÜMELIN (*Ann. Physik*, 1914, [iv], **43**, 821—856).—An account is given of a new method which has been employed in the determination of the rate of recombination of the ions in gases.

From experiments made on air subjected to the action of  $\alpha$ - and  $\beta$ - +  $\gamma$ -rays from uranium and radium, it is found that in all cases the process of recombination diverges from that required by the equation  $q = an^2$ . The difference is much greater for the ions produced by  $\alpha$ -rays than for the corresponding ionisation due to  $\beta$ - +  $\gamma$ -rays. The direction of the divergence suggests that the rate of recombination of newly formed ions is greater than that of ions which have been in existence for some time.

With an arrangement of apparatus in which the influence of the abnormally rapid recombination was reduced to a minimum, it was found that the coefficient  $\alpha$  increases somewhat with increase in pressure. H. M. D.

**Extraction of Radiothorium or Substances Containing Radiothorium which are Used for the Preparation of Solutions Containing Thorium-X.** DEUTSCHE GASGLÜHLICHT AKT.-GES. (AUER-GESELLSCHAFT) (D.R.-P. 269692).—A solution of the substance containing radiothorium is precipitated with ammonia, and the whole evaporated to dryness. From the residue the ammonium salts are removed by repeated washing with water or with dilute salt solution (free from carbonic acid). The hydroxides are now mixed with water or dilute salt solution, and allowed to remain until a sufficient amount of thorium-X is formed (one to two days). The solution of thorium-X obtained in this way is a concentrated one, and is free from ammonium salts. J. C. C.

**Radioactivity of Certain Russian Mineral Waters.** R. SWINNE (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, Phys. Part, 454—459).—In the autumn of 1910 the author examined, according to Kohlrausch and Loewenthal's method with the fontaktoscope, the waters of a number of Russian mineral springs. The values found for the radioactivity in a few instances slightly exceeded one Mache unit, but were mostly very low, especially with sulphur waters.

T. H. P.

**Photo-electric Phenomenon Presented by Liquid Dielectrics.** L. STRAMP (*Bull. Acad. roy. Belg.*, 1914, 45—62).—Ultra-violet rays have a marked influence on the loss of an electric charge by liquid paraffin, light petroleum, shale oil, and Russian mineral oil, the discharge being accelerated to the greatest extent with liquid paraffin and petroleum positively charged, and with shale oil and Russian mineral oil carrying a negative charge. This effect is regarded, not as a result of ionisation of the air, but as a surface photoelectric phenomenon, since the velocity of discharge for either a positive or negative charge may be diminished or increased at will by mixing paraffin and shale oil.

T. H. P.

**Theory of Dielectrics. Variation of the Dielectric Constant with Temperature. Pyroelectricity.** S. BOGUSLAWSKI (*Physikal. Zeitsch.*, 1914, **15**, 283—288).—The temperature variation of  $(\epsilon - 1)/(\epsilon + 2)\rho$ , in which  $\epsilon$  is the dielectric constant and  $\rho$  the density of the dielectric medium, can be readily accounted for if it is assumed that the electrical forces are not strictly quasi-elastic. The occurrence of polar pyro-electric effects may be similarly explained.

H. M. D.

**Contact Electricity of Gases in Relation to Conducting and Non-conducting Liquids.** ALFRED COEHN and HERMANN MOZER (*Ann. Physik*, 1914, [iv], **43**, 1048—1078).—A method is described by which the authors have investigated the electric charge acquired by hydrogen and oxygen when the gases are bubbled through various pure liquids and through aqueous solutions of non-electrolytes and electrolytes.

In the case of non-conducting liquids, it has been found that hydrogen always becomes negatively charged, and that, in general, the intensity of the electrical effect increases with the dielectric constant of the liquid medium through which the gas is bubbled.

On the addition of very small quantities of electrolytes to water, the negative charge acquired by the gases becomes smaller, and with larger amounts the gases become positively charged. Curves are drawn which show the connexion between the electrical effect and the concentration of the solution. From these it is evident that the effect produced by successive small quantities of electrolyte diminishes very rapidly in the initial stages. The concentration at which the sign of the charge acquired by the gas changes from negative to positive has been determined for a number of electrolytes of varying chemical character and valency type. From these

data it is evident that acids are much more active than salts or bases, in that the electrical charge changes sign at a much smaller concentration in the case of the acids.

The question as to whether the electrically charged gases contain charged carriers has been answered in the affirmative. When non-conducting liquids are employed, the gases contain negative carriers only, but when bubbled through solutions of electrolytes positive carriers are also found to be present, the two kinds being equal in number when the concentration of the electrolyte is such that the gas remains unchanged. H. M. D.

**The Electrical Condition of a Gold Surface During the Absorption of Gases and their Catalytic Combustion.** HAROLD HARTLEY (*Proc. Roy. Soc.*, 1914, A, 90, 61—68).—Experiments are described which show the existence of a close relationship between the occlusion of gas by a hot metal surface and the electrical condition of the metal.

On account of its marked catalysing power at moderate temperatures and its chemical inertness, gold was used in most of the experiments as the most suitable metal, and its behaviour in presence of hydrogen, oxygen, and carbon monoxide was examined. The metal becomes negatively charged in contact with hydrogen and carbon monoxide, and positively charged in contact with oxygen. The electrical effect is probably due to occluded gas which is leaving the metal, for any cause, such as a sudden lowering of temperature, which momentarily checks the outflow of occluded gas, reduces the intensity of the electrical effect. Conversely, a sudden diminution in the gas pressure, which will increase the rate of outflow of the occluded gas from the metal, increases the intensity of the electrical effect.

From observations made with mixtures of hydrogen and oxygen, and of carbon monoxide and oxygen, it is found that gold acquires a negative charge during the process of catalytic combustion.

H. M. D.

**Sodium Amalgams. II. The Electrical Conductivity.** ERNEST VANSTONE (*Trans. Faraday Soc.*, 1914, 9, 291—296. Compare A., 1912, ii, 155).—A capillary glass spiral, 1 mm. diameter and 1 metre in total length, is filled with molten sodium or amalgam, and this is allowed to cool slowly from one end, so that a continuous thread of solid, of uniform diameter, is obtained. The specific conductivity of sodium at 12° is found in this way to be  $18.15 \times 10^{-4}$ . The conductivity of the amalgams falls rapidly, being  $7.29 \times 10^{-4}$  at 14.5 atomic % of mercury. At this point there is a discontinuity, followed by a second at 21 atomic % Hg. The conductivity curve then passes through a flat minimum at 35 atomic % Hg, and increases up to 45%. Beyond this point results have not been obtained, owing to frequent breakage of the spiral. C. H. D.

**Molecular Magnitudes and Electrical Conductivity of Certain Molten Salts.** P. WALDEN (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 405—422).—All the methods which have been applied to the

investigation of molten salts are in accord in indicating that such salts are associated, but divergent results have been obtained in regard to the extent of the association. Further, that fused salts exhibit marked ionic dissociation is also generally agreed, but here too discordant views are held as to the degree of the ionisation (compare Walden, A., 1913, ii, 98; Lorenz, A., 1907, ii, 665, 927; Schulze, A., 1911, ii, 790; 1913, ii, 192; van Laar, *Lehrb. der theoret. Elektrochem.*, 1907, 83; Arndt, A., 1907, ii, 598, 842). In general, however, it may be asserted that pure fused salts are strongly ionised, and that salts dissolved in these, when they form no ion in common with the solvent, are virtually completely dissociated into ions.

The author has determined the molecular magnitudes of a number of organic ammonium salts from the results of measurements of their electrical conductivities and capillarity constants. The salts used were anhydrous, and melted at temperatures not exceeding about 100°, so that the experimental conditions approximated, far more closely than is usual with molten salts, with those employed in investigating solutions of salts in water and ordinary organic solvents.

Capillary measurements (compare A., 1911, ii, 97; 1912, ii, 628; 1913, ii, 299) were made with methyl-, ethyl-, dimethyl-, and diethylamine nitrates, tetraisoamylammonium iodide, triisoamylamine thiocyanate, phenyldimethylamine and phenylmethylamine hydrobromides. At 100° the values of  $\eta$  range from 0.0340 to 0.506, those of the surface tension  $\gamma$  from 26.4 to 49.0, and those of the association factor from 1.4 to 8—9. The presence of the phenyl group causes a considerably greater increase in the viscosity and surface tension than that of methyl or ethyl. The association factor diminishes with increase of either the complexity of the organic radicle or the number of such radicles.

Conductivity measurements at various temperatures were made on ethyl-, diethyl-, and dimethylamine nitrates, ethylamine hydrochloride, and phenyldimethylamine hydrobromide. The conductivity-temperature curves are linear within the ranges of temperature employed, independently of the chemical compositions of the salts or of their degrees of association. The molecular conductivities for the different salts increase as the viscosity diminishes, and high values for the viscosity correspond with high temperature-coefficients of the specific conductivity.

In general, the behaviour of these fused organic salts at the low temperature of about 100° corresponds with that of simple inorganic salts at far higher temperatures—300—600°. Complete dissociation of the molten salts does not occur, and the degree of ionisation refers to both simple and also complex ions formed by the gradual resolution of the associated molecules.

T. H. P.

**Some Complex Boric Acids.** NILRATAN DHAR (*Zeitsch. anorg. Chem.*, 1914, 86, 196—200).—The effect of varying quantities of glycerol and mannitol on the conductivity of boric acid solutions has been determined.

C. H. D.



**Allotropy and Electromotive Equilibrium.** ERNST COHEN (*Proc. K. Acad. Wetensch. Amsterdam.*, 1914, **16**, 807—808).—A claim for priority against Smits (this vol., ii, 165) in respect of the statement that the contact of a metal with a solution of one of its salts has an accelerating influence on the setting up of the internal equilibrium in the metal. H. M. D.

**Chemical Action that is Stimulated by Alternating Currents.** S. G. BROWN (*Proc. Roy. Soc.*, 1914, *A*, **90**, 26—32).—It has been found that the polarisation which occurs when a battery, consisting of zinc and carbon poles immersed in dilute sulphuric acid, is joined up in circuit with a low resistance, may be greatly diminished, or even completely eliminated, by passing through the cell a suitable alternating current. When the alternating current is switched on, the evolution of gas at the cathode increases, in consequence of the greater value of the battery current, and it is observed that in these circumstances the gas bubbles appear to be shot off at right angles to the surface of the cathode.

With a battery arranged so as to expose only a small surface of the zinc anode to the action of the electrolyte, polarisation was observed, and the same effect was obtained when the carbon was placed within a porous cell in contact with strong nitric acid. This indicates that the polarisation of the battery is not due to evolution of gas, but to the restricted chemical action at the anode. On passing the alternating current, the current output was increased, as in the first case, showing that the alternating current increases in some way the intensity of the action at the anode.

When the anode surface is small, the chemical effect of the alternating current is most marked, and it has been found that platinum, gold, and carbon are oxidised quite readily when subjected under these conditions to the continued action of direct and alternating current. A similar action is found to take place when direct and alternating currents are passed through a layer of compressed lead monoxide placed between a lead cathode and a platinum anode. It is supposed that the action of the filings coherer is dependent on effects of the same type. H. M. D.

**The Mechanism of Anodic Reactions and the Behaviour of Iron and Steel Anodes.** E. P. SCHOCH (*Trans. Faraday Soc.*, 1914, **9**, 274—280).—The reactions at the anode are better explained by an action of the anions on the anode metal than by the direct emission of cations from the anode. When the surface of an anode is covered with discharged anions in process of reacting, access of other anions to the surface is hindered, and the production of oxygen ions near the electrode begins. The evidence is insufficient to decide whether oxygen accumulates as gas or as an oxide.

The activity of iron or nickel is much greater with haloids than with sulphates in the electrolyte, and the hypothesis of the catalytic influence of hydrogen fails to account for this. C. H. D.

**The Passivity of Metals.** G. SENTER (*Trans. Faraday Soc.*, 1914, 9, 203—213).—Introduction to a general discussion. No one theory accounts for all the phenomena of passivity. The hydrogen activation theory accounts for many phenomena, including those of sudden changes, but is difficult to reconcile with the activating influence of free halogens. The valency theory has been abandoned. The most serious objection to the oxide-film theory is the absence of any difference in the reflecting powers of active and passive iron. C. H. D.

**Anodic and Cathodic Retardation Phenomena, and their Bearing on the Theory of Passivity.** G. GRUBE (*Trans. Faraday Soc.*, 1914, 9, 214—227).—Anodic processes are probably retarded by the formation of an oxygen alloy at the surface. Thus, with platinum anodes, the retardation observed when bromine and iodine are discharged from neutral or alkaline solutions of bromide or iodide may be ascribed to the presence of a platinum oxide, probably  $\text{PtO}$ , in solid solution at the surface of the metal. Still higher potentials observed at platinum anodes are due to higher oxides. This hypothesis differs from that of an oxide film in assuming the presence of only a single solid phase, with continuously varying properties. C. H. D.

**The Passivity of Metals.** G. REICHNSTEIN (*Trans. Faraday Soc.*, 1914, 9, 228—246).—When gold foil is immersed in a solution of potassium cyanide containing oxygen or hydrogen peroxide, a gold-oxygen alloy is formed, which then reacts with the electrolyte. A layer of peroxide does not appear on the surface until the oxygen concentration has reached a high value. In general, passivity is caused by two reactions, such that the velocity of one reaction decreases with increasing oxygen concentration, whilst the velocity of the second increases. C. H. D.

**The Photo-electric Behaviour of Iron and the Theory of Passivity.** H. STANLEY ALLEN (*Trans. Faraday Soc.*, 1914, 9, 247—250).—Chemically active iron is also photo-electrically active, whilst processes which render the iron passive reduce its activity. The cause of both effects is to be found in the condition of the gaseous layer at the surface of the metal rather than in the presence of an actual film of oxide. C. H. D.

**The Phenomena of Passivity.** MAX LE BLANC (*Trans. Faraday Soc.*, 1914, 9, 251—266).—Passivity is not the exception but the rule, and may occur at the cathode as well as at the anode, and with chlorides and other solvents as well as with oxygen compounds. It is to be attributed to changes of valency, and to the changing velocity of hydration of ions of different valency. C. H. D.

**The Hydrogen Theory of Passivity.** G. C. SCHMIDT and W. RATHERT (*Trans. Faraday Soc.*, 1914, 9, 257—265).—The activation potential and the passivation potential are different. Metals which

can be rendered passive are those which dissolve rapidly only in the presence of a catalyst. Hydrogen, which is readily absorbed by many metals, is the most important of these catalysts.

In chromic acid solution, iron may be rendered either passive or active, according to the concentration. With the dilute electrolyte the metal is at first passive, but becomes active when hydrogen reaches it by diffusion. Similar results are obtained with chromium.

C. H. D.

**The Relation of Passivity to the Phenomenon of Electrolytic Valve Action.** GÜNTHER SCHULZE (*Trans. Faraday Soc.*, 1914, **9**, 266—273).—Passivity differs from the valve effect in that the oxide film, if present in the first case, conducts electrically, whilst in the second it offers an obstacle to the passage of the current. Valve action is due to an insulating skin of appreciable thickness, beneath which is a thin layer of gas, and passivity to a conducting skin of molecular thickness, on which is a layer of gas. Iron shows passivity in dilute sulphuric acid, and valve action in the concentrated acid.

C. H. D.

**Magnetic Susceptibilities of the Elements.** F. H. LORING (*Chem. News*, 1914, **109**, 121—123, 133—134).—The author gives two tables in which the magnetic susceptibilities of both para- and dia-magnetic elements are recorded. The existence of relationships between the magnetic susceptibilities of the different elements is discussed in reference to a special grouping, which is very similar to that described in a previous paper (A., 1909, ii, 392).

H. M. D.

**Magnetic Susceptibility of Some Feebly Magnetic Alloys.** EUGÈNE LOUIS DUPUY (*Compt. rend.*, 1914, **158**, 793—794).—A study of the variation in magnetic susceptibility of some alloys with variation in composition and structure. The results are shown by curves. For the system antimony-silver the curve has three angular points corresponding with the compound  $\text{Ag}_3\text{Sb}$  and to its two saturated solid solutions in silver and antimony respectively (compare Petrenko, A., 1906, ii, 667). For the system lead-tin, the solid solution of tin in lead is well shown, and there is indication of a slight solubility of lead in tin (compare Honda and Soné, A., 1913, ii, 919). The curve for the system zinc-aluminium indicates the compound  $\text{Al}_3\text{Zn}$ , partly dissociated, and its solutions in zinc and aluminium (compare Rosenhain and Archbutt, A., 1911, ii, 895).

W. G.

**Magnetic Researches. XII. The Susceptibility of Oxygen in Two Forms.** ALBERT PERRIER and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 894—901. Compare A., 1913, ii, 751).—The transformation from the transparent, vitreous to the blue-grey, opaque form which solid oxygen undergoes at  $-225^\circ$  is not accompanied by any appreciable change in the magnetic properties. The susceptibility of solid oxygen is nearly in-

dependent of the temperature between the freezing point and  $-240^{\circ}$ , and its value is only about one-third of the susceptibility of liquid oxygen at its freezing point. On cooling below  $-240^{\circ}$  there is a further sharp fall in the susceptibility to about half-value, at which it remains practically constant over the range of liquid hydrogen temperatures.

H. M. D.

**Magnetic Researches. XIII. The Susceptibility of Liquid Mixtures of Oxygen and Nitrogen and the Influence of the Mutual Distance of the Molecules on Paramagnetism.**

ALBERT PERRIER and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 901—916; *Compt. rend.*, 1914, **158**, 941—944).

—In order to ascertain the influence of the distance between the molecules of a paramagnetic substance on the coefficient of magnetisation, experiments have been made with oxygen admixed with varying proportions of nitrogen at temperatures between  $-195^{\circ}$  and  $-209^{\circ}$ .

The results obtained show that the specific magnetisation-coefficient of oxygen ( $\chi$ ) increases very considerably as its concentration diminishes, and approaches the value required by the equation  $\chi T = \text{constant}$ , where  $T$  is the absolute temperature. If  $1/\chi$  is plotted as a function of  $T$ , the data obtained for the various mixtures are found to lie on a series of parallel straight lines, which indicates that the variation of the specific magnetisation-coefficient with the temperature can be represented by the equation  $\chi(T + \Delta) = \text{constant}$ , in which  $\Delta$  is a parameter which depends on the concentration of the oxygen in the liquid mixture. The deviations from the Curie-Langevin law exhibited by pure liquid oxygen are therefore caused by the increase in the density or by the diminution in the mean distance between the molecules. In order to account for the observed results on the basis of Langevin's theory, it is only necessary to assume the existence of negative molecular fields, the influence of which increases directly as the density or inversely as the third power of the average distance between the molecules.

H. M. D.

**Magnetic Researches. XIV. Paramagnetism at Low Temperatures.** H. KAMERLINGH ONNES and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 917—920. Compare A., 1913, ii, 473).

—Further measurements have been made of the magnetic susceptibility at low temperatures, according to the method described previously. Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and palladium have been found to deviate appreciably from the requirements of Curie's law. The results for iron alum are in agreement with the law even at  $14.7^{\circ} \text{K}$ . Since the distance between the atoms of iron in this substance is of the same order as that at which the molecular field disappears in the case of liquid oxygen admixed with nitrogen (compare preceding paper), it is supposed that the validity of Curie's law down to the freezing point of hydrogen is due to the wide separation of the atoms of iron. In these circumstances, the individual atoms behave like those of a

normal paramagnetic substance. In general, the deviations exhibited by different substances at low temperatures would seem to make their appearance sooner in proportion as the mean distance between the paramagnetic atoms decreases. H. M. D.

**Electric Vacuum Oven for High Temperatures.** OTTO RUFF (*Zeitsch. Elektrochem.*, 1914, **20**, 177—179).—A comparison is made between the electric furnaces of Wolf and Müller (this vol., ii, 119) and that of the author. A further improved furnace, adapted either for heating crucibles or boats, is described in the present communication. The principle is the same as that previously described (*loc. cit.*). The following quantities of energy are required by the furnace: 2000°, 7.6 kilowatt; 2200°, 9.3 kilowatt; 2400°, 12.0 kilowatt; and 2700°, 18 kilowatt. Working drawings are given in the paper. J. F. S.

**A Modification of the Tammann Furnace.** ULRICH RAYDT (*Zeitsch. Elektrochem.*, 1914, **20**, 185—186).—A modification of the Tammann furnace, in which the iron end pieces used for conducting the current to and from the carbon resistance tube are replaced by copper split rings, which can be bolted together. This makes it much easier to replace the old tubes by new ones. The life of the furnace is much lengthened, since the copper rings can be water-cooled, and there is a somewhat smaller energy quantity required to obtain the desired temperatures. J. F. S.

**Specific Heat at Low Temperatures. VIII.** W. NERNST and F. SCHWERS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 355—370. Compare A., 1913, ii, 103, 104).—The method described in a previous paper (A., 1910, ii, 263) has been improved in detail, and a new series of measurements of specific heat has been made at temperatures varying from 20° to 100° (abs.). The recorded data show that the atomic (or molecular) heat falls in the case of aluminium from 2.355 at 79.1° to 0.066 at 19.1°, thallium from 5.65 at 95.7° to 2.92 at 22.9°, carborundum (SiC) from 1.013 at 96.5° to 0.099 at 52°, calcium oxide from 3.395 at 89.3° to 0.110 at 28.2°, calcium hydroxide from 5.09 at 86.0° to 0.493 at 21.4°, calcium carbonate from 8.683 at 88.2° to 0.996 at 22.3°, silver chloride from 9.820 at 91.4° to 2.780 at 22.5°, silver iodide from 11.355 at 116.5° to 3.287 at 17.8°, potash alum from 165.66 at 90.5° to 27.83 at 25.7°, magnesium from 4.558 at 93.8° to 0.335 at 27.2°, silicon (metallic) from 1.524 at 89.8° to 0.031 at 20.1°, lead monoxide from 6.42 at 92.7° to 1.55 at 21.3°, and lead iodide from 17.3 at 95.6° to 7.05 at 22.3°.

The variation of the specific heat of aluminium, carborundum, and silicon at low temperatures is found to be in approximate agreement with Debye's formula,  $C_v = aT^3$ , in which  $a$  is a constant and  $T$  the absolute temperature. For aluminium  $a = 8.4$ , for carborundum 0.841, and for silicon  $3.90 \times 10^{-6}$ . H. M. D.

**Specific Heat of Solids. III. Correction.** H. VON JÜPTNER (*Zeitsch. Elektrochem.*, 1914, 20, 187).—A correction of numerical details and equations of the author's paper (this vol., ii, 244).

J. F. S.

**Thermodynamic Relation between the Concentration and the Specific Heat of Very Dilute Solutions and the Temperature-coefficient of Concentration Cells.** KARL CZUKOR (*Ber. Deut. physikal. Ges.*, 1914, 16, 228—231).—By means of a cycle of reversible thermodynamic processes, it is shown that the specific heats  $c'_v$  and  $c''_v$ , and the concentrations  $c_1$  and  $c_2$ , of dilute solutions are connected by the equation  $R \log c_1/c_2 = J(c''_v - c'_v)$ , in which  $R$  is the gas constant and  $J$  the mechanical equivalent of heat. According to this equation, the specific heat must increase with the dilution of the solution. By reference to the data for dilute aqueous solutions of various inorganic substances, this is found to be true, and for pairs of solutions which contain 100 and 200 mols. of water per mol. of solute, the difference in the specific heat is approximately constant and independent of the nature of the dissolved substance.

If the above cycle is carried out with a solution of an electrolyte, the further relation  $dE/dT = c''_v - c'_v$  is obtained, in which  $dE/dT$  is the temperature-coefficient of the concentration cell which may be built up from the two solutions of specific heat,  $c'_v$  and  $c''_v$ .

H. M. D.

**Tables of the Relative Depression of Freezing Point 1860/Δ to Facilitate the Calculation of Molecular Weights.** J. ARTHUR HARRIS and ROSS AIKEN GORTNER (*Biochem. Bull.*, 1914, 3, 259—263).—Useful tables the scope of which will be gathered from the title.

W. D. H.

**Potassium Tetroxide.** R. DE FORCRAND (*Compt. rend.*, 1914, 158, 843—846).—A determination of the heat of formation of potassium tetroxide. The oxide was prepared by Vernon Harcourt's method (compare this Journ., 1861, 15, 276). A known weight of the oxide was dissolved in very dilute sulphuric acid in a calorimeter, and the hydrogen peroxide estimated immediately in the resulting liquid. The mean of five determinations gives 133·74 Cal. for the heat of formation of the tetroxide from the metal and 46·94 Cal. for its formation from the protoxide. These values are both lower than those obtained for caesium (compare A., 1910, ii, 584), and from the combined figures the author deduces the values 137·6 Cal. for the heat of formation of rubidium tetroxide and 130·0 Cal. for sodium tetroxide, the corresponding values for their formation from the protoxides being 54·1 Cal. and 29·3 Cal.

W. G.

**Potassium Trioxide and the Stability of Alkaline Peroxides.** R. DE FORCRAND (*Compt. rend.*, 1914, 158, 991—994).—The author has prepared potassium trioxide as a yellow, crystalline mass by heating the tetroxide at 480° in an apparatus in which a vacuum

of about 1 mm. was maintained. With this, by the method already described (compare preceding abstract), the author has obtained the heat of formation of potassium oxide, the trioxide, and the tetroxide. Combining these results with those already obtained (*loc. cit.*) or calculated by analogy, he finds that the heat of formation, starting from the elements, of the four alkali trioxides is sensibly the same, and equal to +126 Cal. The passage from the protoxide to the dioxide liberates quantities of heat, regularly increasing on passing from calcium through lithium, strontium, barium, radium, sodium, potassium, and rubidium to cæsium.

W. G.

**Heat of Combustion of Certain Aromatic Nitro-derivatives.**  
FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1914, 18—44).—The following heats of combustion under constant pressure and heats of formation have been measured; Nitrobenzene, 734·65 cal. (comb.), 3·9 cal. (form.); *m*-dinitrobenzene, 695·1 cal. (comb.), 8·6 cal. (form.); *m*-nitrotoluene, 889·55 cal. (comb.), 11·0 cal. (form.); *o*-nitrophenol, 688·04 cal. (comb.), 50·1 cal. (form.); *m*-nitrophenol, 688·4 cal. (comb.), 53·7 cal. (form.); *p*-nitrophenol, 688·23 cal. (comb.), 50·0 cal. (form.); *o*-nitrophenetole, liquid 1021·2 cal., solid 1017·5 cal. (comb.), 43·4 cal. (form.); *m*-nitrophenetole, 1009·2 cal. (comb.), 55·6 cal. (form.); *p*-nitrophenetole, 1006 cal. (comb.), 58·4 cal. (form.); *o*-nitroaniline, 765·89 cal. (comb.), 6·9 cal. (form.); *m*-nitroaniline, 766·31 cal. (comb.), 6·5 cal. (form.); *p*-nitroaniline, 760·19 cal. (comb.), 12·3 cal. (form.); *o*-nitroacetanilide, 974·12 cal. (comb.), 56·3 cal. (form.); *m*-nitroacetanilide, 969·6 cal. (comb.), 59·8 cal. (form.); *p*-nitroacetanilide, 968·2 cal. (comb.), 61·2 cal. (form.).

Comparison of these results with those for other nitro-compounds shows that the variation of internal energy accompanying the substitution of the nitro-group for a hydrogen atom of the benzene nucleus is far from constant, the divergence between the extreme values being 15 cal. with the mononitro-derivatives, and 18·6 cal. in the case of the dinitro-compounds; with trinitro-derivatives, differences of 112·3 ( $=37·5 \times 3$ ) and 114·2 ( $=38·1 \times 3$ ) are obtained.

Excepting for the phenols and the dinitrobenzenes, the differences between the heats of combustion of isomeric aromatic compounds greatly exceed the experimental errors. In general, the ortho-derivative gives the greatest, and the para-derivative the lowest, heat of combustion; but with the nitrobenzoic acids and the dinitrobenzenes, the lowest values are yielded by the meta-derivatives. That the last observation is related to the orienting capacity of the carboxyl and nitro-groups seems improbable, for the conclusion cannot be drawn that the isomeride produced in largest proportion is the one with the smallest heat of combustion, the relative position of the two substituents in this isomeride depending on the order in which they are introduced.

Whilst the three nitrophenols exhibit equal heats of combustion, the three nitrophenetoles show wide differences in this direction. This is explained by the fact that the nitrophenetoles are of the

same type, and hence directly comparable, whereas the nitrophenols exist in two stable, tautomeric modifications. To an analogous conclusion leads comparison of the results obtained with the three nitroanilines and their acetyl derivatives. T. H. P.

**Pyknometer for Small Quantities of Liquid.** E. SERNAGIOTTO (*Ann. Chim. Applicata.*, 1914, 1, 198—199).—A small cylindrical pipette is fitted with a capillary stem of about 1 mm. bore, partly closed at the point so as to leave an orifice a fraction of 1 mm. in width. The short, upper part of the stem is furnished with a mark to fix the volume of liquid present, and slightly above this a small air-chamber, which is situate immediately below a small tap to prevent entry into the latter of the liquid. Above the tap, the stem has an internal diameter of about 4 mm., and is fitted with two fused-on, glass hooks, by means of which the pyknometer may be hung on the balance. The apparatus weighs about 5 grams, and serves for the determination of density and for the exact weighing of small amounts of liquid removed for quantitative analysis or other purpose. It is filled by suction applied to a rubber tube attached to the top of the stem. T. H. P.

**Influence of Volume Change on the Fluidity of Liquid Mixtures.** WILLIAM HOWIESON GIBSON (*Phil. Mag.*, 1914, [vi], 27, 662—668).—If  $v_1$  and  $v_2$  represent the specific volumes of the constituents of a binary mixture in the mixed liquid, whilst  $F_1$  and  $F_2$  are the fluidities which correspond with these volumes, then the fluidity of a mixture ( $F$ ) may be represented by the formula  $100vF = m_1v_1F_1 + m_2v_2F_2$ , in which  $v$  is the specific volume of the mixture, and  $m_1$  and  $m_2$  are the percentages by weight of the constituents in the mixture. The volumes  $v_1$  and  $v_2$  may be determined by experiment, or calculated from Batschinski's formula  $v - w = cF$ , in which  $w$  is the limiting specific volume at zero fluidity and  $c$  is a constant. It is assumed that when two chemically indifferent, non-associated liquids are mixed together, the specific volumes will change until the free space per unit of co-volume ( $w$ ) is the same for both kinds of molecules in the mixture. In other words, the assumption is made that  $v_1/w_1 = v_2/w_2$ .

If this is true, it would be expected that all normal liquids, for which the ratio  $v/w$  has the same value at one and the same temperature, will exhibit no change in volume on mixing, and that the fluidities of mixtures of two such liquids will be given by  $100vF = m_1v_1F_1 + m_2v_2F_2$ . Carbon tetrachloride and benzene represent such a pair, and it is found that the fluidities of mixtures of these two liquids are in agreement with those calculated by means of the above formula at temperatures from 10° to 70°.

Methyl iodide and carbon disulphide represent two liquids which have different values of  $v/w$  in the free condition. A change in volume on mixing is to be expected, and this is actually found. From the equations  $v_1/w_1 = v_2/w_2$  and  $100v = m_1v_1 + m_2v_2$ ,  $v_1$  and  $v_2$  can be calculated, and by substituting these values in the



Batschinski equation, the fluidities of each constituent in the mixture can then be found. It is shown that the fluidity values of mixtures of these two liquids, calculated from these data by means of the above equation, are in satisfactory agreement with the experimental data recorded by Thorpe and Rodger at temperatures between  $0^{\circ}$  and  $40^{\circ}$ .  
H. M. D.

**The Specific Volume and Constitution of Alloys.** W. M. GUERTLER (*J. Inst. Metals*, 1913, **10**, 175—192).—An explanation of three-dimensional diagrams in which temperature, concentration, and specific volume are used as co-ordinates. Measurements of specific volume may thus be compared with thermal measurements.

C. H. D.

**Theory of Molecular Volumes. II.** GERVAISE LE BAS (*Phil. Mag.*, 1914, [vi], **27**, 740—751. Compare this vol., ii, 173).—By reference to the data for the homologous series of formic esters and normal paraffins, the author discusses the variation in the increment of the molecular volume on the addition of the group  $\text{CH}_2$ . On the assumption that  $\text{C}=4\text{H}$ ,  $\text{O}''=3\text{H}$ ,  $\text{O}'=2\text{H}$ , the values of  $v/w$  have been calculated,  $v$  being the molecular volume and  $w$  the number of hydrogen equivalents in the molecule. In the case of the esters, the value of  $v/w$  falls from methyl to butyl formate, and afterwards increases as a linear function of  $w$ . For the normal paraffins,  $v/w$  decreases very rapidly at first, attains a minimum for  $n$ -pentane, and afterwards increases.

By reference to the data for the methyl and ethyl esters of the fatty acids and the aliphatic ethers, it is found that the molecular volume is to some extent influenced by the symmetry of the molecular structure. This effect is also examined in relation to the variation of  $v/w$  with the number of hydrogen equivalents. In nearly all cases the variations in question are shown in the form of curves  
H. M. D.

**The Critical Point, and the Significance of the Quantity  $b$  in the Equation of Van der Waals.** THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1914, **36**, 617—634).—Consideration of the experimental results hitherto obtained by various investigators for the effect of pressure on gases leads the author to the conclusion that the value of  $b$  (in van der Waals' equation) for carbon dioxide varies with the conditions in such a way that, although fairly constant under moderate pressures, it diminishes greatly with very high pressures. For hydrogen and carbon dioxide, the value of  $b$  is probably affected by the temperature, the nature of this effect being dependent on the value assumed for  $a$ .

The value of  $b$  for helium has a decidedly negative temperature-coefficient, indicating that the helium atoms are compressed by collision, the greater compression at higher temperatures being due to the greater kinetic energy of collision. This suggests, further, that uncombined atoms are not expanded by rise in temperature, which agrees with the solely translatory effect of heat on monatomic

gases. In polyatomic molecules this effect is partly counteracted by some sort of expansion of the molecule due to the energy expended within the molecule, as indicated by their larger specific heat. It follows, since  $b$  is a function of the size of the molecules, that molecules may change the effective size which they assume under collision.

If the atoms and molecules are compressible, van der Waals' conclusion that  $b$  is equal to four times the actual molecular bulk is incorrect; it is possible that the molecular bulk, when the molecules are not compressed by collision or cohesion, is probably even larger than  $b$ , being perhaps about equal to the critical volume. It is pointed out that, as a matter of fact,  $b$  occupies very nearly the bulk of the corresponding liquid at a temperature somewhat above the boiling point in many cases.

The continuity between the liquid and the gaseous states may be supposed to exist only at the critical point. The critical temperature is defined by supposing that it is the point where the kinetic energy of the molecules is just barely enough to separate them when the outside pressure is sufficient to bring, on the average, the molecular surfaces into contact; the critical volume may therefore be about the true volume of the non-cohering molecules.

From the above it is evident that the theory of compressible atoms affords a satisfactory explanation for the inadequacy of the equation of van der Waals, and the equation of corresponding states derived from it.

T. S. P.

**A New Relation between the Critical Quantities, and on the Unity of all Substances in their Thermic Behaviour.** J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 808—822).—The deviations from the van der Waals' ideal equation of condition are discussed, and the view is put forward that these deviations are due to the variability of the quantity  $b$  with the volume and with the temperature.

The assumption that  $b=f(v)$  is shown to lead to the following relations,  $v_k - b_k = 2b_0$  and  $b_k/b_0 = 2\gamma$ , in which  $v_k$  is the critical volume,  $b_k$  the value of  $b$  in the critical condition,  $b_0$  the value at absolute zero, and  $\gamma$  is the coefficient of the rectilinear diameter as given by the equation  $\frac{1}{2}(d_1 + d_2) = 1 + \gamma(1 - m)$ , where  $d_1$  and  $d_2$  are the reduced densities of liquid and vapour, and  $m$  is the ratio of the absolute temperatures  $T/T_k$ . For ordinary substances  $\gamma = 0.9$ , whereas for an ideal substance  $\gamma = 0.5$ , and for argon  $\gamma = 0.75$ .

A further relation obtained is expressed by the equation  $2f' = ss'$ , in which  $f'$  is the critical pressure-coefficient  $(Td p / p d T)_k$ , on the assumption that  $b$  is independent of the temperature,  $s = RT_k / p_k v_k$  and  $s' = v_k / v_0$ . For the ideal substance  $f' = 4$ , for argon  $f' = 5.99$ , and for an ordinary substance  $f' = 7.16$ . For the ideal substance  $s'/s = 1.125$ , and the empirical equalisation of  $s'$  and  $s$ , in accordance with van der Waals, can only lead to approximate relations, whereas the above empirical relations are exact, and appear to hold accurately for all substances.

It is further shown that  $f' = 8\gamma$ , or that the critical pressure-coefficient is equal to eight times the reduced coefficient which determines the slope of the rectilinear diameter.

The values of the above-mentioned quantities and others are recorded in a tabular summary, in which a comparison is made between the data for: (1) a limiting substance of high molecular weight; (2) ordinary substances; (3) oxygen and argon; (4) hydrogen and helium; (5) the ideal substance.

In regard to the variation of  $b$  with temperature, it is supposed that this is very slight at higher temperatures, and increases as the temperature falls. The fact that substances with low critical temperatures approximate more closely to the requirements of the ideal equation of state than do ordinary substances is shown to be in agreement with this hypothesis.

H. M. D.

**The Volume of Molecules and the Volume of the Component Atoms.** J. D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 880—890).—According to the equation  $RT_k/p_k = 8b$ , the quantity  $T_k/p_k$  may be regarded as a measure of the molecular dimensions. The values of  $T_k/p_k$  have been calculated from the critical data for the members of a number of homologous series of organic compounds. The relations exhibited by these numbers show that the volume of the molecules of normal substances is equal to the sum of the volumes of the component atoms. The volume of an atom is not constant, but is dependent on the atoms with which it is combined, and on the mode of combination. In the case of associated substances, the molecular volume, calculated on the basis of the atomic constants, diverges considerably from the value given by the ratio  $T_k/p_k$ . For benzene and other cyclic compounds this ratio is much smaller than the number which is obtained by the summation of the atomic volumes derived from a consideration of saturated compounds.

H. M. D.

**A New Viscometer for General and Scientific Purposes.** EUGENE C. BINGHAM (*J. Ind. Eng. Chem.*, 1914, **6**, 233—237).—A description of a viscometer which can be used for accurate work, and which is standardised by the use of a normal liquid. A general discussion of viscometric measurements is also given (compare T., 1913, **103**, 959).

T. S. P.

**The Viscosity of Certain Gases and the Variation with Temperature at Low Temperatures.** HANS VOGEL (*Ann. Physik*, 1914, [iv], **43**, 1235—1272).—The viscosity of a number of gases and vapours has been measured by the rotating disk method. A form of apparatus is described which has been found to yield satisfactory results down to liquid hydrogen temperatures. By comparison of the results with those of previous observers, it is shown that the rotating disk method is in no way inferior to the transpiration method, and in so far as it permits of measurements being made at low pressures, it is probably superior to the more frequently employed method of determination.

The variation of the viscosity with the temperature which is shown by the low temperature data is not in agreement with Sutherland's formula,  $\eta \sim T^{1/2}/(1 + c/T)$ , in which  $c$  is a constant. The data would, in fact, seem to show that  $c$  is a function of the temperature. The formula  $\eta_r = 2.80 \times 10^{-5}(MT)^{1/2}/V_s(1 + 1.47T_s/T)$  is found to express the temperature variation of the viscosity of the substances examined, with the exception of hydrogen, helium, and ethyl alcohol. In this formula,  $M$  is the molecular weight,  $T_s$  the boiling point, and  $V_s$  the molecular volume of the vapour at the boiling point.

H. M. D.

**Viscosity of Liquid Mixtures.** I. A. N. SACHANOV and N. A. RJACHOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 78—88).—It has been generally assumed that the viscosity of mixtures of liquids is an additive property, and some authors have expressed the relations between the amounts of the components in percentages by weight, and others in molecular or volume percentages. Viscosity curves showing a maximum were formerly regarded as the result of chemical action between the constituents of the mixtures and those showing a minimum as indicating depolymerisation of one or both components. Bingham (A., 1906, ii, 218), however, showed that the equation  $\eta = \eta_1(100 - p)/100 + \eta_2 p/100$  is not in accord with the truth, and that curves expressing the viscosities of mixtures are, in general, hyperbolic in character. Further, Faust (A., 1912, ii, 333) found that a viscosity minimum may be observed when the components of the mixture exhibit no inclination to depolymerise, whilst in certain cases investigated by Bingham (*loc. cit.*) and by Thorpe and Rodger (T., 1897, **71**, 373) no maximum appears, although the constituents show a marked tendency to interact. According to Bingham, the fluidity ( $1/\eta$ ), and not the viscosity, is an additive property, so that

$$\phi = \phi_1(100 - p)/100 + \phi_2 p/100.$$

In some instances this expression corresponds closely with the experimental data, but this ceases to be the case when the fluidities of the components differ considerably.

The viscosity of a liquid depends principally on the attractive forces between the molecules (compare Batschinski, A., 1913, ii, 928), and is, therefore, directly related to the constant of the van der Waals equation. Theoretically, the constant  $a$  for a mixture of two liquids depends on the constants  $a_1$  and  $a_2$  of the components, and on the constant  $a_{12}$  representing the attraction of the molecules of the one component on those of the other, so that  $a = a_1(1 - x)^2 + a_2 x^2 + 2a_{12}x(1 - x)$ , where  $x$  denotes the fractional proportional of the second component present in the mixture. Similarly for the viscosity,

$$\eta = \eta_1 \{(100 - p)/100\}^2 + \eta_2 (p/100)^2 + 2\eta_{12} p(100 - p)/100^2,$$

where  $p$  is the molecular percentage of the second component and  $\eta_{12}$  the mutual internal friction between the components. Now  $\eta_{12}$  is a function of  $\eta_1$  and  $\eta_2$ , and may be taken as proportional to the geometrical mean, that is,  $\eta_{12} = m\sqrt{\eta_1 \eta_2}$  (compare Dolezalek and Schulze, A., 1913, ii, 482). Substitution of this value gives

$\eta = \eta_1 \{ (100 - p)/100 \}^2 + \eta_2 (p/100)^2 + n \sqrt{\eta_1 \eta_2} \cdot p(100 - p)/100^2$ , where  $n = 2$  in the simplest case.

The results obtained by Linebarger (A., 1896, ii, 408), Dunstan (T., 1904, 85, 822), and Faust (*loc. cit.*) for benzene and chloroform at 25° ( $n = 2$ ), carbon tetrachloride and chloroform at 25° ( $n = 1.779$ ), benzene and ether at 25° ( $n = 1.430$ ), nitrobenzene and ethyl acetate at 25° ( $n = 1.581$ ), benzene and carbon tetrachloride at 0° ( $n = 2.076$ ), methyl iodide and carbon disulphide at 0° ( $n = 1.842$ ), and *s*-dichloroethane and benzene at 0° ( $n = 1.602$ ), and are found to be in excellent agreement with the experimental data. The same is the case with the authors' results for chloroform and bromobenzene at 0° ( $n = 2$ ), chloroform and phenetole at 0° ( $n = 2$ ), chloroform and diphenyl ether at 25° ( $n = 1.564$ ), and ethyl iodide and phenetole at 0° ( $n = 1.554$ ).

Certain mixtures, however, have viscosities differing from those calculated by means of the above expression. This is found to be the case when one of the two components has an abnormally high viscosity. With aniline and ether, for example, the viscosities of different mixtures at 0° and at 25° are less than

$$\eta_1 \{ (100 - p)/100 \}^2 + \eta_2 (p/100)^2,$$

the viscosity of the aniline alone being exceptionally high. With abnormally high viscosity there always corresponds abnormally high values of the temperature-coefficient of viscosity, the value of  $d\eta/\eta \cdot dt$  ranging from 0.055 at 0° to 0.029 at 40° (compare Kurnakov and Shemtschushni, A., 1913, ii, 190).

T. H. P.

**The Internal Friction of Aqueous Solutions of Potassium Haloids.** W. HERZ (*Zeitsch. anorg. Chem.*, 1914, 86, 338—340).—Curves are given for the viscosity of solutions of potassium chloride, bromide, and iodide from 0.5 to 6.2*N*.

C. H. D.

**Measurement of Brownian Movement as a Function of the Viscosity, together with a Theory of Distrust of Systematic Errors.** KARL SEELIS (*Zeitsch. physikal. Chem.*, 1914, 86, 682—739).—The viscosity of glycerol-water mixtures containing up to 75% glycerol has been measured at temperatures in the neighbourhood of 25°, and at pressures from 4.45 to 8.43 cm. of water, by means of rate of flow through a capillary tube. It is shown that the Hagenback correction of the Poiseuille formula can be applied to this method. The amount of displacement of cinnabar particles in glycerol-water mixtures has been determined by an ultramicroscopic photographic method. The partition law for the displacement of particles in a plane is developed and confirmed from the experimental results. A method is deduced for calculating the mean error of a single measurement from the mean error of  $n$  measured displacements, and despite the use of a different partition law in this calculation, the same result is arrived at as in the case of the Gauss theory. It is shown that it is less convenient, but more exact, to obtain the mean from the single determinations directly  $\Delta_r = \sqrt{1/n_1^2 \sum x_r^2}$  than from the arithmetic mean of the determinations, and so by means of a factor to obtain the mean error. It is

shown that the glycerol-water mixtures from pure water to 75% glycerol generally confirm the Einstein formula. In the region from 20% to 50% glycerol there is a remarkable divergence, which is to be attributed to an error of principle. The radius of the cinnabar particles was measured by two methods, and in the case of this suspensoid it is shown that Stokes's law does not hold, and corresponding with this it is shown that Einstein's law cannot be strictly applied for these suspensions, the amount of displacement being only about one-half that demanded by the theory. A reason for the divergence from the Einstein law is supposed to be found in the granular nature of the surface of the particles, and in case of the mixtures with 20—50% glycerol, the influence of complex molecules is held to be responsible. A modified Stokes's law is discussed, and the region over which it is applicable examined. It is shown that the conditions examined in the water-glycerol mixtures lie in the region of complete applicability. In place of  $\rho$ , the radius of the particle, a quantity  $P = \gamma/6\pi$  is introduced and determined experimentally. Using this value, there is an approximate agreement with Einstein's law, and the Avogadro constant is found to be  $N = 7.20 \times 10^{23}$ . J. F. S.

**Theory of Liesegang's Stratifications.** EMIL HATSCHEK (*Kolloid. Zeitsch.*, 1914, 14, 115—122. Compare A., 1912, ii, 439; Liesegang, A., 1913, ii, 304).—The author replies to Liesegang's criticism of the interpretation of the observations recorded in the previous paper (*loc. cit.*), and describes a new experiment in which well-marked stratification is set up. A small quantity of a 0.5% solution of potassium dichromate is introduced into a tube containing a 1% agar-agar jelly, in which lead acetate is present to the extent of 0.1%. Diffusion of the solution into the jelly is accompanied by the formation of a stratified system. If a second small quantity of dichromate is added when the first has completely disappeared, it is found that the diffusion of the newly-added dichromate gives rise to a second system of strata, in which the successive bands are much broader than those in the first system. The fact that two different systems can be obtained in the same jelly is considered to be irreconcilable with the supersaturation theory which has been advanced to account for the formation of these stratified systems.

From a study of the behaviour of a large number of diffusing systems, it would appear that the formation of stratified structures only occurs in the case of certain special chemical changes, and that in these cases the phenomenon is dependent on the concentration of the reacting solutions, and also on the nature and concentration of the gel. The substitution of agar-agar for gelatin, or vice versa, may be sufficient for the non-formation of the stratified system in the case of a reaction which gives rise to this structure under certain conditions. In general, agar-agar and silicic acid are more favourable to the development of such stratified systems than gelatin. It is possible that this influence of the gel is connected with its elastic properties. Another point which seems to have been definitely established is that certain reactions give rise to

zonal structures which are most readily obtained by plate experiments, whilst other reactions undoubtedly show the phenomenon best in the form of test-tube experiments.

The changes observable under the microscope during the formation of stratified systems are described in detail. There is a distinct difference in the appearance of the silver chromate rings described originally by Liesegang and the lead iodide and lead chromate rings investigated by the author. The structures characteristic of the lead salts convey no suggestion of empty spaces between the rings, but rather of a difference in the size of the particles in and between the rings. In other words, the stratified system gives the impression of a periodic variation in the degree of dispersity of the precipitate rather than of a variation in the quantity of substance present per unit of volume. The rings contain the more highly dispersed modification, whilst the interzonal spaces are occupied by particles of relatively large size.

H. M. D.

#### The Absorption of Gases by Charcoal at Low Temperatures.

GEORGES CLAUDE (*Compt. rend.*, 1914, 158 861—864. Compare Dewar, *Proc. Roy. Inst.* 1907, June 7th).—A comparison of the absorption of helium, neon, hydrogen, and nitrogen by cocoanut charcoal at temperatures of  $-195.5^{\circ}$  and  $-182.5^{\circ}$ . The results, which are tabulated and shown in curves, show that hydrogen departs entirely from the general rule, that the absorption of a gas is proportional to its ease of liquefaction, since hydrogen is absorbed to a far greater extent than neon at the same temperature and pressure.

W. G.

#### Absolute Measurement of Coefficients of Adsorption. J.

BANCELIN (*Compt. rend.*, 1914, 158, 791—792).—The author has studied the adsorption of colouring matters in solution by a solid having a perfectly defined surface, using glass plates for his solid, the quantity of colouring matter adsorbed being determined by colorimetric measurements of the solution before and after adsorption. The quantity adsorbed per sq. cm. of surface increases with the concentration of the solution, but is not exactly proportional to it. Similar results were obtained by using dilute solutions of sodium chloride, the estimations being made in this case by means of a Richards' nephelometer.

W. G.

**Neutral Salt Reactions with Reference to their Influence in the Acid Dye-Bath.** A. HERZ and C. E. BARRACLOUGH (*J. Soc. Dyers*, 1914, 30, 135—138).—In reference to the neutral salt reactions described by Fort (A., 1912, ii, 1047) and the action of sodium sulphate on the dyeing of wool (A., 1913, ii, 311), the authors have made a number of experiments on the influence of salts on the dyeing of wool, the results of which are opposed to those obtained by Fort, and cannot be accounted for by the assumption that the neutral salt is decomposed with the subsequent absorption of the free acid by the fibre. The explanation of the tendering of cotton warps in lustre goods dyed in a bath containing sodium sulphate

and an organic acid (Lloyd, *J. Soc. Dyers*, 1912, **28**, 337), in terms of the neutral salt reaction, is also found to be inconsistent with the results obtained in similar experiments which have been made by the authors.

H. M. D.

**Osmotic Pressure.** W. R. BOUSFIELD (*Proc. Roy. Soc.*, 1914, **A**, **90**, 41—45).—On the assumption that liquid water consists of a mixture of ice-molecules,  $(\text{H}_2\text{O})_3$ , dihydrol,  $(\text{H}_2\text{O})_2$ , and vapour molecules  $(\text{H}_2\text{O})$ , that the liquid contains molecular interspaces filled with vapour which determines the internal vapour pressure, and that the vapour behaves approximately as a perfect gas, it is shown that the osmotic pressure,  $P$ , of an aqueous solution is related to the lowering of the vapour pressure  $\delta p$  by the equation  $P = V_0 \delta p / ap$ , in which  $V_0$  is the molecular interspace in a litre of the solution under its own vapour pressure  $p$ , and  $a$  is a constant defined by the equation  $\delta V = aP$ . This relation is the same as that which is derived from thermodynamical considerations.

It is probable that the influence of hydrostatic pressure on the vapour pressure of water diminishes as the freezing point is approached in consequence of a reduction in the number of ice-molecules by transformation in accordance with  $2(\text{H}_2\text{O})_3 \rightarrow 3(\text{H}_2\text{O})_2$ , and this may account for the fact that the osmotic pressure of a 0.1 molar solution of sucrose has been found to be greater at  $0^\circ$  than at  $5^\circ$ .

H. M. D.

**Negative Osmosis.** F. E. BARTELL (*J. Amer. Chem. Soc.*, 1914, **36**, 646—656. Compare A., 1912, ii, 628).—Salt solutions of sulphates, chlorides, nitrates, and acetates were placed in osmotic cells constructed of porcelain membranes of the same degree of porosity. Some of the solutions gave positive osmosis, that is, the direction of flow of liquid was from the dilute to the more concentrated solution; others gave negative osmosis. When the cells were set up with pure water inside and salt solutions outside, negative osmosis still occurred with the solutions which had given it before, even though opposed by hydrostatic pressure.

Determination of the quantities of salt diffusing through the membranes showed that the order of the diffusion quantities is practically the same as the order of diffusion velocities when no membrane is present. The smallest quantities of salt diffuse through the membranes which show the greatest negative osmosis.

In all experiments with nitrates and chlorides the flow of the solution as a whole through the membrane was toward the more dilute solution, provided that the anion had a somewhat greater migration velocity than the cation; also, the greater the difference between the migration velocities of anion and cation, the greater the rate of flow.

The appearance of negative osmosis depends on the pore diameter of the membrane. Negative osmosis of magnesium chloride in neutral solution, and with porcelain membranes, predominates only when the pore diameters are somewhat less than 0.4 micron.

Apparently, negative osmosis is dependent on the electrical



polarisation of the capillaries of the membranes; also, it seems probable that this polarisation is largely brought about through ionic adsorption by the membrane.

T. S. P.

**New Method for the Determination of Solubility at High Temperatures.** L. TSCHUGAEV and W. CHLOPIN (*Zeitsch. anorg. Chem.*, 1914, 86, 154—162).—A new apparatus is described, in which, to avoid the use of large thermostats to obtain constant temperatures, all determinations are carried out at the boiling point of the saturated solution, this being varied by varying the pressure. The pressure is reduced by means of a water-pump, and kept constant by a mercury regulator. The actual solubility vessel has a ground-in, double-bored stopper carrying a thermometer, which dips into the liquid, and a narrow tube provided with a tap. At the lower end of this tube is a stopper, to which a small weighing bottle may be attached, and held on by platinum wires. The stopper of the weighing bottle is also provided with a siphon tube containing a filter plug. The solubility vessel has a side neck for a condenser near the top, from which a narrow branch tube re-enters the vessel near the bottom.

The solid is introduced into the solubility vessel, and solvent is then added. The vessel is heated  $5^{\circ}$  or  $10^{\circ}$  above the boiling point of the solvent at the pressure of the experiment by means of an oil-bath, and after a time a part of the solution is siphoned into the weighing bottle and removed. Very exact figures are obtained for the solubility of various salts in water at temperatures between  $50^{\circ}$  and  $95^{\circ}$ .

C. H. D.

**The Influence of a Second Solute on the Solubility of Phthalic Acid.** A. C. D. RIVETT and E. S. ROSENBLUM (*Trans. Faraday Soc.*, 1914, 9, 297—309).—The influence of alcohol, hydrochloric and acetic acids, sucrose, and twenty-one salts on the solubility of phthalic acid in water has been studied. In saturated solutions, the acid may be regarded as a weak, monobasic acid.

Among chlorides, the least electropositive element has the greatest depressing action on the solubility. Among potassium salts, the most electronegative anion has the greatest depressing effect. Oxy-salts give curves passing through a maximum. The depression by potassium chloride and sodium nitrate has been determined at  $35^{\circ}$ , when it is greater than at  $25^{\circ}$ , the curves at higher concentrations running almost parallel.

The first part of each solubility curve is irregular, but by an extrapolation a solubility for phthalic acid may be calculated, assuming the conditions to prevail which determine the remainder of the curve. Relative solubilities, calculated from the ionic and molecular constants of neutral salt action, are in good agreement with the observed values.

C. H. D.

**Relation between the Crystal Symmetry of the Simpler Organic Compounds and their Molecular Constitution.** III. WALTER WAHL (*Proc. Roy. Soc.*, 1914, A, 90, 1—19).—The experimental data recorded in previous papers (A., 1912, ii, 1044; 1913,

ii, 1031) are discussed with reference to the existence of a connexion between the chemical constitution and the crystalline form. Polymorphic forms have been observed in the case of about 50% of the substances investigated, and for these substances the modification which crystallises directly from the liquid is the only one which has been taken into consideration.

From a comparison of the crystalline forms of compounds containing one atom of carbon, it is shown that the crystal form is not an additive property, but that the system to which a particular substance belongs is determined by the symmetry of the molecule. All changes in the symmetry of the molecule which take place as a result of the substitution of one univalent atom or group by another are accompanied by a corresponding change in the symmetry of the crystal. Methane crystallises in the regular system, the mono-substitution products are mostly monoclinic, the di-substitution products orthorhombic, the tri-substitution products hexagonal, and the tetra-substitution products regular. These changes in crystalline form are considered to correspond closely with the changes in the molecular symmetry.

From the difference which has been observed between the crystalline form of the mono-substituted products and that of the tri-substitution products, the author concludes that the atoms or groups connected with the carbon atom modify to some extent the sphere of influence of the carbon atom, whereby the symmetry of the molecule is affected to a greater or less extent.

The phenomena of isomorphism, morphotropy, and enantio-morphism are also discussed, and it is shown that these phenomena are all dependent on the relationship which exists between the molecular constitution and the crystalline form of a substance.

H. M. D.

**Gradual Hydrolysis as Colloido-Chemical Process.** CARL L. WAGNER (*Kolloid. Zeitsch.*, 1914, 14, 149—153).—According to the changes in the electrical conductivity of their aqueous solutions, many salts appear to undergo hydrolysis at quite a slow rate. The cause of the gradual increase in the conductivity of solutions of such salts is discussed with special reference to ferric chloride.

A common characteristic of the salts which exhibit this phenomenon is that one of the products of hydrolytic decomposition is only very slightly soluble. It is supposed that the hydrolytic process itself takes place with great rapidity, and that the subsequent changes in the electrical conductivity of the solution are due to the gradual transformation of the insoluble product. In the case of ferric chloride, the freshly-formed ferric hydroxide is in a highly disperse condition, and in virtue of the large surface which it exposes to the solvent medium it adsorbs larger quantities of hydrochloric acid. As time goes on, the degree of dispersity of the colloidal hydroxide diminishes and the adsorptive capacity falls. In consequence of this change, the quantity of free hydrochloric acid in the solution increases, and this is shown by the rise in the electrical conductivity.

If a ferric chloride solution is diluted with a very weak solution of a sulphate instead of with water, it is found that the rate at which the electrical conductivity changes is very considerably increased. The effect in question becomes more marked as the concentration of the very dilute sulphate solution increases, and is attributable to accelerating influence of the sulphate ion on the coagulation of the ferric hydroxide. H. M. D.

**Processes Occurring on Shaking Dispersoid Solutions with Liquids and Solids Practically Insoluble in the Dispersoid Media.** P. P. VON WEIMARN and A. V. ALEXÉEV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 133—135).—Sahlbom (A., 1911, ii, 100) showed that, when positive colloids are shaken with filter paper, quartz sand, powdered sulphur, or powdered shellac, precipitation takes place, this phenomenon not being observed with negative colloids. The authors have made a number of similar experiments, and find that Sahlbom's results, and also those of Zsigmondy (A., 1913, ii, 847), cannot be regarded as general, since under suitable conditions, and with sufficiently protracted shaking, negative colloids are precipitated and the disperse phase removed from the aqueous layer. T. H. P.

**Combination and the Chemical Individual.** N. S. KURNAKOV (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 321—338).—The author discusses modern physico-chemical methods of investigating the equilibria of systems. T. H. P.

**Equilibria in Ternary Systems. XIII.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 841—857. Compare this vol., ii, 255).—Further special types of equilibrium in three-component systems are discussed in detail. H. M. D.

**Equilibrium of Pairs of Partly Miscible Liquids.** A. CAMPETTI and C. DEL GROSSO (*Nuovo Cim.*, 1913, [vi], **6**, ii, 379—417).—The authors have determined the curves of reciprocal solubility and the corresponding diameters, as well as the critical data for the following systems: water-nitrobenzene, water-*o*-nitrotoluene, aniline- $\beta$ -methylbutane, water-diphenylamine, phenol- $\beta$ -methylbutane, phenol-octane, phenol-hexane (b. p. 67.4°/760 mm.), phenol-heptane (b. p. 97.6°/760 mm.), and nitronaphthalene-paraffin (m. p. 45.5°). Since the hexane and heptane were characterised only by their boiling points, and the paraffin only by its melting point, uncertainty attaches to the results obtained with the last three systems.

The law of rectilinear diameter is found to hold very exactly, excepting for certain of the pairs of liquids in the neighbourhood of their critical temperatures. Under analogous conditions, the law of corresponding states is also applicable as a first approximation.

With water-nitrobenzene, water-*o*-nitrotoluene, and phenol- $\beta$ -methylbutane the curves representing the compositions of the

vapours have also been constructed. The forms of these curves render it probable that molecular association occurs in these cases.

T. H. P.

**Keto-enolic Tautomerism. IX. The Equilibrium of Desmotropic Compounds in Different Solvents.** KURT H MEYER (*Ber.*, 1914, **47**, 826—832. Compare A., 1913, i, 704).—The author has determined the equilibrium constant,  $[\text{enol}]/[\text{ketone}] = K$ , of ethyl acetoacetate, methyl benzoylacetate, acetylacetone, acetylcamphor, benzoylcamphor, benzoylacetone, dibenzoylmethane, acetyldibenzoylmethane, and acetoacetanilide in a large number of different solvents. The ratio of the value of  $K$  for each one of these compounds to the value of  $K$  for ethyl acetoacetate is found to be a constant,  $E$ , which is independent of the nature of the solvent. It follows that the equilibrium constant is a product of two factors, the one,  $E$ , depending on the solute, and the other,  $L$ , depending on the solvent, the relation  $K = EL$  thus holding.  $E$  is called the "enol constant" and  $L$  the "desmotropic constant" of the solvent; since absolute values cannot be given, the value of  $E$  for ethyl acetoacetate is taken as 1.

There is no relation between  $L$  and any other constant, for example, the dielectric constant. The relation between the equilibrium constant and the solubility of the desmotropic forms, as found by van't Hoff and Dimroth, is brought into connexion with  $E$  and  $L$  by the expression  $EL = K = G(\text{solubility of the enol})/(\text{solubility of the ketone})$ .

The enol constants are very different from each other, even when the compounds are closely related. The substitution of the acetyl by the benzoyl group approximately trebles the value of  $E$ , except in the case of the camphor derivatives. Quantitative relations which are generally applicable do not exist.

At the end of his paper the author criticises the recent paper of Leuchs (*A.*, 1913, i, 974), pointing out that his conclusions are not necessarily valid, since asymmetric synthesis may have occurred, the still unbrominated, optically active acid influencing the addition of bromine by the inactive enol in such a way that an optically active bromo-ketone is formed.

T. S. P.

**Keto-enolic Tautomerism. X. The Temperature-coefficient of the Equilibrium between Desmotropic Compounds and their Heat of Transformation.** KURT H. MEYER and FRANCIS G. WILLSON (*Ber.*, 1914, **47**, 832—837).—The authors have determined the equilibrium constants at different temperatures of acetoacetic ester, benzoylacetic ester, acetylacetone, benzoylacetone, and acetyldibenzoylmethane in four different solvents, namely, methyl alcohol, ethyl alcohol, toluene, and hexane. In all cases the percentage of ketone is increased by rise in temperature. With the exception of acetylacetone in hexane as solvent, the various desmotropes in one and the same solvent have approximately the same temperature-coefficient, which, however, varies considerably with the solvent. It follows that the temperature-coefficient depends on,

and is characteristic of, the keto-enol group, and independent of the rest of the molecule.

The heats of transformation of ketone to enol were calculated by the application of van't Hoff's equation, and found to be +2000 cal. in ethyl alcohol, +1000 cal. in toluene, and +2700 cal. in hexane as solvent.

T. S. P.

**Velocity of Hydrolysis of Nitriles by Hydrogen Chloride Solutions.** SULO KILPI (*Zeitsch. physikal. Chem.*, 1914, 86, 641—681).—The rate of hydrolysis of a number of nitriles of aliphatic acids by means of hydrogen chloride has been examined at temperatures between 74° and 110.9° in a 50% alcohol-water solution. The substances investigated include acetonitrile, propionitrile, *n*-butyronitrile, *n*-valeronitrile, methoxyacetonitrile, ethoxyacetonitrile, propoxyacetonitrile,  $\beta$ -methoxypropionitrile,  $\beta$ -ethoxypropionitrile,  $\gamma$ -methoxybutyronitrile, and  $\gamma$ -ethoxybutyronitrile. The course of the reaction is followed by the same method as that used in the determination of the velocity of hydrolysis of amides (Kilpi, A., 1912, ii, 748), from which the concentration of ammonium salt and free acid present in the reaction mixture can be obtained. It is shown that the reaction occurs in two stages, the first being the formation of an amide, which takes place as a bimolecular reaction,  $R \cdot CH_2 \cdot CN + H_2O \rightarrow R \cdot CH_2 \cdot CO \cdot NH_2$ , and the second the hydrolysis of the amide to acid and ammonia,  $RCH_2 \cdot CO \cdot NH_2 + H_2O \rightarrow R \cdot CH_2 \cdot CO_2H + NH_3$ ; this second stage takes place so rapidly in comparison with the first reaction that the velocity of the first stage only can be measured. The temperature-coefficient is deduced from the reactions at 74°, 102°, and 110°, and is shown to be in accord with Arrhenius' equation. The value of the temperature-coefficient is about the same in the various cases, and somewhat larger than that observed in the hydrolysis of amides (*loc. cit.*). It is shown that the rate of hydrolysis is greatest in the  $\alpha$ -ether nitriles and smallest for the  $\beta$ -ether nitriles, and, in general, is in accord with Michael's system for the negative character of the carbon atom of the carbonyl group.

J. F. S.

**Alkaline Hydrolysis of Nitriles.** SULO KILPI (*Zeitsch. physikal. Chem.*, 1914, 86, 740. Compare preceding abstract).—The work of von Peskov and Meyer (A., 1913, ii, 201) on the alkaline hydrolysis of nitriles is criticised; it is shown that the hydrolysis occurs in two stages, first the formation of the amide and then the formation of the acid. The former reaction occurs twenty-eight times as quickly as the latter, which shows that the alkaline and acid hydrolysis of nitriles occurs in the same manner, and can be represented by the same reaction formulæ (compare Kilpi, *loc. cit.*).

J. F. S.

**Hydrolysis of Esters of Substituted Aliphatic Acids. VII. Hydrolysis in Acid and in Alkaline Solution of Ethyl Esters of Hydroxybutyric Acids.** E. W. DEAN (*Amer. J. Sci.*, 1914, [iv], 37, 331—338. Compare Drushel and Dean, A., 1912, ii, 927; Dean, A., 1913, ii, 687).—Since the effect of the hydroxyl group

on the velocity of acid hydrolysis has been shown to be somewhat irregular in the cases of the acids of the acetic and propionic series, the author has examined the rates of decomposition of ethyl  $\alpha$ -hydroxybutyrate, ethyl  $\beta$ -hydroxybutyrate, and ethyl  $\alpha$ -hydroxyisobutyrate in comparison with those of ethyl *n*- and *iso*-butyrate, both in acid and alkaline solution. The first-named substance is most conveniently prepared by boiling  $\alpha$ -hydroxybutyric acid with ethyl alcohol in the presence of finely powdered, anhydrous copper sulphate (compare Bogojavlenski and Narbal, A., 1905, i, 854).

The rate of hydrolysis of the respective esters has been determined in *N*/10-hydrochloric acid solution at 25°, 35°, and 45°. In alkaline solution, measurements have been made by the titration method previously described (A., 1913, ii, 687) and by a modification of the conductivity method of Walker (A., 1906, ii, 732).

The following are the main results. When hydrolysed in acid solution, the three hydroxybutyrates are found to have considerably smaller velocities of reaction than the esters of the acids from which they are derived. Ethyl *isobutyrate* decomposes more slowly than the ester of the normal acid, a difference in the same direction, but of greater magnitude, occurring with the corresponding  $\alpha$ -hydroxy esters. Ethyl  $\beta$ -hydroxybutyrate decomposes more slowly than the  $\alpha$ -ester.

Esters of the butyric acid series appear, in general, to decompose more slowly than the propionates and acetates.

The effect of the hydroxyl group on the velocity of acid hydrolysis is not an additive property.

The velocities of saponification, measured in *N*/100-sodium hydroxide solution at 0°, vary in the following order, with the numerical values representing approximate ratios: ethyl  $\alpha$ -hydroxybutyrate (13.5), ethyl  $\beta$ -hydroxybutyrate (4.5), ethyl  $\alpha$ -hydroxyisobutyrate (3.4), ethyl butyrate (1.5), ethyl *isobutyrate* (1.0).

H. W.

**An Empirical Formula for Protein Hydrolysis by means of Enzymes.** K. G. DERNBY (*Zeitsch. physiol. Chem.*, 1914, 89, 425—431).—The modifications of the mass-action formula put forward by Schütz, Arrhenius and Henri as applicable to the velocity of enzyme actions are shown to give very irregular and inconstant results when applied to the rate of autolysis of yeast. The empirical formula  $k = 1/\sqrt{t} \log(a+x)/(a-x)$  is shown to give approximately constant values for  $k$ , and it is applicable also to the hydrolysis of ethyl acetate by ammonia, and to that of protein by pepsin.

E. F. A.

**Relationship between the Catalytic Action and the Affinity Constant of Acids.** HUGH STOTT TAYLOR (*Zeitsch. Elektrochem.*, 1914, 20, 201—204).—A theoretical paper in which the relationship between the affinity constants of several acids and their catalytic actions is considered. It is shown from the results of

Dawson and Powis (T., 1913, **104**, 2135), Snethlage (A., 1913, ii, 1044), and new determinations of the author that the ratio of the catalytic action of the undissociated molecules of the acid  $k_m$  to the catalytic action of the hydrogen ions  $k_H$  increases regularly with, but not so rapidly as, the affinity constant. A straight-line curve is obtained when  $\log k_m/k_H$  is plotted against  $\log A$ , where  $A$  represents the affinity constant. From the curve, the expression  $A = (k_m/k_H)^2$  is deduced. If  $c_1$  represents the concentration of the hydrogen ions and  $c_2$  that of the undissociated acid molecules, it follows that  $k_m/k_H = c_1/\sqrt{c_2}$ . A number of divergencies from the curve are found among the reactions examined, which are attributed to specific actions occurring in these cases. J. F. S.

**Atomic Weights.** F. H. LORING (*Chem. News*, 1914, **109**, 169—170).—The author has shown previously (*ibid.*, 143) that copper, silver, and gold probably are made up of associate elements (atoms) differing in atomic weight, non-separable by chemical means, and exactly whole numbers; in this connexion, de Heen's experimental demonstration of the variability of the molecule and atom is of interest (this vol., ii, 125). In the present paper it is shown that the same ideas may be extended to the elements chlorine, manganese, iron, nickel, cobalt, ruthenium, rhodium, palladium, magnesium, silicon, bromine, barium, aluminium, and the rare gases. In the great majority of these cases the element may be considered to be made up of 1 part of atomic weight  $x$  and 10 parts of atomic weight  $y$ ; for example, for chlorine  $x=40$  and  $y=35$ , so that its atomic weight is  $(40 \times 1 + 35 \times 10)/11 = 35.45$ . T. S. P.

**The Foundations of Atomic Models.** F. A. LINDEMANN (*Ber. Deut. physikal. Ges.*, 1914, **16**, 281—294).—The question as to what hypotheses are necessary in order to account for the fundamental properties of the atom is discussed in reference to the dimensional evaluation of a general formula for atomic structures. It is shown that the formulæ put forward by Bohr and by Gehrcke may be deduced from the general dimensional formula without the introduction of the special hypotheses which have been suggested by these authors. The possibility that the electrical forces within the atom are subject to a law other than Coulomb's is discussed, and the consequences, resulting from the assumption that the electrical force is inversely proportional to the third power of the distance, are examined in some detail. H. M. D.

**Automatic Gas Generator.** ROBERT W. CURTIS (*Chem. News*, 1914, **109**, 124).—A slightly modified form of a well-known type of automatic gas generator is described. H. M. D.

**Removal of Gas Solutions, especially Radium-emanation Solutions from Receptacles** ARMIN SPITZER (*Chem. Zeit.*, 1914, **38**, 381).—To avoid the introduction of air or other gas into a vessel when a portion of the contents is withdrawn, the author

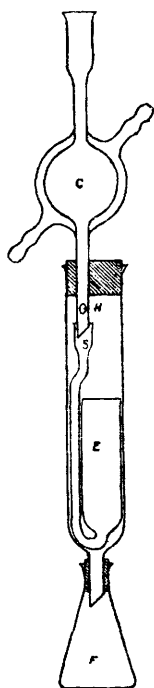
has devised various forms of receptacles. One of these consists of a double-walled vessel for containing the solution; an inverted bell-jar, also provided with double walls, fits into the top of the vessel, the head of the bell resting on the surface of the liquid, whilst its outer wall passes into the space between the two walls of the vessel. This space may be filled with mercury or glycerol. Another form of the apparatus consists of a cylinder having a conical lower end provided with a tap or other closing device, whilst a leather piston rests on the surface of the liquid contained in the cylinder.

W. P. S.

**A New Extraction Apparatus.** S. N. PINKUS (*Biochem. Zeitsch.*, 1914, 60, 311—312).—The apparatus is figured in the text. It is so constructed that the vessel containing the substance to be extracted by the solvent can be placed in a receptacle containing ice or cold water. The extraction can therefore be accomplished at low temperatures. The apparatus is thus adapted to work with protein-containing materials. S. B. S.

**Extraction Apparatus, specially Designed for Solvents of High Specific Gravity.** C. BUDDE (*J. Soc. Chem. Ind.*, 1914, 33, 184—185).—When an ordinary fat or wax is dissolved in a heavy solvent such as chloroform or carbon tetrachloride, the solution has a lower density than the pure solvent itself. In extractions with such solvents, therefore, the solution should be removed from the surface and the solvent be supplied at the bottom of the substance to be extracted if speedy and efficient extraction is to be attained. This is accomplished by means of the apparatus shown in the annexed diagram, which is self-explanatory.

T. S. P.





## Inorganic Chemistry.

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### Apparatus for the Preparation and Storage of Pure Water in Large Quantities.

THEODOR PAUL (*Zeitsch. Elektrochem.*, 1914, **20**, 179—185).—Tap-water is placed in a large glass vessel and stirred with a quantity of freshly-prepared lime and allowed to settle. The clear water is then transferred to a tinned copper still of about 15 litres' capacity. The steam from the still passes along an inverted copper U-tube which leads into a small inner cylindrical copper vessel concentric with the still. This vessel is filled to about one-third of its height with milk of lime, through which the steam passes, and by which it is freed from carbon dioxide and acid gases. The steam then passes into a double-surface tinned copper condenser. After the first

litre of water has passed over, about 10 litres can be obtained, which has a specific conductivity of  $0.80 \times 10^{-6}$ . The still described gives a litre of water in about ten minutes. If the tap-water contains much organic matter, a small quantity of potassium permanganate is added to it, along with the lime in the original storage vessel. The water is stored in a 15-litre Jena-glass flask which has been "steamed out" for two hours. This flask is so arranged by means of stop-cocks and tubes that the water from the condenser receiver can be drawn into it by means of a water-pump, and that a steady stream of carbon dioxide-free air can be bubbled through the water to remove all carbon dioxide. Conductivity water can be kept in this way for very long periods without gaining in conductivity. J. F. S.

**Synthesis of 100% Hydrogen Peroxide by means of a Silent Electric Discharge.** PAUL MAX WOLF (*Zeitsch. Elektrochem.*, 1914, 20, 204—219).—The author has made a number of experiments on the direct combination of hydrogen and oxygen to form hydrogen peroxide. A stream of electrolytic gas, at a pressure (146 mm.) just below that at which the gas will explode, is exposed to a high-tension discharge from aluminium electrodes and cooled by liquid air. A yield of hydrogen peroxide amounting to 17% of the theoretical quantity was obtained in the most favourable experiments. A mixture of hydrogen and oxygen containing quantities of oxygen up to 6% was subjected to a silent discharge in a Berthelot tube. Large quantities of hydrogen peroxide were produced in some cases, the yield being practically 100%. The best yield was obtained under the following conditions: (1) a current strength of 4.6 amperes on the primary of the induction coil; (2) a gas velocity of 400 c.c. per hour; (3) moist gases; (4) a concentration of 3.5% oxygen. Under these conditions at  $-80^{\circ}$  a yield of 99.9% of hydrogen peroxide was obtained, which was 99.9% pure, the residue being water. A series of experiments were made with electrolytic gas diluted with carbon dioxide; in this case a yield of only 4% hydrogen peroxide was obtained; this is explained by the decomposition of the carbon dioxide into carbon monoxide and oxygen, thus largely increasing the amount of oxygen, which is favourable to the formation of ozone. The formation of ozone acts disadvantageously to the hydrogen peroxide formation in two ways: (1) removal of the available oxygen, and (2) decomposition of any hydrogen peroxide which may have been formed. A number of experiments were made with oxygen-hydrogen mixtures in contact with heated wires of platinum, iron, copper, nickel, palladium, and aluminium. Hydrogen peroxide was only formed in those cases where a non-explosive gas containing excess of oxygen was employed, and in every case the yield was very small. J. F. S.

**Lower Limits of Combustible and Explosive Mixtures of Gases and Air.** E. E. SOMERMEIER (*J. Ind. Eng. Chem.*, 1914, 6, 191—198).—The author has collected the various data bearing on

the question of the explosive properties of gas mixtures, and submitted them to a critical examination, for details of which it will be necessary to consult the original paper. Knowing the heat of reaction and the ignition temperature, a method is given for calculating the lower limits of combustible and explosive mixtures of gas. The values obtained by calculation are lower than the actual values, but are useful in that they show the potentially explosive properties of a mixture, and any potentially explosive gas is to be regarded as dangerous.

T. S. P.

**Crude Nitrogen (Nitrogen plus Rare Gases) in Natural Gaseous Mixtures.** CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1914, 158, 839—842).—From a consideration of the analyses of the crude nitrogen fraction of natural gases in mines, thermal waters, or other sources which show these gases to contain the same relative proportions of nitrogen, argon, xenon, and krypton (compare A., 1910, ii, 136; 1911, ii, 392, 602, 1087, 1134), the authors draw the conclusion that the source of this crude nitrogen dates back to the nebulous epoch, any slight variations being accounted for by such processes as occlusion, diffusion, solution, etc., in more recent times.

W. G.

**The Active Modification of Nitrogen.** H. B. BAKER and R. J. STRUTT (*Ber.*, 1914, 47, 801—804).—The authors have repeated the experiments of Tiede and Domcke (this vol., ii, 122), but cannot confirm their results, in all cases obtaining an afterglow of the nitrogen when all the oxygen has been removed. That oxygen is not necessary for the formation of the afterglow is shown by the following: (1) by the action, sufficiently prolonged, of cold phosphorus, oxygen can be removed practically completely from nitrogen, which still gives the afterglow; (2) nitrogen obtained from potassium azoimide (compare Tiede and Domcke, *loc. cit.*) gives the afterglow, as also does nitrogen from which the oxygen has been removed by long contact with the liquid alloy of sodium and potassium; (3) active nitrogen gives hydrogen cyanide by interaction with hydrocarbons in the cold, a fact which cannot be explained by the presence of oxygen.

T. S. P.

**After-glow of Electric Discharge in Mixtures of Nitrogen with Oxygen.** R. J. STRUTT (*Physikal. Zeitsch.*, 1914, 15, 274—276).—In reference to recent criticism (compare Tiede and Domcke, this vol., ii, 122) of the author's work on active nitrogen, attention is drawn to the difference between the after-glow of pure nitrogen and of nitrogen mixed with oxygen. The earlier experiments on the after-glow effects in air (*Proc. Physical Soc.*, 1910, 23; 1911, 24) are again described.

H. M. D.

**The Electrochemical Oxidation of Ammonia.** G. OESTERHELD (*Zeitsch. anorg. Chem.*, 1914, 86, 105—142).—The intermediate stages in the electrolytic oxidation of ammonia have been investigated. Hitherto, only nitrogen, nitrite, and nitrate have been observed.

Using a saturated ammoniacal solution of ammonium carbonate as an electrolyte, the gases evolved at a platinum gauze anode may be washed, dried, and cooled by liquid air, when nitrous oxide condenses in the solid form. The proportion of nitrous oxide increases with the concentration of the ammonia. At low temperatures, chiefly gaseous products are formed, and as the temperature rises the quantity of nitrate increases. The influence of current density and concentration has also been determined. The results are explained by oxidation in stages, but it has not been found possible to isolate hydroxylamine. By determining the oxidation potentialities, the series hydroxylamine-hypoxynitrous acid-nitrous acid has been confirmed. The first attack on the ammonia molecule requires the highest potential, and only under determined conditions can the formation of ammonium nitrate as end-product be checked. Nitrogen is the product of secondary reactions between ammonia and nitrous acid, and between hydroxylamine and nitroxyl, the latter reaction being unimportant.

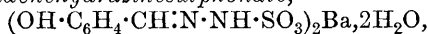
C. H. D.

**Hydrazinesulphonic and Azoimidesulphonic Acids.** WILHELM TRAUBE and O. VOCKERODT (*B.-r.*, 1914, **47**, 938—944. Compare Stollé and Hofmann, A., 1905, i, 28; Ephraim and Piotrowski, A., 1900, ii, 13).—Dry air is drawn slowly through a flask containing fuming sulphuric acid of high anhydride content, and then through a flask containing anhydrous hydrazine. Considerable quantities of hydrazine hydrazinesulphonate are thus formed, according to the equation  $2\text{N}_2\text{H}_4 + \text{SO}_3 = \text{H}_2\text{N} \cdot \text{NH} \cdot \text{SO}_3\text{H} \cdot \text{N}_2\text{H}_4$ . When the reaction product is dissolved in water, the solution heated with excess of barium hydroxide to expel non-combined hydrazine, the excess of barium precipitated with carbon dioxide, and the filtrate from the barium carbonate evaporated in a vacuum, *barium hydrazinesulphonate*,  $(\text{N}_2\text{H}_3 \cdot \text{SO}_3)_2\text{Ba} \cdot 2\text{H}_2\text{O}$ , is obtained; solution in water and precipitation with alcohol gives it in the form of glistening needles. The *calcium* salt,  $(\text{N}_2\text{H}_3 \cdot \text{SO}_3)_2\text{Ca} \cdot \text{H}_2\text{O}$ , is obtained similarly, as also the *strontium* salt,  $(\text{N}_2\text{H}_3 \cdot \text{SO}_3)_2\text{Sr} \cdot 2\text{H}_2\text{O}$ . From the barium salt and ammonium carbonate, *ammonium hydrazinesulphonate*,  $\text{N}_2\text{H}_3 \cdot \text{SO}_3\text{NH}_4$ , is formed as a deliquescent, crystalline mass; it is isomeric with hydrazine amido-sulphonate (Sabanév, A., 1900, ii, 13). Similarly, using potassium and sodium sulphate, the *potassium* salt,  $\text{N}_2\text{H}_3 \cdot \text{SO}_3\text{K}$ , and *sodium* salt,  $\text{N}_2\text{H}_3 \cdot \text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$ , were obtained, the former crystallising in needles and the latter in monoclinic tables.

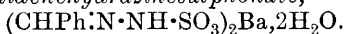
The above salts are stable in alkaline and neutral solutions, but are decomposed by acids into sulphuric acid and hydrazine. Ammoniacal silver nitrate is rapidly reduced, but from the barium salt and silver nitrate *silver hydrazinesulphonate*,  $\text{N}_2\text{H}_3 \cdot \text{SO}_3\text{Ag}$ , is obtained in beautiful, glistening needles. The free acid,  $\text{N}_2\text{H}_3 \cdot \text{SO}_3\text{H}$ , is obtained from the barium salt and sulphuric acid, and forms glistening needles, m. p.  $217^\circ$  (decomp.).

From the barium salt and aldehydes (salicylaldehyde and benz-

aldehyde) the following compounds are readily obtained: *barium hydroxybenzylidenehydrazinesulphonate*,



and *barium benzylidenehydrazinesulphonate*,



Ethylenediamine may be sulphonated in a similar manner to hydrazine; when the reaction product is treated to prepare the barium salt, however, the free acid, *ethylenediaminesulphonic acid*,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_3\text{H}$ , is obtained, obviously as an internal salt,  $\begin{array}{c} \text{CH}_2-\text{NH}-\text{SO}_2 \\ | \qquad \diagup \\ \text{CH}_2\cdot\text{N}\cdot\text{H}_2\cdot\text{O} \end{array}$ ; it forms colourless leaflets, and gives a neutral, aqueous solution.

Treatment of a strongly-cooled, concentrated aqueous solution of potassium nitrite with finely powdered hydrazinesulphonic acid gives rise to the reaction



From the resulting solution, by spontaneous evaporation, the *potassium azoimidesulphonate*,  $\text{N}_3\cdot\text{SO}_3\text{K}$ , is obtained pure by a lengthy process, and then crystallises in long, flat prisms, which explode on heating. The corresponding *sodium*, *ammonium*, and *barium* salts are obtained similarly.

T. S. P.

#### Raschig's Nitrogen Hexoxide and Nitrogen *iso*Tetroxide.

ERNST MÜLLER (*Zeitsch. anorg. Chem.*, 1914, **86**, 230—238. Compare A., 1912, ii, 753; Raschig, this vol., ii, 48).—A further criticism of Raschig's conclusions from his experiments. It is not legitimate to infer the composition of the liquid from that of the vapour, and a recalculation shows that the residual liquid cannot be  $\text{N}_2\text{O}_4$ .

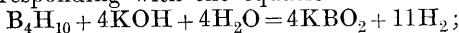
The green substance, assumed to be  $\text{NO}_3$ , is a mixture. The colour may be exactly imitated by dipping a test-tube containing liquid air in liquid nitrogen trioxide, and, after a frozen layer has been formed, in liquid nitrogen tetroxide. The two layers of blue and yellow give a green which is exactly like that of the supposed hexoxide.

C. H. D.

**Boron Hydrides. IV. Hypoborates Resulting from the Interaction of Boron Hydrides and Bases.** ALFRED STROCK and ERNST KUSS (*Ber.*, 1914, **47**, 810—826. Compare A., 1913, ii, 44, 699, 1053; Travers and Ray, A., 1912, ii, 938).—The boron hydrides,  $\text{B}_4\text{H}_{10}$  and  $\text{B}_2\text{H}_6$ , dissolve in aqueous sodium hydroxide, giving solutions which no longer smell of boron hydrides, but which gradually decompose, with evolution of hydrogen and the formation of borate. This decomposition takes place least readily with the hydride,  $\text{B}_4\text{H}_{10}$ , which was consequently used throughout these experiments. The solution first formed, which contains hypoborates, is stable towards oxygen, so that it can be exposed to the air.

By measuring the amount of the hydride dissolved when excess of it was brought into contact with a solution of alkali hydroxide,

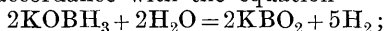
it was found that one mol. of the hydride  $B_4H_{10}$  enters into reaction with four mols. of a monacid and two mols. of a diacid base, in agreement with the equation  $B_4H_{10} + 4KOH = 4KOBH_3 + H_2$ . Solutions of the hypoborates thus formed are stable for hours at  $0^\circ$ , but on boiling they decompose rapidly, giving the amount of hydrogen corresponding with the equation



the solutions are the more stable the greater the excess of free alkali.

Using an apparatus which was specially designed for the purpose, the authors have been successful in isolating pure *potassium hypoborate*,  $KOBH_3$ . Ninety-five % potassium hydroxide was dissolved in one and a-half times its weight of water, and treated with excess of the hydride  $B_4H_{10}$  at  $0^\circ$ ; the solid hypoborate was then obtained as glistening, octahedral, colourless crystals by drying in a high vacuum. The reaction takes place quantitatively according to the equation already given, and the formula  $KOBH_3$  was proved by analysis.

Potassium hypoborate is stable in the absence of moisture; it is deliquescent, and the solutions gradually decompose at room temperature in accordance with the equation



acids, even acetic acid, immediately bring about the decomposition. It is soluble in alcohol with partial decomposition. The aqueous solution is a very strong reducing agent, stronger than potassium hypophosphite, giving precipitates with solutions of most salts, but insoluble hypoborates do not appear to exist. The most characteristic reactions are with solutions of copper and nickel salts, the former giving a precipitate of copper hydride, and the latter one of black, insoluble nickel boride,  $Ni_2B$ . The formation of a boride in this manner is exceptional, since they are generally obtained by the use of high temperatures. It is non-magnetic, but becomes magnetic on heating at  $600^\circ$ , at the same time sintering to a grey, metallic form.

*Sodium hypoborate*,  $NaOBH_3$ , was obtained similarly to the potassium salt, and possesses similar properties. Magnesium hypoborate could not be isolated from solution.

When potassium hypoborate is heated at  $500^\circ$ , metallic potassium, hydrogen, and water are expelled; the reaction is a complicated one, but may be expressed quantitatively by the equation  $5KOBH_3 = K_3B_5O_3 + 2K + 2H_2O + 11H$ . The residue,  $K_3B_5O_3$ , is somewhat hygroscopic, dissolves in water, giving an alkaline solution, which has only a weakly reducing action on permanganate, but gives a characteristic yellow to brownish-red colour when warmed with dilute or concentrated nitric acid. When treated with sulphuric acid, it gives hydrogen and boron hydrides. Its properties are to be further investigated. When magnesium boride, prepared by the interaction of boron trioxide and magnesium, or of borax and magnesium, is treated with water, a solution is obtained which has properties similar to that of the substance  $K_3B_5O_3$ .

T. S. P.

**The True Strength of Carbonic Acid.** A. THIEL and R. STROHECKER (*Ber.*, 1914, **47**, 945—953).—A solution of carbon dioxide in water contains, not only carbonic acid and its ions, but also carbon dioxide (compare Thiel, A., 1913, ii, 396). If the quantity of carbonic acid can be determined, the total quantity of dissolved carbon dioxide being known, the true dissociation constant of carbonic acid can be calculated, the dissociation constant, as ordinarily determined, being known. It has been shown previously (*loc. cit.*) that the carbonic acid actually in solution is immediately neutralised by a base, a slow reaction then taking place, due to the time reaction  $\text{CO}_2 + \text{OH}' \rightarrow \text{HCO}_3'$ . By means of a special arrangement, the authors have been able to arrange for the mixing of solutions of carbon dioxide and a base to be complete in 0.4 second, and by varying the quantity of the base it was possible to determine the quantity of carbonic acid present in the solutions taken, using phenolphthalein as indicator (compare *loc. cit.*). Sodium hydroxide gave anomalous results, owing to the carbon dioxide also entering into reaction, but satisfactory results were obtained with ammonium hydroxide at 4°. It was found that in a 0.00812-*M* solution of carbon dioxide at 4°, only 0.67% is present as carbonic acid. The ordinary dissociation constant of carbonic acid being taken as  $3 \times 10^{-7}$  at 4° (compare Walker and Cormack, T., 1900, **77**, 13), it follows that the true dissociation constant is  $5 \times 10^{-4}$ , that is, it is twice as strong as formic acid. Comparison of the dissociation constants of the hydroxy-substituted acids of the fatty acid series, carbonic acid being hydroxyformic acid, shows that this value is of the right order, qualitatively.

T. S. P.

**Condition of Silica in Diatomaceous Earths.** E. MANZELLA (*Ann. Chim. Applicata*, 1914, **1**, 222—231).—Treatment with sodium hydroxide solution is useless as a means of differentiating the various forms of amorphous and crystalline silica in material to be used for the production of cement, since successive extractions with the alkali solution result in the continued dissolution of the silica. The silica of diatomaceous earths, although in the amorphous condition, cannot be compared with that present in pozzuolane and hydraulic products, and it is difficult to explain, from the chemical point of view, the results of Poulsen (VIth Congress Internat. Ass. Testing Materials Construction, New York, 1912), who found that a mixture of calcined diatomaceous earth with Portland cement yielded a cement resistant to the action of sea-water.

T. H. P.

**Density and Atomic Weight of Neon.** A. LEDUC (*Compt. rend.*, 1914, **158**, 864—866).—Starting with a specimen of neon containing small quantities of helium and nitrogen, the author has carefully purified it by absorption with cocoanut charcoal at the temperature of liquid air, the helium then being pumped off, followed by fractional distillation, the neon distilling first. This operation was twice repeated. The density of neon as determined

on this specimen was 0.695 referred to air as unity, from which, by his formula (compare A., 1911, ii, 792), the author calculates the atomic weight of neon to be 20.15 ( $O=16$ ).

In the course of these experiments, the author has shown that the absorption of neon by charcoal obeys Henry's law. W. G.

**Preparation of Stable Reducing Agents which can be used in a Convenient Form, from easily Oxidisable Materials such as Sodium, Potassium, Calcium, Phosphorus, etc.** PAUL GOLDSTEIN (D.R.-P. 268657).—The substances mentioned in the title are mixed with porous materials, such as kieselguhr, and the mixture is heated at  $100^{\circ}$  in the absence of air or in an atmosphere of nitrogen. J. C. C.

**Isomorphism of Potassium and Rubidium Nitrates.** W. STORTENBEKER (*Rec. trav. chim.*, 1914, 33, 85—90. Compare Wallerant, A., 1905, ii, 237).—The author has examined a series of mixed crystals of potassium and rubidium nitrates obtained by concentration of the mixed aqueous solution at the ordinary temperature. Analyses of such crystals (effected indirectly by prolonged ignition with powdered quartz), density, and specific volume are tabulated.

The author is led to the conclusion that the two substances are isodimorphous, thus resembling the nitrates of potassium and thallium (Stortenbeker, A., 1905, ii, 390). H. W.

**The Heats of Formation and Some Other Properties of Alkali Protosulphides.** E. RENGADÉ and N. COSTEANU (*Compt. rend.*, 1914, 158, 946—948).—An examination of certain physical properties of the anhydrous alkali protosulphides as prepared by the method already described (compare A., 1913, ii, 405). Rubidium sulphide crystallises in regular octahedra. Potassium sulphide crystallises in an analogous form, but the crystals are very small. Cesium sulphide crystallises in long, colourless needles, exhibiting marked birefracton in the blue end of the spectrum, being isotropic in the red. The densities, determined at the laboratory temperature, were: sodium sulphide, 1.856; potassium sulphide, 1.805; rubidium sulphide, 2.912. The values for the heats of solution in water were: sodium sulphide, 15.5 Cal.; potassium sulphide, 22.7 Cal.; rubidium sulphide, 24.6 Cal.; which gave for the heats of formation: sodium sulphide, 89.7 Cal.; potassium sulphide, 87.1 Cal.; rubidium sulphide, 87.1 Cal. W. G.

**Specific Gravities and Coefficients of Dilatation of Solutions of Sodium Sulphate Saturated at Different Temperatures.** N. A. TSCHERNAJ (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 8—13).—The author has determined the weights and volumes of solutions formed by saturating 100 grams of water with sodium sulphate at various temperatures ranging from  $0^{\circ}$  to  $34^{\circ}$ . The weight of the dissolved salt being indicated by  $p$  and the volume of the solution by  $v$ , the values of  $dp/dv$  are: 25.0 at  $0-10^{\circ}$ , 4.8 at  $10-20^{\circ}$ , and 3.7 at



20—30°. For the decahydrated salt, the values of  $dp/dv$  are: 1.73 at 0—10°, 1.55 at 10—20°, and 1.50 at 20—30°. The coefficients of expansion of saturated sodium sulphate solutions at different temperatures have been calculated. T. H. P.

**Silicate Chemistry. I. Compounds of Lithium Oxide and Silica.** F. M. JAEGER and H. S. VAN KLOOSTER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 857—880. Compare Wallace, A., 1909, ii, 665; van Klooster, 1911, ii, 111).—The binary system  $\text{Li}_2\text{O}-\text{SiO}_2$  has been investigated in detail by observations of cooling curves and of the microscopic structure of the crystalline aggregates.

These observations indicate the formation of three compounds: the metasilicate,  $\text{Li}_2\text{SiO}_3$ ; the orthosilicate,  $\text{Li}_4\text{SiO}_4$ ; and the bisilicate,  $\text{Li}_2\text{Si}_2\text{O}_5$ . The metasilicate crystallises in long, opaque porcelain-like needles, which are biaxial, and probably monoclinic. It melts at 1201°,  $D^{25}_D$  2.520,  $n_D=1.609$  and 1.584 for vibrations parallel and perpendicular to the direction of elongation of the needles. By quenching, the metasilicate was obtained in the form of a glass,  $D^{25}_D$  2.330 and  $n_D=1.548$ . The trigonal form of the metasilicate described by Friedel (*Bull. Soc. Min.*, 1901, **24**, 147) could not be obtained, and from experiments carried out under the same conditions the authors conclude that the supposed trigonal form is merely a twin-formation of the original biaxial form imitating very closely a true trigonal individual.

The orthosilicate crystallises in thin, polygonal scales, melts at 1256°,  $D^{25}_D$  2.392,  $n_D=1.614$  and 1.594. Under the microscope, the crystalline aggregates, which approximate in gross composition to the orthosilicate, appear to have undergone some change, and it is suggested that this points to the temperature 1256° being a transition point rather than a true melting point.

The bisilicate crystallises from binary mixtures of the same composition in the form of large, flat tabular crystals. The crystals are biaxial,  $D^{25}_D$  2.454,  $n_D=1.545$  and 1.525. At 1032° it undergoes partial fusion, with the formation of a solid solution of the bisilicate in an excess of metasilicate.

The system is characterised by two eutectics,  $\alpha$ -tridymite + bisilicate in equilibrium with a mixture containing 37.7 mols. %  $\text{SiO}_2$  at 1022°, metasilicate + orthosilicate in equilibrium with a mixture containing 69.4 mols. %  $\text{SiO}_2$  at 1027°.

It has not been possible to determine the behaviour of the components at concentrations between the orthosilicate and pure lithium oxide because of the volatility of the lithium oxide at the crystallisation temperatures. Incidentally, it has been found that lithium oxide, when heated out of contact with the air so as to prevent the formation of peroxide, does not melt below 1625°. The action of the oxide on platinum at high temperatures is due to the formation of peroxide. H. M. D.

**Some Properties of Colloidal Silver Prepared by an Electrical Method.** S. H. LONG (*Kolloid. Zeitsch.*, 1914, **14**, 136—139).—The properties of colloidal silver have been examined, the sub-

stance being obtained by the high-frequency arc method described in a previous paper (Morris-Airey and Long, A., 1913, ii, 1033). Such solutions of colloidal silver are very stable, and can be concentrated by boiling without decomposition. The behaviour of the solutions under the influence of an electrical field shows that both positive and negative particles are present. When the field was allowed to act for a sufficiently long time, the cathode solution was found to have a deep red colour, whilst that of the anode solution was yellow. On slow evaporation of the two solutions, the anode liquid gave a brilliant deposit of metallic silver, whilst the cathode liquid gave a deposit of silver hydroxide.

The colour of the colloidal silver solutions depends on the size of the colloidal particles, the yellow solutions containing the smallest, and the blue solutions the largest, particles. During the process of coagulation, such as may be brought about by the addition of a small quantity of  $N/100$ -sodium hydroxide, the colour of the solution changes gradually in the order yellow, red, green, blue. The colour change is accompanied by a considerable increase in the electrical conductivity of the solution.

From a series of experiments in which the colloidal solutions were absorbed by filter paper and exposed to the action of ultra-violet light, it has been found that the more highly disperse solutions are particularly sensitive to the action of light rays.

H. M. D.

**Thermal Analysis of Binary Mixtures of Chlorides of Uni- and Bi-valent Elements.** CARLO SANDONNINI (*Gazzetta*, 1914, 44, i, 290—386).—The author gives a complete and connected account of his investigations in this direction during the past few years (A., 1911, ii, 606, 800, 984; 1912, ii, 47, 50, 160, 162, 350, 764, 918, 941, 1172; 1913, ii, 137, 588, 853, 965; this vol., ii, 204).

The following conclusions are drawn. The results obtained with pairs of chlorides of univalent elements are in complete accord with the regularities foreseen from the periodic system and with the isomorphous relations and the tendency to unite observed even at low temperatures. The inclination to form mixed crystals increases with rise of temperature. In general, the results given by pairs of chlorides of bivalent elements are in similar accord, but the relations are here less simple. The chlorides of the metals of the alkaline earths show but slight tendency to yield mixed crystals either with one another or with magnesium chloride. The singular relations exhibited by the alloys of magnesium, zinc, and cadmium are repeated with the chlorides of these metals, magnesium and cadmium chlorides showing pronounced analogy, whilst the behaviour of the intermediate zinc chloride is quite abnormal. In only four out of thirty-seven cases is there any tendency of pairs of chlorides of bivalent metals to combine. In certain cases, formation of solid solutions, sometimes in all proportions, occurs between a chloride of a univalent metal and one of a bivalent metal.

The results of Schaefer (this vol., ii, 204) and of Korreng (this vol., ii, 205) are discussed. T. H. P.

**Preparation of Metallic Strontium.** BERNHARD NEUMANN and EINAR BERGVE (*Zeitsch. Elektrochem.*, 1914, **20**, 187—188).—It is shown that a eutectic point for the binary mixture strontium chloride-potassium chloride occurs with the mixture containing 15% of potassium chloride; this mixture melts at 628°, which is 220° lower than the melting point of strontium chloride. The authors show that on electrolysing such a molten eutectic mixture by the method used in the manufacture of calcium, sticks of strontium 10 cm. long and 1—2 cm. diameter can be obtained. A current density of 20—50 amperes per sq. cm. cathode is required, and a current efficiency of 80% is obtained. Metallic barium has been obtained in a similar manner. J. F. S.

**Electrolysis of Barium Chloride Solutions with Mercury Cathodes.** P. P. FEDOTÉV and I. WEIZER (*Zeitsch. anorg. Chem.*, 1914, **86**, 325—337).—The electrolysis of barium chloride solutions differs from that of the alkali chlorides in the greater stability of barium amalgam towards water and in the lesser solubility of barium hydroxide. Using the Kellner form of apparatus, in which the electrolysis is performed in one vessel and the amalgam is transferred to a separate vessel for decomposition, the yield increases with the current density and with the rate of flow of mercury through the apparatus. A carbon anode cannot be used with high current densities. In the Solvay modification of this process, the rate of flow of the liquid diaphragm is the determining factor. The decomposition of the amalgam by water is greatly accelerated by the presence of iron.

The Castner process, in which the electrolysing and decomposing vessels are connected by the layer of mercury at the bottom, is less suitable, but on raising the temperature to 40°, the solubility of barium hydroxide is sufficiently increased. C. H. D.

**Application of the Laws of Transparency of Matter for X-Rays to Fixing Some Contested Atomic Weights. Case of Glucinum.** LOUIS BENOIST and HIPPOLYTE COPAUX (*Compt. rend.*, 1914, **158**, 859—860. Compare this vol., ii, 272).—A comparison of the transparency of glucinum oxide with the transparencies of aluminium, sulphur, carbon, lithium, and lithium hydroxide fixes the atomic weight of glucinum at 9.1. W. G.

**The Intercrystalline Cohesion of Metals. II.** WALTER ROSENHAIN and DONALD EWEN (*J. Inst. Metals*, 1913, **10**, 119—149. Compare A., 1913, ii, 119).—Experiments with lead, tin, aluminium, and bismuth confirm the view that the crystal grains of a metal are united by a thin layer of an amorphous cement. Cold lead elongates under tensile stress, the crystals being deformed, whilst at a temperature only 4° below the melting point the fracture is entirely intercrystalline, and the crystal grains are

not deformed. Tin and aluminium behave in a similar manner. Bismuth is not ductile, but the fracture of the cold metal takes place along the cleavage planes, and of the hot metal between the crystal grains. The eutectic alloy of lead and tin behaves like a pure metal. It is not possible to account for the results by the presence of impurities in the intercrystalline films. C. H. D.

**The Constitution of White Lead.** EDWIN EUSTON (*J. Ind. Eng. Chem.*, 1914, 6, 202—203).—Analyses of the precipitates formed by the action of carbon dioxide on a solution of basic lead acetate lead the author to the conclusion that white lead is a mixture in varying proportions of the two amorphous compounds  $\text{PbCO}_3$ ,  $\text{Pb(OH)}_2$  and  $\text{PbCO}_3$ , and is not  $2\text{PbCO}_3$ ,  $\text{Pb(OH)}_2$ , as is generally assumed. The precipitates produced are not appreciably soluble in a solution of sucrose, so that they cannot be mixtures simply of normal lead carbonate and lead hydroxide.

In stack white lead, some lead carbonate may be present in crystalline form, and occasionally some form of lead hydroxide is present, owing to abnormal conditions in the corroding stack.

T. S. P.

**Metallographical Researches on Egyptian Metal Antiquities.** H. GARLAND (*J. Inst. Metals*, 1913, 10, 329—343).—A copper knife of the 18th dynasty proved to have been made by cold hammering from impure cast copper containing 0.63% lead, 1.18% iron, 0.44% bismuth, 0.81% arsenic, as well as tin, nickel, and oxygen. The cored structure of the  $\alpha$ -crystals was still distinct, and disappeared on annealing. The cores were also present in other ancient copper and bronze objects. A copper dagger, probably of the 1st dynasty, contained 0.39% of arsenic and 0.08% of iron, and recrystallisation was confined to the areas rich in arsenic.

C. H. D.

**The Copper-rich Kalchoids (Copper-Tin-Zinc Alloys).** SAMUEL L. HOYT (*J. Inst. Metals*, 1913, 10, 235—274).—The ternary alloys within the limits of 50% of zinc and 30% of copper are quite similar to the binary alloys. The liquidus surfaces and the limits of saturation of the  $\alpha$ -phase, and the position of the eutectoid line, have been determined. The eutectoid surface has a maximum at  $590^\circ$ , corresponding with 66% Cu, 17% Sn, and 17% Zn. The  $\beta$ -solid solutions are isomorphous throughout, and may be obtained in a homogeneous condition by quenching from above the eutectoid surface. The resolution of  $\beta$  into  $\alpha$  and  $\gamma$  is facilitated by the presence of tin. A new thermal effect has been observed in the pure alloys of copper and tin at  $590^\circ$ , occurring within the  $\alpha$  and  $\beta$  range.

C. H. D.

**The Corrosion of Brass Tubes.** GUY D. BENGOUGH and RICHARD M. JONES (*J. Inst. Metals*, 1913, 10, 13—118).—Experiments are described dealing with the corrosion of brass, used in the form of tubes, by sea-water of various concentrations. The earliest visible sign is usually the formation of a layer of oxide, and the corrosion

is thus facilitated by access of oxygen. The corrosion increases with the concentration of the electrolyte. Contact with particles of carbon, metallic oxides, and other substances capable of acting as cathodes is without appreciable influence. At the ordinary temperature, both copper and zinc are removed, and the residual metal retains its original composition. At 40° and 50° dezincification takes place. The usual brass tubes contain 30% of zinc, but greater resistance to corrosion is obtained when a part of the zinc is replaced by 1% of tin or 2% of lead. C. H. D.

**The Micro-chemistry of Corrosion. I. Some Copper-Zinc Alloys.** CECIL H. DESCH and SAMUEL WHYTE (*J. Inst. Metals*, 1913, **10**, 304—328).—Small polished specimens of the alloys are submitted to electrolytic corrosion for short periods in contact with a 5% solution of sodium chloride, using a platinum cathode. The metals in the electrolyte, including the flocculent precipitate, are estimated separately from those in the adherent layer. With the  $\beta$ -alloys, zinc is almost completely removed, and the adherent, spongy layer contains as much as 99.6% of copper. There is a sharp boundary between the completely dezincified layer and the unaltered metal. The presence of iron in solid solution accelerates corrosion. Tin retards it, but the effect is mainly a mechanical one, the tin forming a very tough and adherent layer of oxychloride, which protects the underlying metal. C. H. D.

**Volume Changes in Alloys.** J. H. CHAMBERLAIN (*J. Inst. Metals*, 1913, **10**, 193—234).—Expansion is observed in the solidification and cooling of alloys of copper and aluminium, and the expansion-composition curve shows a distinct relation to the curve of crystallisation intervals. Alloys of copper and zinc containing the  $\delta$ -phase show a large expansion during the transformation into  $\epsilon$ -crystals. These alloys contract when slowly heated up to their melting points. Continued growth takes place on repeated heatings. The volume changes in aluminium are partly connected with the presence of dissolved gases. C. H. D.

**The Basic Carbonates of Copper.** V. AUGER (*Compt. rend.*, 1914, **158**, 944—946).—A study of the conditions of the formation of azurite from malachite and basic carbonates of copper. The amorphous basic carbonate  $8\text{CuO} \cdot 5\text{CO}_2 \cdot 7\text{H}_2\text{O}$  is converted into hydrated malachite in the presence of carbon dioxide under 40 atmos., but at higher pressures its transformation into azurite takes place, the time required varying from a few days to a few months, according to the pressure, but is considerably shortened if a certain amount of azurite is previously added to the system. Azurite can be rapidly prepared in quantity by the addition of small amounts of a soluble copper salt to a solution of sodium carbonate and hydrogen carbonate containing an excess of azurite in suspension. The double salt  $\text{CuCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , in the presence of a little water, furnishes in a few days, by the action of carbon dioxide under a pressure of 40 atmos., a mixture of

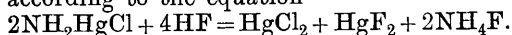
azurite and sodium hydrogen carbonate. The author suggests that the reaction  $\text{malachite} + \text{CO}_2 \rightleftharpoons \text{azurite} + \text{H}_2\text{O}$  is reversible, the action from right to left being extremely slow. W. G.

**Constitution of Hydrates. I. JAMES MACLEOD-BROWN** (*Chem. News*, 1914, 109, 123).—Two constitutional formulæ are suggested for copper sulphate pentahydrate. These formulæ are consistent with the fact that removal of water from the pentahydrate leads to the formation of trihydrate, and eventually monohydrate. The second formula, in which copper is represented as a quadrivalent element, is also in agreement with the fact that compounds are well known which may be regarded as derived from copper sulphate pentahydrate by substitution of four of the molecules of water by other molecular groups. H. M. D.

**Mercuric Oxide Jellies. E. H. BUNCE** (*J. Physical Chem.*, 1914, 18, 269—277).—The author has repeated the work of Emerson Reynolds (A., 1871, 561) on the formation of mercuric oxide gels in acetone-water solutions. The best method for preparing a strong solution of the acetone mercuric compound consists in dissolving 40 grams of mercuric chloride in 500 c.c. of hot water and 29 grams of potassium hydroxide in 300 c.c. of water. A solution of 20 c.c. of acetone in 250 c.c. of water is placed in a large flask, and 150 c.c. of the alkali solution added to it, then 250 c.c. of the mercuric chloride; this is shaken until all the mercuric oxide has dissolved; the residue of the alkali solution is then added, and finally the mercuric chloride. The solution thus obtained is turbid, and should be filtered and then dialysed. It is shown that the amount of mercuric chloride to be used may only be varied within narrow limits. Addition of potassium sulphate or sodium nitrate has no effect on the gelatinisation of the solution; potassium carbonate causes a thick, viscous liquid to be formed, and copper sulphate or cobalt nitrate brings about the formation of a granular precipitate. There is no precipitation of metallic mercury on a bright copper gauze immersed in the solution. The solution on keeping is transformed into a clear, transparent jelly, whilst a slight elevation of temperature brings this about much more rapidly. If the solution is kept at  $63^\circ$  for some minutes there is no gelatinisation. The jellies when heated with water break up and form a granular precipitate. When the jellies are heated with water to which a few drops of concentrated hydrochloric acid or nitric acid have been added, no jelly is formed, but a black, granular precipitate, which contains mercurous oxide, is formed. No jelly is formed when the solution is again made alkaline. Hydrogen sulphide precipitates mercuric sulphide from the solutions of the jellies. An *alcosol* can be formed by adding an equal volume of alcohol to a 1% aqueous solution and evaporating over lime. This liquid can be boiled without gelatinising, but if ebullition is continued for some time, a jelly is suddenly formed.

J. F. S.

**Constitution of "Infusible" White Precipitate.** HARIDAS SAHA and KUMUD NATH CHOUDHURY (*Zeitsch. anorg. Chem.*, 1914, **86**, 225—229).—Cold hydrofluoric acid reacts with infusible white precipitate according to the equation



Platinum chloride yields a yellow, crystalline precipitate with a dilute ammoniacal solution of the white compound, having the composition  $\text{NH}_2\text{HgCl}, \text{PtCl}_4$ . These reactions favour the view that the compound is  $\text{NH}_2\cdot\text{Hg}\cdot\text{Cl}$ , the chlorine being attached to mercury, and not to nitrogen.

C. H. D.

**Action of Ammonia on Mercurous Carbonate and Sulphate.** HARIDAS SAHA and KUMUD NATH CHOUDHURY (*Zeitsch. anorg. Chem.*, 1914, **86**, 239—240. Compare A., 1912, ii, 1174).—Ammonium hydroxide and mercurous carbonate yield an amorphous substance,  $(\text{NH}_2\text{Hg})_2\text{CO}_3, 3\text{HgO}, 5\text{H}_2\text{O}$ , and the sulphate yields a product,  $(\text{NH}_2\text{Hg})_2\text{SO}_4, 2\text{HgO}, 2\text{H}_2\text{O}$ .

C. H. D.

**Scandium.** IV. R. J. MEYER [and, in part, ALEXANDER WASSJUCHNOV, NELLY DRAPIER, and EMMA BODLÄNDER] (*Zeitsch. anorg. Chem.*, 1914, **86**, 257—290. Compare A., 1909, ii, 45; 1910, ii, 853; 1912, ii, 768).—Largely a recapitulation and summary of previous work on scandium. Some new compounds are also described.

Solutions of scandium chloride are considerably hydrolysed. The alkali chlorides do not form double salts with it, with the exception of caesium chloride, which yields a very soluble double salt. Caesium chloride yields highly crystalline compounds with the other rare earths; thus the *praseodymium* salt,  $\text{Cs}_3\text{PrCl}_6, 5\text{H}_2\text{O}$ , forms large, green crystals. The *neodymium*,  $\text{Cs}_3\text{NdCl}_6, 5\text{H}_2\text{O}$ , and *samarium*,  $\text{Cs}_3\text{SmCl}_6, 5\text{H}_2\text{O}$ , salts also form very large crystals. The *lanthanum* salt,  $\text{Cs}_3\text{LaCl}_6, 4\text{H}_2\text{O}$  (?  $5\text{H}_2\text{O}$ ), forms small, opaque crystals, which are apparently not isomorphous with the other salts.

Scandium fluoride dissolves in solutions of alkali fluorides. *Scandium ammonium fluoride*,  $(\text{NH}_4)_3\text{ScF}_6$ , forms large, transparent crystals, and its solution is not precipitated even by boiling with ammonia. The *potassium* salt,  $\text{K}_3\text{ScF}_6$ , crystallises well, is less soluble in water, and is less complex in solution. The *sodium* salt,  $\text{Na}_3\text{ScF}_6$ , crystallises with difficulty.

The solutions of scandium sulphate,  $\text{Sc}_2(\text{SO}_4)_3, 6\text{H}_2\text{O}$ , are shown to be largely complex. This is confirmed by migration experiments, more than half of the scandium travelling towards the anode. The solubility of scandium potassium sulphate,  $\text{K}_3[\text{Sc}(\text{SO}_4)_3]$ , has been determined. The *ammonium* salt is anhydrous; the *sodium* salt contains  $5\text{H}_2\text{O}$ . When the solution of the ammonium salt with an excess of ammonium sulphate is evaporated or boiled, a second salt is obtained as sparingly soluble leaflets,  $(\text{NH}_4)_4\text{Sc}_2(\text{SO}_4)_5$ .

*Scandium sulphite*,  $\text{Sc}_2(\text{SO}_3)_3, 6\text{H}_2\text{O}$ , is very sparingly soluble. An anhydrous sulphite was obtained by Crookes. Sodium and

potassium sulphites do not form complex salts, but *ammonium scandium sulphite*,  $\text{Sc}_2(\text{SO}_3)_3 \cdot (\text{NH}_4)_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , may be obtained in a crystalline condition by evaporation in an atmosphere of sulphur dioxide. The *thiosulphate* has only been obtained in a basic form,  $\text{Sc}(\text{OH})\text{S}_2\text{O}_3$ . Other salts prepared by Crookes have been re-examined. The solubility of scandium oxalate in sulphuric and hydrochloric acids of varying concentrations at  $25^\circ$  and  $50^\circ$  has been determined.

*Potassium scandium oxalate*,  $\text{KSc}(\text{C}_2\text{O}_4)_2$ , and the *sodium salt*,  $\text{NaSc}(\text{C}_2\text{O}_4)_2$ , are sparingly soluble, whilst the *ammonium salt*,  $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 4(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$ , is readily soluble, and is not resolved by boiling with water.

C. H. D.

**The Separation of Yttrium from the Yttrium Earths.** H. C. HOLDEN and C. JAMES (*J. Amer. Chem. Soc.*, 1914, **36**, 638—646).—The authors have investigated various fractional precipitation methods in order to find the best method for the separation of yttrium from the yttrium earths. The methods used were fractional precipitation of the dimethyl phosphates, the cacodylates, the phosphates, the monomethyl phosphates, the arsenates, the phosphites, the chromates, the iodates, and the bromates, and also fractional precipitation by means of hypophosphorous acid. The chromate and phosphate methods gave the greatest efficiency.

T. S. P.

**The Double Sulphates of Samarium with Sodium and Ammonium.** D. B. KEYES and C. JAMES (*J. Amer. Chem. Soc.*, 1914, **36**, 634—638).—The following *double sulphates* have been isolated, the various systems being studied by determining the mutual solubilities of the salts at  $25^\circ$ :  $2\text{Sa}_2(\text{SO}_4)_3 \cdot 3\text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sa}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  (compare Cleve, A., 1885, 636).

T. S. P.

**Physico-chemical Researches on the Electrometallurgy of Aluminium.** PAUL PASCAL and A. JOUNIAUX (*Bull. Soc. chim.*, 1914, [iv], **15**, 312—321. Compare A., 1913, ii, 508; Fedotéev and Iljinski, A., 1913, ii, 324).—A study of the variations with temperature of the densities of aluminium, cryolite, mixtures of cryolite and silica, cryolite and fluorspar, and cryolite fluorspar and alumina. The density of molten aluminium steadily diminishes with the temperature, the curve of variation being a straight line. Cryolite undergoes very considerable expansion on melting, and for the molten substance there is a maximum density a few degrees above the melting point. The presence of small amounts (3%) of silica notably lowers the density of fused cryolite, whilst the presence of fluorspar, on the other hand, causes an increase in the density, the maximum density of the binary mixture increasing regularly with the amount of fluorine present. The presence of alumina produces a marked diminution in the density of cryolite, and also a lowering in the temperature of maximum density. For the ternary mixtures of cryolite, alumina and fluorspar, within the limits commonly employed in the manufacture of aluminium, the



maximum density of the molten mass at the temperature used, is always less than that of molten aluminium at the same temperature; thus the metal sinks and collects at the cathode. Rise in temperature or increase in the percentage of fluorspar tends to bring the maximum density nearer the density of aluminium, and favours the formation of a "cloud" of aluminium in the bath.

W. G.

#### Preparation and Properties of Manganous Arsenate Jellies.

EUGEN DEISS (*Kolloid. Zeitsch.*, 1914, 14, 139—146).—If concentrated solutions of manganous chloride and potassium dihydrogen arsenate are mixed together at the ordinary temperature, a solid jelly is formed. Suitable conditions for the formation of the jelly are obtained if a 0.5 molar solution of manganous chloride is diluted with an equal volume of water and rapidly mixed with one to ten volumes of a 0.5 molar solution of the arsenate. The jellies prepared in this way are very stable, and can usually be kept for weeks without appreciable change. Sooner or later, however, rose-coloured crystals begin to separate, and this process is accompanied by a partial liquefaction of the jelly. The crystallisation process is accelerated by rise of temperature, but is retarded by the use of excess of arsenate solution in the preparation of the jelly. The analytical data indicate that the essential constituent of the jelly is the secondary arsenate,  $\text{MnHAsO}_4$ , and that the crystals which separate out correspond with the formula  $\text{MnHAsO}_4 \cdot \text{H}_2\text{O}$ .

Other observations have reference to the influence of the relative quantities of manganous chloride, potassium dihydrogen arsenate, and water on the rate of formation and properties of the jelly, and on the yield of the crystalline secondary arsenate. H. M. D.

**The Embrittlement of Iron by Sodium Hydroxide.** J. H. ANDREW (*Trans. Faraday Soc.*, 1914, 9, 316—329).—Wrought iron and electrolytic iron are rendered highly brittle by concentrated solutions of sodium hydroxide at 100°. Steel containing 0.5% C is much less affected. A polished surface is much less corroded at first than an unpolished surface, but as the outer layer is removed the actions become nearly equal. Hydrogen is evolved, and iron passes into solution. The brittleness appears to be caused by the diffusion of hydrogen between the crystals. Should an amorphous, intercrystalline cement be present, as assumed by Rosenhain, this would permit the diffusion of hydrogen more readily than the crystalline metal, and the expansion due to the absorption of hydrogen would loosen the crystals and cause brittleness. Iron originally saturated with hydrogen corrodes at a slower rate. Iron in tension is much more affected than iron in compression. C. H. D.

**Some of the Ternary Alloys of Iron, Carbon, and Phosphorus** J. E. STEAD (*J. Soc. Chem. Ind.*, 1914, 33, 173—184).—After a summary of the results hitherto obtained in the investiga-

tion of iron-carbon and iron-phosphorus alloys, the author deals with a few of the triple alloys, iron-carbon-phosphorus. The changes which occur during solidification, re-heating, and slow cooling are described by the aid of numerous photomicrographs, which it is necessary to refer to in order to understand the results obtained. The order of crystallisation when white and grey phosphoretted pig-irons solidify and cool down has been traced. Reference is also made to a mass of metal found in the hearth of a blast furnace at Skinningrove, which had crystallised in columnar form resembling the basaltic formation of the Giant's Causeway; it was nearly free from phosphorus, practically the whole of the ternary eutectic having been squeezed out of it by circumferential pressure during the time it was solidifying. T. S. P.

**Equilibrium of Carburation of Steels in Molten Mixtures of Potassium Cyanide and Chloride.** A. PORTEVIN (*Compt. rend.*, 1914, 158, 1025—1027).—On heating a piece of steel and a piece of iron side by side in a bath of molten potassium chloride and cyanide, the steel undergoes superficial decarburation and the iron carburation, both tending towards the same carbon content, which after five hours' heating at  $900^{\circ}$  is 0.25% for the steel and 0.26% for the iron. These values are apparently independent of the amount of potassium cyanide added to the potassium chloride. W. G.

**Iron Nitride.** G. CHARPY and S. BONNEROT (*Compt. rend.*, 1914, 158, 994—996).—The nitride of iron,  $\text{Fe}_2\text{N}$ , can be obtained by heating a fragment of iron or steel in a current of ammonia gas at a red heat, the nitride peeling off in thin flakes. The formation of the nitride proceeds most rapidly at  $650\text{--}700^{\circ}$  with a rapid current of ammonia. If the metal contains carbon, this combines with nitrogen, and is removed. The reduction of the nitride by hydrogen commences at  $350^{\circ}$ , and the velocity of the reaction increases rapidly with rise in temperature, being very rapid at  $600^{\circ}$ . The nitride heated in nitrogen at the atmospheric pressure begins to decompose at  $550^{\circ}$ , and this takes place even under a pressure of 18 atmos. at  $600\text{--}800^{\circ}$ . Under the same conditions of temperature reduced iron does not absorb nitrogen when heated in an atmosphere of this gas. W. G.

**Ferrous and Chromous Metaphosphates.** A. COLANI (*Compt. rend.*, 1914, 158, 794—796. Compare Lüdert, *Zeitsch. anorg. Chem.*, 1894, 5, 37).—The author has obtained anhydrous ferrous metaphosphate,  $\text{Fe}(\text{PO}_3)_2$ , in the form of a white powder by the action of fused metaphosphoric acid on metallic iron or on ferrous chloride or oxalate, or, best of all, ferrous phosphate, in a gold, Rose crucible in an atmosphere of carbon dioxide, in the manner already described for molybdenum metaphosphate (compare this vol., ii, 280). The substance so obtained is insoluble in hydrochloric or nitric acid, but is attacked by hot concentrated sulphuric acid.

All attempts to prepare chromous metaphosphate by a similar method were unsuccessful. W. G.

**Cobalt-Magnesium Red.** J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1914, **86**, 296—300).—A red substance, mentioned by Berzelius, is obtained in similar manner to Rinman's green (this vol., ii, 133) when magnesia is substituted for zinc oxide.

When magnesia and cobalt oxide are heated together with potassium chloride, products are obtained which vary in colour from light to dark red, according to the composition. The crystals are very minute octahedra and cubo-octahedra. Boiling water decomposes them, so that the potassium chloride must be removed by means of 30% alcohol. Between 38 and 79% CoO the product consists of homogeneous crystals, and it is possible that complete miscibility exists throughout the series. C. H. D.

**Experiment on the Colours of Some Cobalt Salts in Solution.** J. E. MARSH (*Chem. News*, 1914, **109**, 171).—A solution of sodium chloride (1 part by weight) and cobalt chloride (2 parts) in a mixture of water (8·7 parts) and acetone (7·7 parts), which is pink when cold, separates on warming into two solutions, the upper one being light blue in colour and the lower dark blue. The upper layer is expelled gradually, and the lower layer changes its colour gradually as the temperature is raised. The solutions will mix again on cooling to the original homogeneous pink solution; when cooled without mixing, the upper layer fades to an almost colourless solution, which becomes blue again on warming, while the lower layer changes in colour from blue to pink.

The concentrations of the solution, which should be contained in a sealed tube and heated by placing in hot water, may be varied within certain limits. Lithium chloride may be used instead of sodium chloride; potassium and cobalt bromides also give similar results. Cobalt chloride alone, without the sodium chloride, will bring about the separation in much the same way, but a higher temperature is required. T. S. P.

**Chromous Oxide.** TH. DIECKMANN and O. HANF (*Zeitsch. anorg. Chem.*, 1914, **86**, 301—304).—Chromous oxide is most conveniently prepared by the action of dilute nitric acid on chromium amalgam. Only mercury is dissolved, and the oxide CrO is obtained as a black powder. The properties agree with those observed by Féréé (A., 1901, ii, 513). Carbon monoxide at 1000° converts it into a mixture of oxide and carbide, whilst hydrogen at 1000° reduces it to metal. C. H. D.

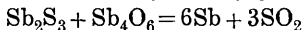
**The Absorption of the Carbonic Acid of the Air by Chromium Hydroxide.** MIL. Z. JOVITSCHITSCH (*Compt. rend.*, 1914, **158**, 872—874).—Chromium hydroxide carefully prepared, free from all traces of alkalis and ammonia, absorbs carbon dioxide from the atmosphere until the saturation limit is reached. Analyses of the compound obtained lead the author to ascribe to it the formula  $\text{CO}_3[\text{Cr}_2(\text{OH})_5]_2 \cdot 8\text{H}_2\text{O}$ , and show that it can be dried at 100° without losing its carbon dioxide, which is, however, liberated by acids. W. G.

**Some Arsenides and Phosphides of Chromium.** TH. DIECKMANN and O. HANF (*Zeitsch. anorg. Chem.*, 1914, **86**, 291—295).—When finely divided chromium, prepared from the amalgam, is heated with an excess of arsenic at 700° in a sealed exhausted tube, the product powdered and again heated, a product is obtained the composition of which is not altered by prolonged heating in hydrogen at 400°. This is a grey *arsenide*,  $\text{Cr}_2\text{As}_3$ ,  $D_4^{22}$  6.2. When heated in hydrogen at 480—500°, a second *arsenide*,  $\text{CrAs}$ , is obtained,  $D_4^{16}$  6.35. Both compounds are insoluble in acids.

When chromium and red phosphorus are used, the *phosphide*  $\text{Cr}_2\text{P}_3$  is obtained, yielding  $\text{CrP}$  on heating at 440° in hydrogen. Both phosphides are grey, and insoluble in acids. C. H. D.

**Oxygen and Metallic Antimony in Crude Antimony.** W. R. SCHOELLER (*J. Soc. Chem. Ind.*, 1914, **33**, 169—170).—In a previous paper (A., 1913, ii, 415) the author has shown that the percentage of sulphur in crude antimony from Hu-nan is much lower than that corresponding with the formula  $\text{Sb}_2\text{S}_3$ . The results of the complete analysis also gave a more or less considerable deficit, which was assumed to be due to the presence of oxygen. This assumption has now been proved to be correct, and the percentage of oxygen has been estimated by fusing the material in a current of dry hydrogen sulphide, and weighing the water formed. The complete analyses also indicated the presence of metallic antimony in the crude, and this was confirmed by experiment.

The presence of oxygen is due to oxidation occurring during the process of liquation, as carried out in China. The content of metallic antimony would indicate that the reaction



takes place to a limited extent, although this is usually stated not to be the case. T. S. P.

**Reduction of Quilquevalent Columbium.** ARTHUR STÄHLER (*Ber.*, 1914, **47**, 841—843).—The electrolytic reduction of a hydrochloric acid solution of columbium pentachloride was carried out by the method used for compounds of titanium and vanadium (compare Stähler and Wirthwein, A., 1905, ii, 40, 41, 595), but the results were altogether different (compare Ott, A., 1912, ii, 771); neither a chloride nor a sulphate of tervalent columbium could be obtained. The brown solution by reduction at amalgamated lead cathodes gives reactions similar to those of tervalent titanium (*loc. cit.*).

When columbic acid is dissolved in concentrated sulphuric acid, the solution diluted, and then reduced with zinc, an indigo-blue solution is obtained which reduces a solution of copper sulphate to metallic copper; the solution is thus more strongly reducing than one containing tervalent titanium.

Reduction of a solution of columbium pentachloride at a platinum cathode gives a blue solution, which is of a colloidal character; with gold chloride it gives a magnificent purple liquid, from which, on boiling, a purple precipitate deposits. This pre-

cipitate is similar to Purple of Cassius; it colours glass a violet-red.

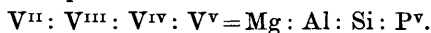
The results show that the lower oxidation stages of columbium, as far as salt-forming power is concerned, are more similar to the elements of the sixth group than to titanium and vanadium.

T. S. P.

**The Annealing of Gold.** THOMAS KIRKE ROSE (*J. Inst. Metals*, 1913, **10**, 150—174).—Impurities raise the temperature at which hard-worked gold is annealed, hydrogen having the greatest effect. Copper has a greater effect than silver. The hardness test, after heating at 150° for thirty minutes, may be used as a test for the purity of gold, one or two parts of impurity in 100,000 being detected in this way. The mechanism of recrystallisation is described.

C. H. D.

**Systematic Chemistry: Ruthenium, Rhodium, and Palladium.** G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 334—340).—The periodic classification does not indicate the fact that heterologous elements may give perfectly analogous compounds when in the same form of combination below their highest valency. This similarity is made obvious if the compounds of an element in which it has different valencies are regarded as belonging to so many different elements. For instance, the compounds of vanadium, in its different valencies, resemble those of magnesium, aluminium, silicon, and (quintivalent) phosphorus, a fact which the author expresses as follows:



Other instances are also given. In this paper the author records the results of experiments on the preparation of compounds of ruthenium, rhodium, and palladium, having for their object the preparation of analogous compounds.

Tervalent ruthenium forms with acetylacetone a red, crystalline compound,  $\text{Ru}(\text{C}_5\text{H}_7\text{O}_2)_3$ , which is unimolecular in bromoform, and is soluble in the solid state in aluminium acetylacetonate.

Rhodium forms rhodimolybdates, which are chemically and crystallographically analogous to the corresponding complex molybdates of Al,  $\text{Fe}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ , and  $\text{Co}^{\text{III}}$ . Ammonium rhodimolybdate,  $3(\text{NH}_4)_2\text{Rh}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$ , forms minute, yellow laminae, and potassium rhodimolybdate is of similar appearance and composition.

Bivalent palladium gives an acetylacetonate,  $\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$ , a canary-yellow, crystalline substance which is unimolecular in bromoform, and forms mixed crystals with cupric acetylacetonate.

R. V. S.

## Mineralogical Chemistry.

**Posthumous Transformations in the Stassfurt Salt Deposits.** M. RÓZSA (*Zeitsch. anorg. Chem.*, 1914, **86**, 163—168. Compare A., 1913, ii, 231).—Tables of the thickness of the layers are given. The principal changes which have taken place in the deposits are those of kieserite and rock salt into vanthoffite and loewite, and of carnallite into sylvite. The vanthoffite crystals are almost pure. The transformation products in the hard salt zone are in accordance with the results obtained by van't Hoff at elevated temperatures. These salts are not primary products of crystallisation. The rock salt is a transformation product of the kieserite transition layer, and the hard salt a transformation product of the kieseritic halite-carnallite.

C. H. D.

**The Minervites.** ARMAND GAUTIER (*Compt. rend.*, 1914, **158**, 912—920).—The author has analysed a sample of minervite taken from the grotto of Minerva (Hérault), and has compared its composition with that of minervites of other and known sources (compare Lacroix, *Min. France et Colonies*, **4**, 466). Expressing the various alkalis and ammonia as  $K_2O$ , and ferric oxide as  $Al_2O_3$ , he assigns the formula

$(Al_2O_3, P_2O_5, 7H_2O)_7, (2K_2O, P_2O_5, H_2O)(K_2O, P_2O_5, 2H_2O), H_2O$   
to his minervite, and the formula

$(Al_2O_3, P_2O_5, 7H_2O)_6, (2K_2O, P_2O_5, H_2O)$   
to that of Réunion and Misserghin, and the formula

$(Al_2O_3, P_2O_5, 7H_2O)_4, (2K_2O, P_2O_5, H_2O), 2H_2O$   
to the palmerite and minervite of Mount Alburno. In all of these minerals the analyses indicate the existence of mono- and di-hydrogen phosphates in the complexes. These minerals in the form of powder, although containing 10% or more of alkali phosphate, can be boiled with water without losing more than a trace of their alkali. The minervites are soluble in ammonium citrate, and should form excellent phosphatic manures.

W. G.

**Monazites from Some New Localities.** SYDNEY J. JOHNSTONE (*J. Soc. Chem. Ind.*, 1914, **33**, 55—59).—The method of analysis used by the author has been tested over a period of five years. The principles of the method are as follows: 1—2 grams of the finely powdered monazite is taken into solution by digestion with concentrated sulphuric acid; the silica in the residue is estimated by evaporation with hydrofluoric and sulphuric acids, and any residue remaining is examined separately for bases. In the filtrate the total rare earths are estimated by twice precipitating as oxalates and ignition to oxides; the solution remaining after collecting the precipitates is examined for further traces of rare earths. The filtrate from the oxalate precipitates is treated by Glaser's method

(A., 1897, ii, 190, 349) for the estimation of iron, aluminium, calcium, and phosphoric acid. The thorium in the total rare earths is estimated by means of a slight modification of the thiosulphate method of Fresenius and Hintz (A., 1896, ii, 677). The total thiosulphate filtrates are evaporated to a small bulk, and the thiosulphate destroyed by nitric acid, after which the solution is evaporated to dryness, the residue dissolved in hydrochloric acid, and the remaining rare earth precipitated as oxalates. The collected and washed oxalates are ignited, transformed into chlorides, and the cerium and lanthanum earth precipitated as the double sulphates with potassium sulphate; the yttrium earths remaining in solution are precipitated with ammonia, the precipitate redissolved in hydrochloric acid, and the earths precipitated as oxalates and weighed as oxides. The ceria is separated from the lanthana, etc., by a slight modification of Mosander's chlorine method (*J. pr. Chem.*, 1843, **30**, 276).

Analyses are given of nineteen different monazites from Ceylon, Travancore, the Malay States, Nyassaland, Nigeria, and Brazil, as also of four monazites from the United States, Canada, Australia, and S. Norway for comparison. The results obtained do not support either Penfield's (A., 1883, 162; 1889, 356) or Kress and Metzger's theory (A., 1909, ii, 588) as to the constitution of monazite.

T. S. P.

**Meerschaum from Grant Co. in New Mexico.** H. MICHEL (*Kolloid. Zentsch.*, 1914, **14**, 146—149).—In a previous paper (A., 1913, ii, 518) it was shown that meerschaum consists of an intimate mixture of a definite crystalline silicate and a gel. A sample of meerschaum from the Dorsey Mine in New Mexico has been examined in a similar way, and found to contain the same components, although the proportion of the crystalline constituent is much larger than in the mineral from Asia Minor. The chemical and physical properties of the mineral indicate that the crystalline constituent is an  $\alpha$ -sepiolite corresponding with the formula  $2\text{MgO} \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ , in which two of the molecules of water behave like the water in zeolites.

H. M. D.

**Composition of the Syenite from the Plauenschen Grund, Dresden.** RICHARD NACKEN (*Centr. Min.*, 1914, 183—185).—New analyses of this well-known rock agree closely with those given by H. S. Washington in 1906.

L. J. S.

**Physico-chemical Principles of Rock Metamorphism.** JOHN JOHNSTON and PAUL NIGGLI (*J. Geology, Chicago*, 1913, **21**, 481—516, 588—624); PAUL NIGGLI and JOHN JOHNSTON (*Jahrb. Min., 1914, Beil.-Bd.*, **37**, 495—575).—The second paper is a translation of the first, with some modifications. In an attempt to apply the principles of physical chemistry to geological problems, the authors discuss at length the effects of temperature and pressure (both uniform pressure and variable stresses) on solid and on solid-fluid systems, the application of the phase rule to such systems, etc.

L. J. S.

**A Meteoric Iron from Winburg, Orange Free State.** W. A. DOUGLAS RUDGE (*Proc. Roy. Soc.*, 1914, **A**, **90**, 19—25).—An account is given of the composition, internal structure, mechanical and magnetic properties of a meteorite, weighing nearly 50 kilograms, which was seen to fall in 1881.

The observations show that the meteorite consists of a mass of ferrite crystals with veins of iron nickel alloy running through, and with flakes and crystals of the alloy disseminated through the mass. It contains 92·54% of iron, 90·67% of which is soluble in dilute sulphuric acid, 6·905% of nickel, and 0·555% of carbon and other substances. After digesting in 1*N*-sulphuric acid for three days, a residue was obtained which consisted of a mixture of iron nickel alloy and carbon. The alloy was separated by means of a magnet, and found to contain 29·57% of nickel. The mechanical strength of the meteorite is not so great as that of ordinary iron, although its elastic modulus is nearly as large before rupture occurs. The magnetic properties are practically identical with those of Swedish iron. H. M. D.

**Manganese in Some Springs in the Vosges Mountains.** F. JADIN and A. ASTRUC (*Compt. rend.*, 1914, **158**, 903—905 Compare A., 1913, ii, 870).—The results of the examination of the waters from twenty-five springs in seven places in the Vosges Mountains for manganese are given. The mineral waters of this region do not all have the same manganese content, those of Luxeuil, rich in sodium and sulphates, and those of Bussang, rich in mixed carbonates, being the richest in manganese. The manganese content varies with different springs in the same town, and appears to be related to the amount of iron present in the water. W. G.

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### Analytical Chemistry.

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**The Ives Replica Diffraction Grating in Spectroscopic Analysis.** GORDON J. SAXON (*J. Biol. Chem.*, 1914, 17, 103—106).—This apparatus is recommended for the examination of absorption spectra; it is more sensitive than the ordinary spectroscope provided the column of fluid is a long one. W. D. H.

**Electrolytic Rectifier and its Application to Analysis by Electrolysis.** R. BELASIO (*Ann. Chim. Applicata*, 1914, 1, 114—121).—The author has devised a form of electrolytic rectifier, arranged conveniently for obtaining the small current densities used in electrolytic analysis. Some of the results obtained when this apparatus was employed for the estimation of metals are as follows: copper in nitric-sulphuric acid solution, 0.7186 instead of 0.7185

gram; tin in presence of oxalic and hydrochloric acids, 0.5104 instead of 0.5108 gram; iron in ammonium oxalate solution, 0.1442 instead of 0.1440 gram; copper and nickel in nitric acid solution: copper, 0.7465 instead of 0.7464 gram, and nickel, 0.1186 instead of 0.1184 gram; copper and zinc in sulphuric acid solution: copper, 0.2765 instead of 0.2764 gram, and zinc, 0.2471 instead of 0.2468 gram.

T. H. P.

**The Estimation of Chlorine in Blood-serum.** S. GUTMAN and F. SCHLESINGER (*Biochem. Zeitsch.*, 1914, **60**, 283—285).—The authors show that the wet-ashing method of von Bogdany, in which the organic matter is destroyed by a mixture of fuming sulphuric acid, sulphuric acid, and copper and potassium sulphates, yields results which are too low, owing chiefly to the oxidation of hydrochloric acid to chlorine. To destroy the organic matter in serum, they heat 10 c.c. of the material with 0.5 gram of sodium carbonate, and moisten the charred mass from time to time with water.

S. B. S.

**[Bromides. VII] Detection of Gases and Vapours Containing Bromine.** I. GUARESCHI (*Atti R. Accad. Sci. Torino*, 1914, **49**, 401—414. Compare this vol., ii, 214).—When air containing traces of bromine (either in the free state or as vapour of a large number of bromine compounds) is passed over hot chromic acid, the presence of bromine can be detected by means of paper impregnated with the decolorised magenta solution already described. The reaction is very sensitive, and can be employed even when a large excess of chlorine or iodine is present. Volatile bromine compounds can be detected in such products as animal tissues and fluids in the same way, air being passed through the material or through a suspension of it in water. The method is therefore capable of application in cases of poisoning by anæsthetics containing bromine.

R. V. S.

**Use of Telluric Acid in the Estimation of Bromine Associated with Chlorine in Haloid Salts.** F. A. GOOCH and H. ISABELLE COLE (*Amer. J. Sci.*, 1914, [iv], **37**, 257—262).—About 0.5 gram of the haloid mixture is introduced into a Voit distillation flask with 1 gram of telluric acid and water up to 40 c.c. Ten c.c. of dilute sulphuric acid (1:1) are added through the separating funnel, and the whole distilled in a slow current of carbon dioxide. The bromine liberated is collected in a receiver (with trap) containing 300 c.c. of a 1% solution of potassium iodide. When about 18 c.c. have passed over, the flask is disconnected, and the iodine set free by the bromine titrated with standard sodium thiosulphate.

L. DE K.

**Sources of Error in Iodometry.** A. LECLÈRE (*J. Pharm. Chim.*, 1914, [vii], **9**, 341—345).—There is a very considerable error in titrating solutions of iodine with sodium thiosulphate in the presence of alkaline substances such as sodium or potassium

hydrogen carbonates, borax, or disodium hydrogen phosphate, the error varying from 7 to 55%. It is reduced by adding the iodine solution to the thiosulphate. Temperature and the rate of titration also have an effect on the result in the presence of these substances. The satisfactory method of performing the titration is as follows. A known volume of the iodine solution is decolourised with excess of sodium thiosulphate, and its alkalinity determined by means of *N*/10-sulphuric acid, methyl-orange being the indicator. To a fresh portion of the iodine solution add the calculated quantity of *N*/10-sulphuric acid for neutralisation, and then titrate with the standard sodium thiosulphate. W. G.

**A Field Method for Estimating Dissolved Oxygen in Water.** JAMES MILLER (*J. Soc. Chem. Ind.*, 1914, **33**, 185—186).—Linossier's method (A., 1891, 616), which is essentially a laboratory one, is modified as follows. To 50 c.c. of the water contained in a 100 c.c. Nessler cylinder are added 5 c.c. of alkaline tartrate solution (as used in making Fehling's solution) and one drop of phenosafranine solution (1 in 2000 of water); then, from a 10 c.c. graduated pipette, a solution of ferrous sulphate (0.22 gram and 1 c.c. of concentrated sulphuric acid in 100 c.c.) is run in just below the surface of the liquid, stirring gently with the pipette until the colour is discharged, looking through the cylinder horizontally. The pipette reading gives the amount of oxygen in c.c. per litre. The ferrous sulphate should be standardised against water of known oxygen content. Nitrites have no effect on the method, but it cannot be used in the presence of cyanides. T. S. P.

**The Estimation of Oxygen in Copper and Brass.** T. WEST (*J. Inst. Metals*, 1913, **10**, 371—384).—Oxygen in copper or ordinary brass may be estimated by ignition in carbon monoxide, but the method is not applicable to alloys containing either tin or nickel, on account of the decomposition of carbon monoxide which is brought about. C. H. D.

**The Colorimetric Estimation of Small Quantities of Hydrogen Sulphide.** WERNER MECKLENBURG and FELIX ROSENKRÄNZER (*Zeitsch. anorg. Chem.*, 1914, **86**, 143—153).—The formation of methylene-blue may be used as an accurate method for the colorimetric estimation of hydrogen sulphide in very dilute solution. Using 15 mg. of dimethyl-*p*-phenylenediamine sulphate and 1.5 c.c. of a 2.7% solution of pure, crystallised ferric chloride, the coloration is proportional to the quantity of hydrogen sulphide when the absolute quantity of the latter ranges from 5 to 810 micrograms, provided that the temperature and acid concentration are the same in each experiment. At high dilutions the colour cannot be directly compared with that of pure methylene-blue, but standard solutions of hydrogen sulphide or sodium hydrogen sulphide must be used, the concentration of which has been determined iodometrically. The most suitable proportions are: for 100—500 c.c. of hydrogen sulphide solution, 10 c.c. of concen-

trated sulphuric acid, 25 mg. of the sulphate, and 2.5 c.c. of the ferric chloride solution. This suffices for hydrogen sulphide up to 3 mg. For very dilute solutions, 10 c.c. of hydrochloric acid, 10 mg. of sulphate, and 1 c.c. of ferric chloride solution may be used. Half an hour or more is required for the full development of the colour.

C. H. D.

**Some Limitations of the Kjeldahl Method.** H. D. DAKIN and H. W. DUDLEY (*J. Biol. Chem.*, 1914, 17, 275—280).—Pyrrole and its derivatives present no difficulty provided heating is continued for an hour after charring has disappeared. Most pyridine derivatives give only approximate results. In the case of piperidine and its derivatives, and quinoline and its derivatives, great care and prolonged heating are required. Pyrazole derivatives all gave unsatisfactory results. Piperazine, quinoxaline, acridine (with prolonged heating), most pyrrolidine, pyrimidine, and glyoxaline derivatives (including histidine and proline), and substances containing the hydantoin nucleus present no difficulties.

W. D. H.

**Some Modifications of Kjeldahl's Method for the Estimation of Nitrogen.** ROB. HOTTINGER (*Biochem. Zeitsch.*, 1914, 60, 345—351).—A modification is suggested in the method of distilling off the ammonia formed. The diluted acid liquid is mixed with half its volume of absolute alcohol in an Erlenmeyer flask, the alkali is then added through a rubber valve, which serves later to prevent the suction backwards of the standard acid. The ammonia is then distilled off through an indented tube (designed to prevent the alkali from being mechanically carried over) dipping some way into the flask, at the upper end of which is a thermometer. As soon as the temperature is nearly that of the boiling point of water, the distillation may be regarded as complete. The apparatus is figured in the text.

S. B. S.

**A New Ammonia Distillation Apparatus.** CL. GRIMME (*Chem. Zeit.*, 1914, 38, 404).—A description of a bank of ammonia distillation apparatus for the Kjeldahl estimation of nitrogen. The apparatus is made completely of glass, no new principle being involved.

T. S. P.

**Detection of Nitric Acid in Fruit Juices.** J. TILLMANS and A. SPLITTGERBER (*Zeitsch. öffentl. Chem.*, 1914, 20, 90—91).—A criticism of a method described by Cohn (*A.*, 1913, ii, 723); the test does not appear to be as sensitive as claimed, and any traces of nitric acid detected in fruit juices may have been derived from the sulphuric acid employed.

W. P. S.

**Detection of Nitric Acid in Fruit Juices.** ROB. COHN (*Zeitsch. öffentl. Chem.*, 1914, 20, 82—93).—A reply to Tillmans and Splittgerber (preceding abstract); the sulphuric acid employed did not contain nitric acid.

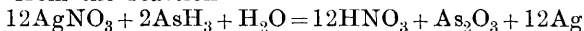
W. P. S.

**Estimation of Phosphorus in Iron and Steel.** HARCOURT PHILLIPS (*Chem. News*, 1914, 109, 170—171).—In the direct method for the estimation of phosphorus, if the tared filter paper containing the phosphomolybdate precipitate is heated too long in the oven, a greyish-blue stain develops on the paper. Accompanying the formation of the stain is a loss in weight, and for correct results the filter should not stay in the water-oven longer than fifteen to twenty minutes.

The author proposes the following plan for dealing with the precipitate; using a solution of sodium phosphate (50 c.c. contain 0.00798 gram of phosphorus), the method of estimation is as follows. To 50 c.c. of the solution contained in a stoppered flask are added 30 c.c. of nitric acid (D 1.2), 10 c.c. of ammonia solution (1:1), and then 30 c.c. of a nitro-molybdate solution prepared according to the formula of Brearley and Ibbotson. After vigorous shaking and warming to 40°, the contents of the flask are allowed to settle for an hour, after which the precipitate is collected, washed with 2% nitric acid to remove all salts, and then with cold water to remove all acid. The precipitate is then dissolved from the filter paper with ammonia, the solution being run into a weighed dish; the contents of the dish are evaporated to dryness on the water-bath, and the residue heated to constant weight. Knowing the strength of the sodium phosphate solution used, the factor necessary to convert the weight of the residue into percentage of phosphorus can be calculated. The factor found by the author was 0.0151, and using this factor the percentages of phosphorus in iron and steels could be estimated with satisfactory results, the tendency, however, being for the results to be high. In the presence of iron it is necessary to refilter the ammoniacal solution of the phosphomolybdate precipitate through the same filter paper. T. S. P.

[**Analysis of Monazite.**] SYDNEY J. JOHNSTONE (*J. Soc. Chem. Ind.*, 1914, 33, 55—59).—See this vol., ii, 376.

**A Method of Estimating Traces of Arsenic of the Order of One-thousandth of a Milligram.** L. MORFAU and E. VINET (*Compt. rend.*, 1914, 158, 869—871).—A description of a simple apparatus by means of which it is possible to estimate one-thousandth of a milligram of arsenic by comparing a ring deposit of silver from the reaction



with standard rings. The apparatus consists essentially of two U-tubes, one of which (A) contains a solution of silver nitrate, and serves to purify the hydrogen used to wash out the last traces of hydrogen arsenide from the second tube. The second tube (B) contains 0.5 gram of pure zinc and a few drops of distilled water. One limb is connected to the U-tube (A), and also carries a dropping funnel. The second limb is connected to a glass tube (C), 0.5 cm. internal diameter, bent twice at right angles, containing 0.5 c.c. of N/10-silver nitrate solution, and is kept suitably

inclined, the open end carrying a thread of glass to prevent the silver nitrate solution being blown out of the tube. A steady stream of pure hydrogen is maintained through the apparatus, and then into the second tube is run, by the dropping funnel, 0.5 c.c. of 20% sulphuric acid, followed by the solution containing the arsenic. A ring of silver slowly forms in the tube *C* at the front surface of the liquid, and when deposition is complete the liquid is drained off and the tube put to dry in the dark, the ring being compared the next day with standard rings, thus giving the percentage of arsenic in the original liquid. The presence of antimony or sulphides is indicated by the difference in the appearance of the ring deposit. W. G.

**Quantitative Estimation of Arsenic in Metals by Hypophosphorous Acid.** L. BRANDT (*Chem. Zeit.*, 1914, **38**, 461—463, 474).—The process already described (this vol., ii, 68) is not interfered with by the presence of manganese, nickel, cobalt, zinc, chromium, tin, lead (traces), copper (traces), aluminium (traces). Silver is, of course, excluded, as it is already eliminated as chloride. Mercury, being readily reduced to mercurous chloride in the cold, may thus be got rid of. Bismuth is also reduced on boiling, but it redissolves when heated with strong hydrochloric acid. The sparingly soluble cadmium compound formed may also be redissolved in this manner. Antimony does not form an obstacle; the exact details will be published later. L. DE K.

**Standardising Arsenite Solutions.** E. DEISS (*Chem. Zeit.*, 1914, **38**, 413—415).—The author calls attention to the fact that the ordinary standard iodine solution may contain potassium iodate either by the use of impure potassium iodide or by oxidation on keeping. It is therefore recommended to acidify the solution with hydrochloric acid before final standardisation. The best way, however, is to prepare an iodine solution of definite strength by starting from pure potassium iodide, and adding to this, in the presence of hydrochloric acid, a definite volume of accurately standardised potassium permanganate. Excess of sodium hydrogen carbonate is now added, and then the arsenite solution to be tested, until all free iodine has disappeared. L. DE K.

**Estimation of Carbon Monoxide in Air [and Waste Gases].** FRANK STURDY SINNATT and BARNETT JOSEPH CRAMER (*Analyst*, 1914, **39**, 163—167).—A known volume of the gas is drawn through washing-bottles containing fuming sulphuric acid, aqueous potassium hydroxide, concentrated sulphuric acid, then through two long tubes containing solid potassium hydroxide so as to remove any carbon dioxide, unsaturated hydrocarbons, and moisture.

The gas then passes through a long tube filled with alternate layers of iodine pentoxide and glass-wool, and heated at 140—160°. About 1 litre per hour should be passed. The iodine liberated is absorbed in a tube containing mercury, and the carbon dioxide formed is absorbed in aqueous barium hydroxide of known strength,

the excess of which is then titrated, without transferring the solution, with  $N/20$ -hydrochloric acid (Pettenköfer's process).

A special mercurial vacuum apparatus is described and figured (also compare A., 1913, ii, 432). L. DE K.

**Estimation of Carbon Monoxide by means of Yellow Mercuric Oxide.** L. MOSER and O. SCHMID (*Zeitsch. anal. Chem.*, 1914, **53**, 217—233).—The gaseous mixture is passed through a U-tube made of dark glass filled with 20 grams of precipitated mercuric oxide and heated at  $100^{\circ}$ , in such a manner that for 100 c.c. of carbon monoxide the experiment occupies at least twenty minutes. This converts the carbon monoxide into carbon dioxide, which is absorbed in three receivers containing a known volume of  $N/4$ -barium hydroxide, the excess of which is titrated as usual with  $N/4$ -hydrochloric or oxalic acid.

Owing to its method of preparation, the yellow mercuric oxide may contain traces of sodium hydroxide, and, therefore, it should be submitted for some time to the action of a current of carbon dioxide, and then again to a current of pure air. The presence of hydrogen, or methane, does not interfere; any pre-existing carbon dioxide can be readily removed by a wash-bottle containing barium hydroxide. L. DE K.

**Approximate Estimation of Free Carbon Dioxide in Mineral Waters.** R. FRESSENIUS and L. GRÜNHUT (*Zeitsch. anal. Chem.*, 1914, **53**, 265—274).—The process is based on the fact that on shaking, mineral waters part with most of their free carbon dioxide, which may then be measured.

A considerable amount of the gas, however, remains in solution depending on temperature, etc. From the authors' tables given in the original this amount may be readily ascertained. A convenient graduated shaking tube is described and figured. The sample should be collected at the source. L. DE K.

**Detection of Soluble Silicates in Soaps and the Action of Sodium Chloride on Soluble Silicates.** E. ISNARD (*Ann. Chim. anal.*, 1914, **19**, 98—100).—The soap is dissolved in water, acidified with hydrochloric acid, and the fatty acids are separated by filtration. The filtrate is then rendered slightly ammoniacal, when a precipitate is obtained if silicates are present. The test may be rendered more sensitive by concentrating the filtrate before the ammonia is added.

When a dilute potassium silicate solution is saturated with sodium chloride, the silica is separated in the form of a gelatinous precipitate. This reaction may be used for detecting silica in the presence of alumina. The solution containing the two substances is rendered alkaline with sodium hydroxide, and then saturated with sodium chloride; the silica is precipitated whilst the alumina remains in solution. W. P. S.

**Convenient Standard End Point in the Titration of Alkali Carbonates with Hydrochloric Acid.** GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1914, **36**, 656—657).—Küster (A., 1897, ii, 74) has recommended the colour of a saturated aqueous solution of carbon dioxide containing methyl-orange as a standard end-point in the titration of alkali carbonates with hydrochloric acid. This standard end-point is not permanent, however, even in corked vessels, owing probably both to the escape of carbon dioxide and to the solubility of the alkaline constituents of the glass, and hence the solution must be renewed frequently. Solutions of 17·5 grams of sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , or of 15·3 grams of potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , in 100 grams of water give, with methyl-orange, the same colour as the saturated aqueous solution of carbon dioxide, and thus form a convenient standard end-point; they can be used in the titration of solutions from half- to tenth-normal. Both salts should be recrystallised before use, the potassium salt being the more easily purified.

T. S. P.

**Detection of Magnesium Sulphate in Saffron.** A. NESTLER (*Zeitsch. Nahr. Genussm.*, 1914, **27**, 388—391).—When a drop of a mixture consisting of equal volumes of saturated magnesium sulphate solution and glycerol is mixed with a drop of chloral hydrate solution (5:2), crystals of magnesium sulphate are formed almost immediately; without the addition of the chloral hydrate, drops of the magnesium sulphate-glycerol mixture do not yield crystals even when exposed to the atmosphere for many hours. This reaction may be applied to the detection of magnesium sulphate in saffron by treating a portion of the sample with water and filtering the solution; the filtrate is concentrated at the ordinary temperature to a syrupy consistence, and a drop of this syrup is then mixed on a microscope-slide with a drop of chloral hydrate solution. Crystals form within three minutes if magnesium sulphate is present. The crystalline mass may be washed with alcohol (to remove chloral hydrate, colouring matters, etc.), and the crystals further identified by the application of suitable microchemical tests.

W. P. S.

**The Estimation of Zinc in Coinage Bronze by Volatilisation.** T. K. ROSE (*J. Soc. Chem. Ind.*, 1914, **33**, 170—172).—The method consists in heating the bronze in a carbon crucible, driving off the zinc by volatilisation, and weighing the residue. The crucibles, each containing 1 gram of bronze, are placed close together inside a salamander crucible, and completely covered by powdered charcoal. The cover pot is then strongly heated for two hours in an ordinary gas injector furnace, the final temperature being 1375°. The use of check or proof assay pieces is necessary, since the loss varies considerably with the temperature, and some copper and tin also volatilise.

The various sources of error are discussed. The errors may reach about 0·03%, or about the same as may be expected in the



gravimetric or volumetric processes, but the saving of time is very considerable.

T. S. P.

**A Very Delicate Test for Lead [in Water].** V. N. IVANOV (*Chem. Zeit.*, 1914, 38, 450).—About 50 c.c. of the sample are mixed with an equal volume of a freshly prepared 2% solution of sodium hydrogen sulphite (neutral to methyl-orange). In the presence of lead a white turbidity is formed; if this does not occur until after a few minutes, the lead may be taken as something like 1 part per million. Copper, silver, nickel, iron, aluminium, magnesium, and calcium do not interfere. Barium and stannous tin should be absent. Normal sodium sulphite gives the reaction with all these metals.

L. DE K.

**Estimation of Small Quantities of Lead.** I. M. SIEGFRIED and W. POZZI (*Biochem. Zeitsch.*, 1914, 61, 149—156).—The method is a colorimetric one, based on the depth of colour produced by hydrogen sulphide. The liquid under examination is introduced into a 120 c.c. flask, and diluted if necessary to the 100 c.c. mark; 9 c.c. of *N*/100-hydrochloric acid are then introduced (this prevents precipitation of iron), and 1 c.c. of a 1% solution of the purest gum arabic, which maintains the sulphide in colloidal form. The mixture is then diluted to the 120 c.c. mark with saturated hydrogen sulphide solution. For comparison a lead nitrate solution containing 0.1599 gram of lead nitrate is employed; 1 c.c. of such a solution contains 0.0001 gram of lead. Enough of this is introduced into a second 120 c.c. flask to give a colour near that of the test solution, and this is diluted with water, and the hydrochloric acid, gum arabic, and hydrogen sulphide solutions added in the same way as with the test solution. The final comparison of the two solutions is then made in a Duboscq colorimeter, with a special method of illumination described by the authors. It is incidentally mentioned that nitric acid produces a quantity of insoluble lead compound, and lead estimations give too low a result when this acid is used for destruction of the organic matter.

S. B. S.

**Lux's Method for the Estimation of Lead Peroxide.** A. IPIENS (*Zeitsch. anal. Chim.*, 1914, 53, 261—265).—Lux's process consists in treating the lead peroxide with dilute nitric acid and a known amount of oxalic acid, and titrating the excess of the latter with permanganate. The results are, however, somewhat irregular.

The author has improved the process by neutralising the solution before titration with sodium hydroxide, and then re-acidifying with sulphuric acid.

L. DE K.

**Commercial Copper Sulphate. Estimation of Copper.** F. MACH and P. LEDERLE (*Landw. Versuchs-Stat.*, 1914, 84, 129—143).—The following method for estimating copper in copper sulphate is recommended. The salt (10 grams) is dissolved in about 200 c.c. of hot water, made slightly ammoniacal, treated with about 5 c.c.

of 2% hydrogen peroxide, boiled for two minutes, and filtered from the ferric hydroxide. The precipitate is then dissolved in hydrochloric acid, precipitated with ammonia, and the filtrate added to the first filtrate, which is made slightly acid, with hydrogen chloride, and diluted to 1000 c.c. A portion of this (25 c.c.) is boiled with 10—20 c.c. of hydrochloric acid (D 1.125) for one minute, and the flask at once closed with a double-bored cork provided with two tubes, one of which is connected with a carbon dioxide generator. The contents of the flask are then quickly cooled under a tap. The cork is removed, and 5 c.c. of 10% potassium thiocyanate and two drops of *N*/10-ferric chloride are added. Carbon dioxide is passed through, and the solution is titrated with a solution of titanium trichloride until the reddish-brown colour changes to white. The strength of the titanium trichloride solution is best estimated by means of a solution of copper sulphate in which the copper has been estimated electrolytically.

It is considered desirable to examine samples of commercial copper sulphate, at any rate qualitatively, even when in the form of large crystals of the right colour. Ground samples have occurred which contained very large amounts of iron sulphate.

N. H. J. M.

**Electrolytic Analysis of Delta Metal.** R. BELASIO and M. MARCHIONNESCHI (*Ann. Chim. Applicata*, 1914, 1, 127—133).—The ordinary methods for analysing brasses and bronzes are inapplicable in the case of delta metal, which contains, besides copper and zinc, 0.5—3% of manganese, 0.4—1.2% of iron, 0.02—2.5% of aluminium, 0.02—0.5% of lead, and 0—3% of tin.

The presence of manganese renders impossible the simultaneous deposition, from nitric acid solution, of the copper at the cathode and of the lead as peroxide at the anode, as the manganese is also deposited in small proportion at the anode as peroxide. This difficulty is met by Foerster's method (A., 1906, ii, 805; 1907, ii, 54), in which the copper is deposited from sulphuric acid solution and the lead is estimated as sulphate.

No exact method exists for the electrolytic separation of zinc from iron. Jerre (*Chem. Zeit.*, 1905, 29, 803) proposed the estimation of the zinc in sodium hydroxide solution in presence of ferric hydroxide, but under these conditions the whole of the zinc cannot be removed from the iron precipitate, and at the same time small quantities of the precipitate are held mechanically on the electrode, the deposited zinc having a brown appearance. Vortmann (A., 1894, ii, 34; see also A., 1895, ii, 89) separates iron from zinc in presence of potassium cyanide, the iron being thereby converted into potassium ferrocyanide, from which it is not deposited by the current, but, with this method, which was used by Hollard and Bertiaux (A., 1903, ii, 513), the iron tends to become precipitated as hydroxide, and to carry down with it some of the zinc, whilst the deposited zinc contains a little iron; this difficulty is intensified if manganese and aluminium are also present.

By means of a modification of the ordinary treatment with

sodium hydroxide, the author has succeeded in effecting a satisfactory separation of iron from manganese (compare *Ann. Lab. Gabelle*, 8), and a method has been devised which yields excellent results when applied to delta metal. The estimations of the various constituents are described in detail. A control analysis of a mixture of copper, zinc, ferrous ammonium, and manganous ammonium sulphates with ammonium-alum and lead nitrate gave the following weights in grams, the actual quantities present being given in brackets: copper, 0.5987 (0.5985); zinc, 0.3406 (0.3411); iron, 0.0194 (0.0197); manganese, 0.0352 (0.0355); aluminium, 0.0151 (0.0151); lead, 0.0172 (0.0177). Analysis of a commercial ingot of delta metal gave: copper, 54.04%; zinc, 40.50%; manganese, 2.72%; iron, 0.86%; aluminium, 0.85%; and lead, 0.81%.

T. H. P.

**A New Reaction of Copper, Cobalt, and Nickel.** G. MALATESTA and E. DI NOLA (*Boll. Chim. farm.*, 1913, 52, 855—860. Compare this vol., ii, 220).—In this paper further details are given regarding the influence of electrolytes on Uhlenhuth's reaction. In the case of copper the addition of electrolytes which do not give rise to secondary reactions (such as alkali salts) does not affect the coloration, but the presence of acids, ammonium salts, aluminium salts, and, to a less degree, magnesium and calcium salts does interfere with the reaction.

R. V. S.

**Analysis of Commercial Aluminium and its Light Alloys.** R. BELASIO (*Ann. Chim. Applicata*, 1914, 1, 101—110).—In commercial samples of aluminium and in the light alloys of this metal the preponderating proportion of the latter renders the estimation of the separate constituents difficult. In order to overcome this difficulty, the author subjects the metal or alloy to preliminary treatment with sodium sulphide in presence of sodium tartrate. In this way the copper, lead, iron, nickel, cobalt, zinc, and manganese are precipitated, whilst the aluminium passes into solution accompanied only by the tin, which can be readily estimated electrolytically even in presence of a very large excess of aluminium. The above method of separation possesses, however, the inconvenience that it cannot be applied in presence of nickel, since nickel sulphide dissolves partly in alkali sulphide solution. Hence, when nickel is present, it is eliminated and estimated by means of diacetyldioxime prior to the treatment with alkali sulphide.

Details are given for estimating in these alloys: (1) the heavy metals, and (2) the aluminium, magnesium, silicon, carbon and sodium. Test experiments show that the procedure employed leads to excellent results.

T. H. P.

**The Precipitation of Aluminium in the Presence of Fluorides.** (Mlle.) H. CAVAGNAC (*Compt. rend.*, 1914, 158, 948—950).—The precipitation of aluminium by ammonium hydroxide is incomplete either in the cold or at the boiling point in the presence of small quantities of hydrofluoric acid, the precipitation being more complete in the cold than in the hot. The precipi-

tate obtained yields hydrogen fluoride on warming with sulphuric acid. W. G.

**Volumetric Estimation of Nickel in Argentans, Nickeliferous Bronzes and Brasses, and Nickel steels.** R. BELASIO and M. MARCHIONNESCHI (*Ann. Chim. Applicata*, 1914, 1, 133—138).—This method, which is not affected by the presence of zinc or of small proportions of iron, manganese, aluminium, lead, etc., makes use of a solution prepared by dissolving 1.582 gram of pure dimethylglyoxime (compare Brunck, A., 1907, ii, 582, 989) in 1500 c.c. of 95% alcohol and making up to 2 litres with water. The solution is standardised in the manner described below.

In estimating the nickel in one of the above alloys, a certain quantity of the solution of the metal is rendered alkaline with ammonia and diluted so that the resultant liquid contains about 0.05% of nickel. A number of equal volumes of the solution are pipetted into small beakers. Into one of these the dimethylglyoxime solution is run from a burette as long as the precipitate increases visibly in amount. A drop of the liquid is then placed on a doubled filter paper, and the wet spot on the lower layer tested for the presence of nickel by means of the dimethylglyoxime solution. If nickel is not detected in this way, a little of the liquid is filtered into a test-tube, and if this gives no more than a faint red coloration with the reagent, the remaining volumes of the liquid are treated. Assuming 9.2 c.c. of the dimethylglyoxime solution to have been used in the preliminary test, 9.2, 9.4, 9.6, 9.8, and 10.0 c.c. are added to the other flasks. After five to ten minutes the different liquids are filtered into two series of test-tubes, and to each of those of one series a little 1% alcoholic dimethylglyoxime solution is added, and to each of those of the other, a few drops of dilute nickel sulphate solution. After about fifteen minutes it can be seen which of the tubes corresponds with exact precipitation of the nickel.

Test estimations with nickel sulphate in presence of salts of zinc, or of iron, aluminium, and manganese show that the method gives exact results, and estimations of nickel in argentan, nickeliferous bronze or brass, and similar alloys give results in good agreement with those obtained electrolytically. T. H. P.

**Apparatus for the Combustion of Highly Volatile Liquids.** E. SERNAGIOTTO (*Ann. Chim. Applicata*, 1914, 1, 195—198).—A small test-tube holding about 3 c.c. is fitted with an inlet-tube reaching nearly to the bottom of the test-tube, so that air or oxygen can be passed through the liquid, the vapour of which is thus carried through an outlet-tube into the combustion tube. The inlet- and outlet-tubes are each provided with a three-way tap, the two taps being connected by a side-tube, passage of oxygen through the latter driving the vapour from the taps and outlet-tube into the combustion apparatus. The connexions are accurately ground, and are kept tight by means of fused-on glass lugs pulled together by steel springs. The test-tube is graduated with arbitrary divi-

sions, so that a suitable quantity of liquid may be burnt, the exact amount taken being determined by weighing the apparatus before and after the combustion. The apparatus serves well for the combustion of a small quantity of a hygroscopic liquid, the latter being placed in the test-tube together with the drying agent. Test experiments with acetone and ether yielded excellent results. T. H. P.

**Colour Reactions of Organic Compounds with Trichloroacetic Acid.** K. V. CHARITSCHKOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 76—78).—A number of organic compounds and different naphtha distillates have been tested to ascertain which of them give a colour reaction with trichloroacetic acid, which has been proposed as a reagent for detecting the presence of cholesterol. It is found that, with the exception of benzene hydrocarbons and of unsaturated aliphatic hydrocarbons of low boiling point, almost all the compounds giving colorations with tetranitromethane (compare Ostromisslenski, A., 1912, i, 1) react with trichloroacetic acid. Neither reaction is shown by unsaturated, dibasic, aliphatic acids or by cyclic compounds with a double linking in the nucleus (terpenes and menthene), and both are given or both fail with the various naphtha products. Trichloroacetic acid gives a yellow coloration with triphenylmethane, and a reaction is also obtained with mesitylene, but this may depend on the presence of impurities.

Although no final conclusion can yet be drawn, it would appear that trichloroacetic acid constitutes, equally with tetranitromethane, a reagent for cyclic double linkings. T. H. P.

**The Heat Test of Explosives.** A. C. EGERTON (*J. Soc. Chem. Ind.*, 1914, **33**, 112—116).—The results of further experiments on the author's heat test for explosives (A., 1913, ii, 534) are described, and the criticisms of Smart and Robertson (A., 1913, ii, 1080) replied to. T. S. P.

**Source of Error in Estimating Sugar by Clerget's Method.** VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1914, **38**, 289—298).—It is shown that whilst the Herzfeld constant 132.66 for  $N/2$ -solutions and 20° holds good when the inverted solution is polarised within three to five minutes, it is too low if the polarisation is delayed (as, for instance, when the solution has to be decolorised) to from fifteen to thirty minutes. The constant should then be 132.95 (or 133.00). N. H. J. M.

**A Micro-analytical Method for the Estimation of Sugar in the Blood.** OSCAR KRAUS (*Biochem. Zeitsch.*, 1914, **60**, 344).—The author calls attention to the fact that he has already published a method for estimation of sugar in blood (*Wiener Med. Woch.*, 1913, Nos. 18, 26, 47), which is very similar to that recently described by Michaelis (this vol., ii, 223). S. B. S.

**A Rapid Clinical Test for Hyperglycæmia.** S. GITLOW and B. HOROWITZ (*Biochem. Bull.*, 1914, **3**, 272—274).—The Molisch test is recommended for the detection of sugar in blood; the colour

differences between normal and hyperglycæmic bloods is very marked and readily detected. W. D. H.

**Colorimetric Estimation of Sugar in Urine.** E. RIEGLER (*Zeitsch. anal. Chem.*, 1914, **53**, 245—249).—The process is, briefly, as follows: 1 c.c. of the urine (suitably diluted) is added to 10 c.c. of the author's copper solution and heated to boiling. After centrifugating the liquid, the solution is poured off from the cuprous oxide deposit, and the excess of copper determined colorimetrically, preferably in an Autenrieth-Königsberger apparatus. Albumin, if present, should be removed by means of  $\beta$ -naphthalene-sulphonic acid (see this vol., ii, 395) before applying the test.

The reagent, which is also a very convenient one for qualitative purposes and keeps for an indefinite period, is made by dissolving 10 grams of pure copper sulphate in 50 c.c. of water, adding 10 c.c. of pure glycerol and diluting with 3% sodium hydroxide solution to a litre. Its exact reducing power is found experimentally by means of a 1% solution of dextrose. L. DE K.

**Difference between Acid-content and Degree of Acidity of Wine.** C. VON DER HEIDE and M. I. BARAGIOLA (*Zeitsch. anal. Chem.*, 1914, **53**, 249—260).—A lengthy article with tables and curves, and containing the results of both chemical and physico-chemical analyses of wines.

From two cases occurring in actual practice it is shown that the degree of acidity (hydrogen-ion concentration) is not necessarily proportional to the acid-content. L. DE K.

**Estimation of Tartaric Acid in Wine by a Physico-chemical Volumetric Method.** MARCEL DUBOUX (*Ann. Chim. anal.*, 1914, **19**, 89—97. Compare A., 1913, ii, 888).—The principles of the method described previously by the author and Dutoit (*loc. cit.*) may be applied to the estimation of tartaric acid alone in wine. Having ascertained the total acidity and the quantity of sulphate present in the wine, the tartaric acid is estimated as follows: When the total acidity is equivalent to less than 90 c.c. of *N*/1-solution per litre of wine, 15 c.c. of the sample are treated successively with a quantity of barium hydroxide solution exactly sufficient to precipitate the sulphates, 0.15 c.c. of *N*/1-uranium nitrate solution, 5 c.c. of glacial acetic acid, 1 c.c. of *N*/1-sodium hydroxide solution, and 80 c.c. of 95% alcohol, and the solution is titrated with barium acetate solution as described. In the case of wines where the total acidity corresponds with from 90 to 115 c.c. of *N*/1-solution per litre, 30 c.c. of the wine are treated with the requisite amount of barium hydroxide, 0.3 c.c. of *N*/1-uranium acetate solution, 8 c.c. of glacial acetic acid, 1 c.c. of *N*/1-sodium hydroxide solution, 0.5 c.c. of *N*/1-tartaric acid solution (this is added to facilitate the precipitation of the barium tartrate, and the quantity is deducted from the tartaric acid found), and 70 c.c. of 90% alcohol and the mixture is titrated with *N*/4-barium hydroxide solution. The same procedure is followed with wines in which the total

acidity is equivalent to 115—140 c.c., and more than 140 c.c., respectively, of *N*/1-solution, except that in the first case 60 c.c. of 95% alcohol are added and in the second 50 c.c. Citric acid, when present, is estimated with the tartaric acid. W. P. S.

**Detection of Picric Acid in Urine.** E. ISNARD (*Ann. Chim. anal.*, 1914, **19**, 100—101).—Five c.c. of the urine to be tested are heated to boiling in a test-tube with 5 c.c. of saturated sodium hydroxide solution; 1 c.c. of ammonium sulphide solution is then allowed to flow on to the surface of the mixture. If picric acid is present, a red zone appears at the junction of the two liquids. The test is rendered more sensitive if the urine is shaken with ether, the ethereal solution separated and evaporated, and the residue thus obtained treated as described. W. P. S.

**Determination of the Freezing Point of Milk.** L. TH. REICHER (*Chem. Werkblad*, 1914, **11**, 323—324).—A description of a form of Beckmann depressimeter employed by the Municipal Public Health Department, Amsterdam, for estimating the percentage of added water in milk by determining the freezing point. A. J. W.

**Estimation of Fat in Small Quantities of Blood.** W. R. BLOOR (*J. Biol. Chem.*, 1914, **17**, 377—384; *Proc. Amer. Soc. Biol. Chem.*, 1913, xxxvii—xxxviii).—Two c.c. of blood are withdrawn and stirred with 30—40 volumes of a mixture of alcohol and ether, and boiled on the water-bath, which dissolves the fat and coagulates the protein. An aliquot portion of the filtrate from this is saponified with sodium ethoxide; a few c.c. of the alcohol-ether mixture are added, and stirred into 100 c.c. of water. This is acidified with 10% hydrochloric acid, and compared with a standard fat solution by a nephelometer. After feeding with fat, after starvation, and during ether-anæsthesia, the fat of the blood increases. W. D. H.

**Estimation of Total Fats of Undried Fæces and other Moist Masses.** GORDON J. SAXON (*J. Biol. Chem.*, 1914, **17**, 99—102).—The method described is a combination of Folin and Wentworth's method for fat estimation in dried fæces, and that of Meig's for fat estimation in milk. W. D. H.

**Action of Diazo-derivatives on Vegetable Oils.** P. SISLEY and FREHSE (*Bull. S.c. chim.*, 1914, [iv], **15**, 295—298; *Ann. Falsif.*, 1914, **7**, 130—132).—The authors have studied the colour reaction given by certain oils with diazonium salts, which Kreis discovered in the case of sesame oils and diazotised naphthionic acid (A., 1904, ii, 75). Whereas benzene- and naphthalene-diazonium salts do not give interesting results, it is found that a solution made by diazotising *p*-nitroaniline is a useful reagent. Ten c.c. of the oil are mixed with 5 c.c. of 20% sodium acetate and a few drops of the reagent, when a coloration varying from brownish-red to currant-red develops in a short time, with a number of oils. Olive oil

gives only an orange-yellow colour, that is, a negative result, and the test may serve to detect foreign oils in a sample.

The authors hope to be able to isolate the substance which enters into condensation. It is probably phenolic in character.

J. C. W.

#### Estimation of Colophony in Varnishes, Oils, and Soaps.

H. WOLFF and E. SCHOLZE (*Chem. Zeit.*, 1914, 38, 369—370, 382—383).—The method recommended by the authors depends on the esterification of the fatty acids present by treatment with alcohol and sulphuric acid, and the subsequent separation and titration of the resin acids. From 2 to 5 grams of the mixture of fatty and resin acids separated from the sample are boiled for two minutes with 10 to 20 c.c. of methyl alcohol and 5 to 10 c.c. of a mixture of 1 part of sulphuric acid with 4 parts of methyl alcohol. The solution is then mixed with ten times its volume of 10% sodium chloride solution, extracted with ether, and the ethereal solution is titrated with  $N/2$ -alcoholic potassium hydroxide solution. In calculating the quantity of resin from the result of the titration, it must be assumed that the resin acids have a mean molecular weight of 160, and that 1.5% of the fatty acids present remain unesterified. More accurate results are obtained by repeating the esterification process. Five grams of the mixed fatty and resin acids are esterified as described (ethyl alcohol may be used in this case in place of methyl alcohol), and the ethereal extract is titrated. The neutral solution is shaken with water, the aqueous solution obtained is acidified, sodium chloride is added, and the fatty and resin acids are extracted with ether. The residue obtained on evaporating the ether is again esterified with alcohol and sulphuric acid, but this time the action is allowed to proceed at the ordinary temperature for two hours; the resin acids are then extracted with ether and titrated. A correction for unesterified fatty acids is unnecessary, but in this estimation, as in the former, the amount of resin acids found is multiplied by 1.07 when it is desired to obtain the amount of colophony present, since the latter contains on the average about 6.5% of unsaponifiable substances. Oxidised fatty acids do not esterify readily, and, when the double-esterification process is not utilised, it is advisable to estimate the amount of these acids separately; from 7 to 18% of the oxidised fatty acids may remain unesterified by a single treatment with alcohol and sulphuric acid.

W. P. S.

**Use of Carbon Tetrachloride for the Extraction and Estimation of the Active Principles in Drugs and Medicinal Plants.** GIULIO GORI (*Boll. Chim. farm.*, 1913, 52, 891—895).—Theobromine is insoluble in carbon tetrachloride. The solubilities of a number of other alkaloids in carbon tetrachloride have been measured by the author. From examples given it appears that carbon tetrachloride can be advantageously used instead of chloroform in the estimation of caffeine in kola nuts or green coffee, whilst caffeine and theobromine can be separately estimated in mixtures of the two



(such as extracts of kola nut) by taking advantage of the fact that theobromine is insoluble in carbon tetrachloride. R. V. S.

**The Ninhydrin Reaction.** PAUL E. HOWE (*Biochem. Bull.*, 1914, **3**, 269—271).—The triketohydrindene hydrate (ninhydrin) test is very satisfactory for compounds with free amino- and carboxyl groups attached to aliphatic radicles—amino-acids, peptone, protein, etc. The typical blue colour may result under other conditions than in the presence of amino-acids and related substances. But when the reagent is used in a neutral solution, distilled water, with a negative or very low salt content, a positive test results only in the presence of amino-acids. W. D. H.

**The Detection of Monoamino-acids.** R. ENGELAND (*Zeitsch. Biol.*, 1914, **63**, 470—476).—The hydrolysis products are exhaustively methylated by means of methyl sulphate, and thereby converted into the betaine derivatives. These can be separated and quantitatively estimated by means of their mercuric, gold, and platinum chloride derivatives. Examples are given by the isolation of the proline derivative from spongin, isolated in the form of its platinum-chloride, and of the betaine of glycine from ergot of rye, isolated as its mercurichloride. It is, incidentally, shown to be partly precipitable by phosphotungstic acid. S. B. S.

**Displacement Curves of Some Organic Bases: Application to the Estimation of Certain Alkaloids.** R. GOUBAU (*Bull. Acad. roy. Belg.*, 1914, 63—90).—The author has studied the variations in electrical conductivity occurring on continued addition of *N*-sodium hydroxide solution to a solution of an organic base containing excess of acid. The curves obtained exhibit, in general, two points of inflection, one separating the curve of neutralisation of the excess of acid from that of displacement of the base by the sodium hydroxide, and the other this from the curve showing the increase of conductivity due to the growing excess of sodium hydroxide. In some cases these curves serve well for the estimation of alkaloids, the measurements being made in aqueous alcoholic solutions.

Thus, cocaine can be estimated in a capsule containing as little as 0.01 gram of this base. With homoatropine, 0.09951 gram was obtained instead of 0.1 gram. Atropine may also be accurately estimated in this way; with pharmaceutical preparations of belladonna, it is first necessary to remove foreign substances, such as resins, chlorophyll, etc., by extraction with ether or chloroform, as described in the Belgian Pharmacopœia. Coniine gives good, but nicotine unsatisfactory, results. With pharmaceutical preparations of aconitine, preliminary removal of the resins by means of ether is necessary. Pilocarpine, morphine, and codeine also give satisfactory results, and the same is the case with strychnine and brucine, if the fat contained in pharmaceutical preparations is previously extracted by means of ether. The displacement curves

do not admit of the estimation of the cinchona alkaloids, but the total proportion of acid in salts of these alkaloids can be determined.

T. H. P.

**Conversion of Creatine into Creatinine.** FRANCIS G. BENEDICT (*J. Biol. Chem.*, 1914, 17, 363).—The method of employing a high temperature for converting creatine into creatinine was published as by the author in conjunction with V. C. Myers (*Amer. J. Physiol.*, 1907, 18, 1907); this was an inadvertence; the method is that of Myers only.

W. D. H.

**Colorimetric Estimation of Albumin.** E. RIEGLER (*Zeitsch. anal. Chem.*, 1914, 53, 242—245).—The process is based on the fact that an alkaline solution of albumin dissolves copper hydroxide, and that the intensity of the violet colour is proportional to the amount of the albumin present. Hence by means of a standard solution and an Autenrieth-Königsberger colorimeter, a determination may be rapidly made. This comparison liquid is prepared by dissolving 0.5 gram of dry egg-albumin in 80 c.c. of 3% sodium hydroxide solution, adding 2 c.c. of 20% copper sulphate solution, and then soda solution up to 100 c.c. After settling, the solution is filtered, and is then ready for use.

In order to apply the process to urine, 10 c.c. of the sample are placed in a graduated tube and mixed with 5 c.c. of 5%  $\beta$ -naphthalenesulphonic acid, and submitted to centrifugal force for three to four minutes. The liquid is poured off, and the deposit dissolved in 9.8 c.c. of the soda solution, and the copper solution is then added up to the 10 c.c. mark. After vigorous shaking and again centrifugating for one minute, 2 c.c. of the liquid are examined in the colorimeter.

L. DE K.

**Estimation of the Proteins of Wheat.** G. SILVESTRI (*Ann Chim. Applicata*, 1914, 1, 214—222).—In consequence of the discordant values which have been assigned to the specific rotation of gliadin, the author has extracted this from flours of different characters by means of 70% alcohol, and determined the rotation of a solution containing 5.79 grams per 100 c.c. of 70% alcohol, the result being  $[\alpha]_D - 70.29^\circ$ .

Estimations were made, with flours from various hard and soft wheats of different origins, of the total nitrogen, that soluble in potassium sulphate solution, that soluble in 70% alcohol, and that extracted by 70% alcohol from the residue remaining after treatment with potassium sulphate solution. Numbers were thus obtained for the proportions of total protein, gliadin, glutenin, and proteins soluble in salt solutions. The results show that estimation of the proteins of these three different classes does not alone permit of differentiation between hard and soft wheats.

T. H. P.

**A New Method of Estimating Tryptophan in Proteins.** ANNIE HOMER (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, 48, iv—v).—The method is based on the fact that when baryta acts on

protein, the tryptophan liberated during hydrolysis is not destroyed. Excess of baryta is removed with sulphuric acid; the tryptophan is precipitated as usual with mercuric sulphate, and washed free from tyrosine. The mercury sulphate compound is decomposed with hydrogen sulphide; the filtrate is freed from hydrogen sulphide and sulphuric acid, and the tryptophan content is estimated against both nascent and molecular bromine which have been standardised against a known solution of pure tryptophan.

W. D. H.

**A Simple Method for the Determination of Colloids in Effluents and the Application of the Liquid Interferometer in the Examination of Waters Generally.** R. MARC and K. SACK (*K. U. Chem. Beihefte*, 1914, 5, 375—410. *Comptes A.*, 1912, ii, 1150; 1913, ii, 113; this vol., ii, 35).—The method described in a previous paper has been applied in the examination of a large number of waters. As a result of further experience, the author recommends the use of specially prepared barium sulphate instead of barium carbonate for the adsorption of the colloids. In this way, changes in the refractivity due to the reaction of barium carbonate with dissolved calcium sulphate are avoided. By combining the refractometric determination which affords a measure of the total colloids, with an estimation of the oxygen absorption before and after treatment with barium sulphate, it has been found possible to differentiate between the inorganic and organic colloids.

The recorded observations also show the existence of a close connexion between the original refractivity of the water and the total solid residue which is obtained on evaporation. For waters of a similar type the ratio of the refractivity to the total solids is practically constant, but varies considerably for waters of different kinds. Neither the refractivity nor the total solid residue is of much significance when waters of different types are compared, but the ratio of these quantities would seem to afford a means of distinguishing between these with comparative ease.

H. M. D.

**Critical Observations with Reference to the Measurement of the Adsorption Capacity of the Soil.** TADEUSZ ORYNG (*Kolloid. Zeitsch.*, 1914, 14, 105—108).—A criticism of the colorimetric method for determining the adsorption capacity of soils, with special reference to Górski's measurements (*Zeitsch. landw. Versuchswesen, Oesterreich*, 1912, 15, 1201), in which crystal-violet was used. Since the colour of a colloidal dye is to some extent dependent on the degree of dispersity, and since changes in this may be brought about under the coagulating influence of the electrolytes present in the soil, the author considers that trustworthy results cannot, in general, be obtained by this method. H. M. D.

## General and Physical Chemistry.

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**The Refractive Index of Mixtures of Gases.** S. VALENTINER (*Ber. Deut. physikal. Ges.*, 1914, **16**, 363—366).—By application of the method proposed by Richarz and Neumann (Marburg Universitätsprogramm, 1909) for the detection of systematic errors in experimental observations, it is found that the conclusions drawn in a previous paper (Valentiner and Zimmer, this vol., ii, 81) are completely justified. H. M. D.

**Indices of Refraction of Binary Mixtures of Isofluidic Compounds.** (MLLE.) O. M. MORGULEVA (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 235—246).—The author has measured the indices of refraction at 20° for the *C*, *D*, *F*, and *G* lines of the following binary mixtures of non-associated, non-dissociated, isofluidic liquids, with which there is no tendency to chemical interaction: chloro- and bromo-benzenes; ethyl *isovalerate* and *isobutyl acetate*; propyl acetate and ethyl propionate; ethyl butyrate and *isobutyrate*; *m*- and *o*-xylenes; *p*- and *m*-xylenes; *o*- and *p*-xylenes; ethylbenzene and *o*-xylene; ethylbenzene and *m*-xylene; ethylbenzene and *p*-xylene. Comparison of the experimental values with those calculated on the assumption that the index of refraction is an additive property shows that only with the various mixtures of *m*- and *p*-xylenes do the differences exceed the limits of accuracy of the measurement. The conclusion is drawn that the index of refraction is additive in character, independently of the nature of the light.

A table is given which shows for the various mixtures the values of the above difference for the *C* line, the differences between the critical pressures of the two components, and the contraction constants *K* (compare Biron and Morguleva, A., 1913, ii, 174; Biron, Nikitin and Jakobson, A., 1913, ii, 175). T. H. P.

**Spectroscopy of the Electric Brush Discharge in Weak Acids and Solutions.** HAROLD SMITH (*Phil. Mag.*, 1914, [vi], **27**, 801—823. Compare A., 1913, ii, 360).—The earlier experiments have been extended in order to include the ultra-violet spectrum of the discharge, and also to investigate the differences between the positive and the negative brush.

The series and secondary spectrum of hydrogen, which are characteristic of the brush discharge, are obtained in much greater intensity when the discharge takes place in distilled water in place of aqueous solutions. These spectra depend on the potential to a much greater extent than do any of the other spectra. Since the spectra are not affected by the nature of the ions contained in the solution or by the sign of the brush, it follows that their appearance is not determined by electrolytic action.

In all salt solutions, the spectrum of the metal appears at the

negative pole only when the solution is dilute; in stronger solutions it begins to show at the positive pole, but the intensity is relatively small. For a constant current, the intensity increases with increasing concentration, and reaches a maximum for salts of the alkali metals between 0.005 and 0.01%. For solutions of magnesium sulphate, the maximum is reached at 0.02%, and for zinc sulphate at 0.1%. These solution spectra can be accounted for on the basis of the electrolysis which accompanies the discharge.

The elementary line spectrum of oxygen is found in both the positive and negative brush with distilled water. It is much more intense in the positive for solutions of acids and salts. The "water vapour" bands are equally developed in the positive and negative brushes.

H. M. D.

**The Atomic Weights of the Elements of Nebulæ.** J. W. NICHOLSON (*Compt. rend.*, 1914, 158, 1322—1323).—The author claims that the work of Bourget, Fabry and Buisson (compare this vol., ii, 313) supports his view as to the existence of a number of "simple elements" in nebulæ and Wolf-Rayet stars (compare Monthly Notices Roy. Astron. Soc., November, 1911, *et seq.*). The element they call nebulium he has called archonium.

W. G.

**Certain Doublets of Lithium and their Resolution in a Magnetic Field.** NORTON A. KENT (*Physikal. Zeitsch.*, 1914, 15, 383—385).—The four lithium lines  $\lambda$  6708.2, 6103.77, 4972.11, and 4602.37 have been found to be true series doublets corresponding with the doublets shown by the other alkali metals. A detailed examination of the behaviour of the lines in magnetic fields of varying intensity has shown that all four pairs are resolved into normal triplets in strong magnetic fields.

H. M. D.

**Ratio of the Intensities of the D-Lines of Sodium.** R. W. WOOD (*Physikal. Zeitsch.*, 1914, 15, 382—383).—From photographs of the sodium D-lines, which were obtained by exposure to a very weak sodium flame, it has been found that the intensity of the  $D_2$  line is from three to four times as great as that of the  $D_1$  line. The values of the intensity ratio recorded by previous observers vary from 1.3 to 1.6. The difference is probably due to variations in the intensity of the sodium flame, for with a very strong sodium flame the author finds that the two lines are of nearly equal intensity. It is probable that the higher value represents the true ratio, for in the case of a weak sodium flame the disturbing effects of absorption are reduced to a minimum.

H. M. D.

**Flame Reactions. II.** WILDER D. BANCROFT and HARRY B. WEISER (*J. Physical Chem.*, 1914, 18, 281—336).—The cause of the luminosity of flames is discussed in reference to the literature of the subject, and the authors draw the conclusion that a transparent gas will not emit light at any temperature unless some reaction takes place.

Some experiments have been made to determine the nature of the reactions which occur in flames containing tin and copper or

the salts of these metals. These would seem to show that the reaction  $\text{Sn} \rightarrow \text{Sn}$  produces a carmine-red luminescence, whilst the reaction  $\text{Sn} \rightarrow \text{Sn}$  is the cause of the green colour of flames containing tin. The differences between the spectra of tin chloride, bromide, and iodide are due to the absorption of light by the halogens and the salts, and also to the emission of light by the reactions of the halogens.

The colours shown by flames containing copper are said to be due to the following changes:  $\text{Cu} \rightarrow \text{Cu}'$ , giving a green colour;  $\text{Cu}' \rightarrow$  cuprous salt, a red colour; and  $\text{Cu}' \rightarrow$  cupric salt, a blue colour. The intensity of the green colour is so great that the blue colour cannot be directly observed even when the third reaction is the principal reaction taking place in the copper flame. No characteristic luminescence has yet been detected for the reverse reactions.

H. M. D.

**A New Absorption Spectrum of Oxygen in the Extreme Ultra-violet.** LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1914, 158, 1161—1164).—The spark spectra from various metals such as bismuth, aluminium, cadmium, tin, thallium, after long-continued sparking, exhibit a certain number of bands, which, while differing in intensity from metal to metal, are identical as regards structure and situation. In the interior of the band, the dark rays, which are relatively sharp at the beginning of the band, gradually broaden and extend to several Ångström units, whilst the clear spaces separating them become narrower. Five bands were discovered, three of which, namely, 1864·0—1881·3, 1882·0—1899·4, 1900—1919·2, are identical with those obtained by Steubing using a mercury arc (compare A., 1910, ii, 913). The other two, 1923·4—1936·5 and 1946·5—1957·4, are new. All the bands possess the same structure, and are capable of representation by Deslandres' formula. The results point to the probability that the absorption by the air in the extreme ultra-violet commences at  $\lambda$  1957, and is manifested by a spectrum of regular bands, very probably belonging to oxygen.

W. G.

**Calculation of the Absorption Spectrum of a Substance from its Chemical Constitution.** JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1914, 158, 1114—1117. Compare this vol., ii, 318, 319).—The authors show that it is possible to calculate the absorption spectrum of a substance containing two chromophores by means of the general formula

$$\epsilon = p\alpha_1\nu e^{-\beta_1(\nu - \nu_1 - \Delta\nu)^2} + p\alpha_2\nu e^{-\beta_2(\nu - \nu_2 - \Delta\nu)^2},$$

where  $\epsilon$  is the molecular constant of absorption,  $\alpha_1$ ,  $\beta_1$ , and  $\nu_1$ ;  $\alpha_2$ ,  $\beta_2$ , and  $\nu_2$  the constants characteristic of each chromophore;  $p$  is the hyperchrome effect; and  $\Delta\nu$  the hypsochrome effect exerted by the two groups on each other. If the two chromophores are adjacent,  $p$  is small and  $\Delta\nu$  large, while if the groups are far apart in the molecule,  $p$  is large and  $\Delta\nu$  is small. The curves measured and calculated, as given for phorone, show close agreement.

W. G.

**Absorption Spectra of Several Aromatic Nitro-compounds in Mixtures of Alcohol and Water.** FR. BORTINI (*Zeitsch. physikal. Chem.*, 1914, 87, 104—115).—The absorption spectra of picric acid, 2:4-dinitrophenol, and *p*-nitrophenol have been determined in aqueous, alcoholic, and aqueous alcoholic solutions. It is shown that the absorption spectrum of the three substances in absolute alcohol changes rapidly on the addition of small quantities of water, and that the addition of only a small percentage of water changes it entirely into the same spectrum as that obtained for an aqueous solution of the same concentration. The amount of water to be added to bring this about is largest in the case of *p*-nitrophenol and least in the case of picric acid. Thus the amount of water to be added increases with the strength of the acids. The quantity of water is not proportional to the quantity of nitro-compound in the solution. It is shown that Beer's law holds approximately for picric acid in water and in 90% alcohol solution, and for dinitrophenol in absolute alcohol solution, but it does not hold for an absolute alcohol solution of picric acid. J. F. S.

**Ultraviolet Absorption Spectrum of Buchu-camphor.** MARIO MAYER (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 439—442).—The ultraviolet absorption spectrum of synthetic buchu-camphor shows a band (maximum at 3750) as well as the usual absorption of the extreme ultraviolet rays shown by many substances. This is consistent with the existence of an equilibrium in the solution between two isomerides, but as the band corresponds with one of those of benzene, it may be due to the presence of the benzene nucleus.

R. V. S.

**Absorption Spectrum of Alcoholic Solutions of Santonin and its Derivatives in Presence of Alkali.** M. MAYER (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 442—446).—The paper deals with the absorption spectra of the reddish-violet solutions of santonin and dihydrosantonin in alcoholic potassium hydroxide, and of the hydroxysantonins in alcoholic sodium ethoxide. The examination of the visible spectra shows that the reaction, lactone  $\rightarrow$  hydroxy-acid, proceeds very similarly in all three cases, the principal band lying at 540—440  $\mu$ . The small differences noticed are, however, accentuated in the ultra-violet, where the curves of dihydrosantonin and hydroxysantonin resemble one another, whilst that of santonin differs from them.

R. V. S.

**The Spectral Structure of Substances of the Hæmoglobin Group.** FRED VLÈS (*Compt. rend.*, 1914, 158, 1206—1208).—A comparative examination of the spectra of substances of the hæmoglobin group shows a certain number of coincidences in these spectra. It seems probable that these spectra can be represented by a law similar to one of the laws of Deslandres for the band spectra of nitrogen. In the law for the spectra of these colouring matters, the superposition of at least three principal series probably intervenes. The most important series is apparently more specially

dependent on the pyrrolic nuclei of the molecule, whilst the others are dependent rather on certain of the side-chains W. G.

**Absorption Phenomena of Hæmatoporphyrin and of Mesoporphyrin in the Grating Spectrum.** O. SCHUMM (*Zeitsch. physiol. Chem.*, 1914, **90**, 1—31).—The absorption spectra of hæmatoporphyrin and mesoporphyrin in aqueous hydrochloric acid (D 1·124) differ in that the bands lie  $2\cdot5\mu$  nearer the red in the hæmatoporphyrin solution. In both cases, all the bands are displaced towards the violet when the amount of hydrochloric acid present is decreased. For instance, the position of the sixth hæmatoporphyrin band is at  $407\cdot5\mu$  in 25% acid, at  $401\mu$  in 0·1% acid. The spectrographic observation of this band permits of the detection of very small quantities of the porphyrins, as apparently almost colourless solutions show it very plainly.

Willstätter's phylloporphyrin in hydrochloric acid (D 1·124) gives a spectrum which differs only very slightly from that of mesoporphyrin.

The spectra of alcoholic solutions of hæmatoporphyrin hydrochloride and mesoporphyrin hydrochloride are very similar to one another, and are markedly altered by the merest trace of hydrochloric acid. The spectra of solutions of the same substances in alcohol containing ammonia are also very similar, the bands of the hæmatoporphyrin solution lying about  $1\text{--}1\cdot5\mu$  nearer the red.

Fresh alkaline solutions of hæmatoporphyrin hydrochloride containing a considerable excess of alkali have four absorption bands. The fifth band, described by Lewin, Miethe and Stenger (*Pflüger's Archiv*, 1907, **118**, 80), appears only when the solution has been exposed to the light of the lamp for some time. Fresh alkaline solutions show no violet band, and thereby differ distinctly from hydrochloric acid solutions.

The spectrum of alkaline solutions of mesoporphyrin hydrochloride changes with the quantity of alkali present, and with their treatment (action of the air). They show the blue band of Lewin, Miethe and Stenger only when decomposition has begun. Solutions in *N*/10-potassium hydroxide have no band in the violet, differing, thereby, from the solutions in hydrochloric acid.

R. V. S.

**Fluorescence of Gases Excited by Ultra-Schumann Waves.** R. W. WOOD and G. A. HEMSALECH (*Phil. Mag.*, 1914, [vi], **27**, 899—908 \*).—The ultra-violet luminosity observed in the neighbourhood of the condensed spark discharge (A., 1910, ii, 915) has been further investigated with an improved form of apparatus. The fluorescence excited by the radiation from the spark was resolved by a quartz prism placed in front of a quartz-fluorite achromatic lens, behind which was situated the plate on which photographs were taken. In this way, the spectra obtained in an atmosphere of oxygen, nitrogen, air, carbon dioxide, hydrogen, and coal gas have been examined. The most interesting results are those

\* and *Physikal. Zeitsch.*, 1914, **15**, 572—578.



obtained by comparing the fluorescence of gases in a stationary and in a moving condition. Some gases show a much more brilliant fluorescence when moving across the jet of rays from the spark, whilst others show no luminosity in these circumstances, although they respond vigorously to the excitation when quite stagnant.

H. M. D.

**The Biochemistry of the Action of Rays. I. The Relation-ship between the Action of Mineral Catalysts and Fluorescent Dyes.** C. NEUBERG and A. GALAMBOS (*Biochem. Zeitsch.*, 1914, **61**, 315—331).—The action of dyes from the following groups on glycerol, alanine, and tartaric acid was investigated: fluorescein, rhodamine, anthracene, acridine, triphenylmethane dyes, ethyl-red, nigrosine, and æsculine. Of the dyes investigated, sodium dichloroanthracenedisulphonate, and sodium anthracene-2:7-disulphonate, were the only substances which were found capable of inducing decomposition of chemical substances in light, and they produced in this way degradation of a large number of organic substances. The theory of the action is discussed by the authors, who reject von Tappeiner's idea that dyes act catalytically in light by virtue of their fluorescing properties. They suggest that the active substances can function as oxygen acceptors in light.

S. B. S.

**Deductions from the Valency Theory. III. Natural Rotation of the Plane of Vibration of Light.** J. STARK (*Jahrb. Radioaktiv. Elektronik*, 1914, **11**, 194—211. Compare A., 1912, ii, 403. 621; this vol., ii, 86).—The author's valency hypothesis (A., 1908, ii, 138) is applied to the rotation of the plane of polarised light. It is shown that the field of the valency electron and the electrostatic field of the light wave act on one another with a slight rotation of the plane of vibration of the light. This is developed for numbers of valency electrons up to four, and it is shown that only in the case of four unsymmetrically arranged valency electrons is there a definite resultant twist given to the plane of vibration. This conception is then applied to various cases, and the influence of changing the position of two of the substituting groups, namely, two of the valency fields, is shown to reverse the direction in which the plane is rotated. Similarly, when two of the valency fields are made equal, it is shown that no resultant twist is given to the vibration plane. The Walden inversion is discussed on this hypothesis, and an explanation of the mechanism of the change given.

J. F. S.

**Theory of the Rotatory Power of Liquids.** ARRIGO MAZZUCHELLI (*Gazzetta*, 1914, **44**, i, 410—417).—According to van't Hoff's theory and to Guye's results, the rotatory power of a substance depends on the degree of asymmetry of the molecule, but since this varies with the orientation of the molecule, it would seem that the observed rotatory power represents the mean of a number of values differing more or less among themselves. If, therefore, the molecules can be constrained, wholly or partly, to assume a

definite orientation, the optical activity should be changed. With the liquid crystals examined by Vorländer (A., 1908, i, 641), the great superiority of the rotations over those exhibited by the same compounds in solution renders it probable that the liquid crystal consists of an asymmetric aggregate of many simple molecules. That liquid crystals are highly polymerised is, indeed, indicated by their relatively slight solubility.

In the case of an electrolyte, the charges of the ions are regarded as localised at certain points occupying invariable positions in the molecule. If the electrolyte is optically active, the action of a current passing in the direction of the ray of polarised light constitutes a force applied only at one portion of the molecule, and should hence tend to orientate the latter in a definite direction. Any variation in the rotation would depend solely on the direction, and not on the sense, of the electric field, since, according to Helmholtz's principle of reciprocity, all modifications produced in a ray of light in its passage through any medium are independent of the direction of that passage.

Experiments made with solutions of potassium uranylmalate showed, however, that the passage of a current is accompanied by no appreciable alteration in the rotation. The author draws the conclusion, which is confirmed by calculation, that the directive force of the current is very small in comparison with the active forces exerted between the molecules.

T. H. P.

**Influence of Solvents on the Optical Activity of Camphoric Esters.** J. MINGUIN and R. BLOC (*Compt. rend.*, 1914, 158, 1273—1276).—The authors have determined the optical activity of the methyl, ethyl, propyl, and butyl hydrogen esters of ortho- and *allo*-camphoric acids, and also of the normal esters in alcohol, benzene, and toluene. In the ortho-series, leaving out the methyl ester, the molecular rotation is practically constant for all the esters in each solvent, but the value is much higher in solution in benzene and toluene than in alcohol. This increase with the solvent is not noticeable in the *allo*-series, whilst the normal esters, on the other hand, resemble the ortho-esters in this respect. Molecular-weight determinations in benzene solution show that the normal esters are not molecularly associated, whilst the ortho- and *allo*-esters are partly associated.

W. G.

**Kinetics of Photochemical Reactions.** FRITZ WEIGERT (*Zeitsch. physikal. Chem.*, 1914, 87, 87—92).—A criticism of Bodenstein's hypothesis of the mechanism of photochemical reactions (A., 1913, ii, 1039). It is shown that the reactions, anthracene  $\rightarrow$  dianthracene (A., 1904, ii, 463; 1905, ii, 785; 1909, ii, 632), the polymerisation of  $\beta$ -methylantracene (this vol., ii, 11, 159), *o*-nitrobenzaldehyde  $\rightarrow$  *o*-nitrosobenzoic acid (A., 1913, i, 872; ii, 370), and other reactions, all of which Bodenstein classifies as primary photochemical reactions, fail to fulfil the essential condition of primary photochemical reactions. This condition is that the quantity of absorbed light energy is strictly proportional to

the velocity of the reaction. The decomposition of ozone by chlorine in the presence of light is classified by Bodenstein as a primary reaction, but the author gives reasons which show that it must be regarded as a secondary reaction. J. F. S.

[Kinetics of Photochemical Reactions.] MAX BODENSTEIN (*Zeitsch. physikal. Chem.*, 1914, 87, 93—103. Compare preceding abstract; also Bodenstein, A., 1913, ii, 1039).—An answer to Weigert; it is shown that the non-agreement of the reaction anthracene  $\rightarrow$  dianthracene, and the polymerisation of  $\beta$ -dimethylanthracene, with the condition for primary reactions, is to be explained by the assumption that in the process, after the initial separation of an electron from the reacting molecule, the positive residue does not combine quickly enough with a similar residue, and consequently must recombine with an electron, with the reformation of the original molecule. This brings about a decrease in the reaction velocity, which ought to have resulted from the absorbed energy. J. F. S.

Photochemistry of Ammonia. ALFRED COEHN and GEORGES PRINGENT (*Zeitsch. Elektrochem.*, 1914, 20, 275—278).—It has been shown by Regener (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1228), Berthelot and Gaudechon (A., 1913, ii, 458), and others that ammonia is practically completely decomposed by ultra-violet light. The object of the present work was to see whether this decomposition was complete or whether a determinable amount of ammonia still remained undecomposed. Ammonia was sealed up in quartz tubes and exposed to the light of a quartz mercury lamp, and the gas examined after various periods of exposure. It was found that after one hour ammonia was still present, but after six hours ammonia could not be detected by means of Nessler's reagent, thus showing that the decomposition was complete. Weigert (A., 1908, ii, 5) has shown that when a mixture of nitrogen and hydrogen is sensitised by the addition of chlorine, ammonia is formed by ordinary visible light. The authors have passed similar mixtures, dry and damp, through a quartz tube which passed down the centre of a quartz mercury lamp, and have been unable to show the formation of ammonia even in such small amounts as would give the reaction with Nessler's reagent. J. F. S.

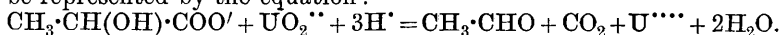
Photochemistry of the Hydrates of Chromic Chloride. B. KURILOV (*Kolloid. Zeitsch.*, 1914, 14, 171—172. Compare A., 1913, ii, 31).—The behaviour of the green and violet solutions of chromic chloride on exposure to light has been examined by measurements of the extinction coefficient for light of wave-length  $\lambda = 485 \mu$ . Comparative observations were made on solutions which were kept in the dark. The author considers that the results afford evidence of a photo-effect in the transformation of the green into the violet salt. H. M. D.

Supposed Chemical Changes in Light. E. SERNAGIOTTO and A. BARON HOSCHEK (*Zeitsch. physiol. Chem.*, 1914, 90, 437—440).—A

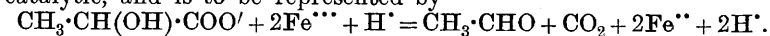
repetition of Inghilleri's work on this subject (A., 1911, i, 354, 709; 1912, i, 831) does not give the results obtained by that author. When formaldehyde and water are exposed to light, no methyl alcohol is formed. When formaldehyde, water, and methyl alcohol are exposed to light, methylal is produced, but not methyl formate. The exposure to light of a mixture of formaldehyde, water, and ammonia yields hexamethylenetetramine, which is presumably Inghilleri's "new alkaloid." When a mixture of glycerol and oxalic acid is kept either in the light or in the dark, formic acid is produced; a relatively small quantity of butyric acid can also be found, but this can be obtained in control experiments with glycerol alone.

R. V. S.

**The Photochemical Decomposition of Lactic Acid in Presence of Uranyl Sulphate.** IWAN BOLIN (*Zeitsch. physikal. Chem.*, 1914, 87, 490—506).—The decomposition of lactic acid by light in the presence of uranyl sulphate has been examined with the object of determining whether the uranyl salt acts catalytically or whether the action is purely one of oxidation by the uranium salt. The experiments were carried out in flat, thin glass flasks, in which the reaction mixture, in the absence of air, was subjected to the light from a carbon arc. The reaction consists in the decomposition of lactic acid into acetaldehyde and carbon dioxide. Experiments were also carried out with sodium lactate under the same conditions. It is shown that the amount of acetaldehyde and carbon dioxide produced is proportional to the amount of uranyl sulphate reduced to the uranous condition, and the reaction is to be represented by the equation:



Consequently, in the absence of oxygen, the reaction is not catalytic. Experiments were then carried out in which the original conditions were maintained, with the exception that oxygen was slowly passed through the solution, and in this case the reaction is strictly catalytic, since the uranous salt is oxidised by the oxygen to the uranic condition, and can consequently convert an indefinite amount of lactic acid into acetaldehyde. The reaction is strictly photochemical, for there is no change at all in the dark, and the effect of sunlight is the same as that of the arc light. Experiments were then carried out with ferric sulphate as the oxidising agent, and the conditions here found to be the same as in the preceding case, namely, that in the absence of oxygen the reaction is not catalytic, and is to be represented by



In the presence of air or oxygen, this reaction is catalytic.

J. F. S.

**Influence of Occluded Gases on the Selective Photoelectric Effect.** R. POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1914, 16, 336—344).—According to Wiedmann and Hallwachs (this vol., ii, 162), the photo-electric activity of potassium is dependent on the presence of gases in the surface layers of the metal. In

view of the importance of this result for the explanation of the nature of the selective photo-electric effect, the authors have made a further examination of the photo-electric behaviour of potassium on similar lines to those adopted by Wiedmann and Hallwachs. The observations show that potassium which has been boiled for 180 to 430 hours at  $350^{\circ}$  to  $400^{\circ}$  in the highest vacuum attainable by the continuous action of a Gaede pump, exhibits the same photo-electric activity as the original metal from which the gases have not been removed when light of frequency corresponding with the selective effect is allowed to act in the metal. Under the above treatment, the gas evolution per c.c. of potassium was reduced to  $4 \times 10^{-4}$  c.c. of hydrogen per hour, whereas the original metal was found to give off 2 c.c. of hydrogen per hour under similar conditions.

The authors draw the conclusion that the presence of hydrogen in the metal is not essential for the development of the selective photo-electric effect.

H. M. D.

**The Tyndall Phenomenon in Liquids.** WALTHER KANGRO (*Zeitsch. physikal. Chem.*, 1914, **87**, 257—292).—Attempts have been made to prepare an optically clear liquid by the settling of precipitates in liquids; the liquids were examined by means of a photographic photometric method, and it is shown that by this method optically clear liquids cannot be obtained. It is shown also that the use of the light deflection as a differential method is not possible. The Rayleigh theory of the dependence of the intensity of the deflected light on the wave-length is confirmed qualitatively, and the conclusion is drawn that deflected light of different coloured solutions cannot be directly compared. The great difference in the nature of the deflected light from crystalloid and colloid solutions is confirmed. A method of producing optically clear solutions by means of distillation was tried, and in this way it is shown to be possible to effect a purification of the solutions, but not to obtain absolute optical homogeneity.

J. F. S.

**The Variations in the  $\alpha$ -Rays Emitted from a Radioactive Solution.** THE SYEDBERG (*Physikal. Zeitsch.*, 1914, **15**, 512—516).—In place of an earlier view that the probability variation in the emission of  $\alpha$ -particles from a radioactive solution involves the spontaneous concentration variations according to the kinetic theory, the author accepts Schweidler's result that there should be no difference between a radioactive solution and solid, and gives a simple proof of it. The experiments show, however, a very large departure from the theoretical formulæ in case of solutions. The part of the radioactive solution near the bounding surfaces gives out radiation of special character, the intensity of which depends on the nature and treatment of these surfaces. The variations for this "surface radiation" obey the simple law for solids. Working with liquid solutions of polonium or gaseous solution of radium emanation, the surface effect can be eliminated, and the frequency numbers experimentally found agree with another formula, which

departs so largely from the simple formula that the difference cannot be due to error of experiment. A solution of radium-barium chloride was laid on a fluorescing diamond and covered with a cover-glass, kept at a distance of 0.1 mm. from the diamond by a ring of platinum wire. The radium was carefully freed from disintegration products before use. The results showed clearly that the  $\alpha$ -particles from the inner part of a radioactive solution do not obey the simple law, but another, which cannot be theoretically explained. The law experimentally obeyed was derived from a theory which implied a connexion between the concentration and the variations of disintegration, which shows that there is some connexion between these. The cause of this connexion, however, remains unknown. It is possible that along the paths of the  $\alpha$ -rays there may be a short-lived accumulation of radioactive atoms, in the neighbourhood of each disintegrating atom, which may account for the effect, but there is no experimental or theoretical foundation for such an accumulation. F. S.

**The Passage of  $\alpha$ -Particles through Hydrogen.** E. MARSDEN (*Phil. Mag.*, 1914, [vi], 27, 824–830).—In the collision of an  $\alpha$ -particle with an atom of hydrogen, on the nucleus theory of the atom, if the direction of projection of the hydrogen atom makes the angle  $\theta$  with the direction of the  $\alpha$ -particle, and the latter is moving with velocity  $V$ , the velocity of the hydrogen atom will be  $1.6V \cos \theta$ . In an “end-on” collision, where  $\theta=0$ , it can be deduced that the “H-particle” so resulting will have a range about four times that of the  $\alpha$ -particle. In the first experiments, a movable source of 25 millicuries of radium emanation contained in an  $\alpha$ -ray tube was placed in a wide tube filled with hydrogen at variable pressure, and the scintillations counted on a zinc screen cemented to the end of the wide tube. Whereas the  $\alpha$ -rays did not traverse a distance beyond 24 cm. in hydrogen at atmospheric pressure, scintillations, similar to, but less intense than, those produced by  $\alpha$ -particles, at the rate of ten per minute, were observed at 38 cm., and these continued in diminishing number up to a distance of 82 cm. In air at 17 cm. pressure, in which the range of the  $\alpha$ -particle was the same as that in hydrogen at atmospheric pressure, only 0.5 scintillation per minute were observed at a distance of 26 cm. By inserting a screen of aluminium leaves, sufficient to stop the  $\alpha$ -particles, near the source the H-particles were suppressed; but with the same screen near the zinc-sulphide screen, the scintillations were again observed. This shows that these scintillations have their origin in the hydrogen by the impact of the  $\alpha$ -particles.

In the next series of experiments, the hydrogen was contained in a metal vessel at 4.5 atmospheres' pressure, and the distances between source and screen reduced to one-fourth. A magnetic field was used to deflect the  $\beta$ -rays. An arrangement of metal foils mounted on a disk was employed, so that any one of four different foils could be introduced directly in front of the zinc-sulphide screen without opening the apparatus. The pressure was

one-sixth greater than that which would stop the  $\alpha$ -particles. In experiments on the absorption of the H-particles in aluminium, copper, tin, and platinum, a similar law of absorption to that for the  $\alpha$ -particles was found, the weights per unit area of different metals necessary to produce the same absorption being proportional approximately to the square roots of the atomic weights. Experiments are in progress to measure the number of H-particles produced by a known number of  $\alpha$ -particles of definite velocity, and their distribution in direction, by passing the  $\alpha$ -particles through films of substances rich in hydrogen, such as indiarubber or paraffin wax. F. S.

**Intensity Distribution in the Magnetic Spectrum of the  $\beta$ -Rays of Radium  $B+C$ .** J. CHADWICK (*Ber. Deut. physikal. Ges.*, 1914, **16**, 383—391).—The magnetic spectrum of the  $\beta$ -rays emitted by radium  $B+C$  has been investigated by Geiger's counting method (A., 1913, ii, 745), and also by a method depending on the ionisation produced by the rays.

The results obtained by both methods indicate that the  $\beta$ -radiation yields a continuous spectrum, on which is superposed a line spectrum of relatively small intensity. Both methods indicate the existence of four lines (or groups of lines) in the region of the slowly moving  $\beta$ -rays. The observations are accordingly at variance with the results obtained by photographic methods, for these are supposed to indicate that the  $\beta$ -radiation of radium  $B+C$  consists of a large number of groups of homogeneous rays. The discrepancy is attributed to the very large variation in the sensitiveness of photographic plates for small changes in the intensity of the rays.

H. M. D.

**The Wave-lengths of the Soft  $\gamma$ -Rays from Radium- $B$ .** SIR ERNEST RUTHERFORD and E. N. DA C. ANDRADE (*Phil. Mag.*, 1914, [vi], **27**, 854—868).—It was anticipated that each of the various homogeneous types of  $\gamma$ -rays given by the radio-elements should give definite line-spectra when reflected from crystal surfaces. The determination of the wave-lengths of  $\gamma$ -rays by this method was found to be more difficult than for the X-rays, long exposures, of twenty-four hours or more, being necessary, with special precautions to protect the plate from the penetrating  $\gamma$ -rays and from the swiftest primary and the secondary  $\beta$ -rays. The source was a tube of emanation 1 cm. long, behind a massive block of lead, in a strong magnetic field, provided with a slit 3 mm. wide. The crystal of rock-salt or heavy spar was mounted on a turn-table, and the plate and source were equidistant from the crystal. The lines due to the penetrating  $\gamma$ -rays of radium- $B$  and - $C$  are faint compared with those due to the soft  $\gamma$ -rays of radium- $B$ , and have not yet been fully investigated. The stronger lines of radium- $B$  appear with great distinctness. The main features of the spectrum with a rock-salt crystal are two strong lines at almost exactly  $10^\circ$  and  $12^\circ$  ( $10^\circ 3'$  and  $12^\circ 3'$ ), and a number of fainter ones between  $8^\circ$  and  $14^\circ$ . There is also a large group of lines, too faint to measure

accurately, between  $18^\circ$  and  $22^\circ$ , some of which are probably second-order repetitions of the first order. With a heavy-spar crystal the lines for the soft rays were less intense. The angles of the two strong lines of radium-*B* were  $7^\circ 52'$  and  $9^\circ 28'$ , which, multiplied by the factor 1.278, as determined experimentally with the *X*-rays for the two crystals, agree closely with those found with rock-salt, and shows that the lines are true diffraction-lines. The wave-lengths of the two strong lines of radium-*B* are 0.982 and  $1.175 \times 10^{-8}$  cm. The detailed structure of the images of these lines shows the sharp and well-marked edges and less intense centre characteristic of  $\alpha$ -rays when the image of a cylindrical  $\alpha$ -ray tube produced through a narrow parallel slit is photographed by its own rays.

The spectrum of radium-*B* was examined to see whether it was identical with that of the *X*-ray spectrum of lead, as is to be expected on the general theory of Soddy and Fajans, since radium-*B* has been shown by Fleck to be isotopic with lead. Moseley has found for the nucleus charge, or atomic number, of gold, 79, so that of lead should be 82, and the strongest line of lead, as calculated from this number, should be reflected from rock-salt at  $12^\circ 07'$ , which is in very close agreement with the angle,  $12^\circ 05'$ , actually found.

To test the point directly, the  $\gamma$ -ray spectra of radium-*B* was compared with the strong, characteristic "L" type of radiation excited by the  $\beta$ -rays of radium-*B* and -*C* in lead, as discovered by Richardson. A piece of lead was put in place of the emanation tube and exposed to the  $\beta$ -rays from the emanation tube, which was placed at one side out of the line through the slit. Only a few faint lines of lead could be measured under these conditions. Two of these gave reflexion angles of  $10^\circ 2'$  and  $12^\circ 0'$ , in good agreement with the strong lines of the radium-*B* spectrum. On substituting the piece of lead for a piece of platinum, the position of the lines was quite distinct, in fair agreement with those given by Moseley and Darwin for platinum. The reflexion angles of the  $\gamma$ -rays of radium-*B* are believed to be correct to 0.3%, whereas a mistake of one unit in the atomic number would make a difference of 2% in the angle. According to radioactive calculation, the atomic weight of radium-*B* is 214, whilst that of lead is 207. These results, therefore, confirm the deduction of Soddy and Fajans in an unexpected way, and verify the hypothesis that two elements of different atomic weights may have identical spectra and identical chemical properties.

F. S.

**The Absorption of  $\gamma$ -Rays.** S. OBA (*Phil. Mag.*, 1914, [vi], 27, 601—607).—The effect of passing  $\gamma$ -rays through various metals before determining their absorption coefficient in a given metal has been examined in detail. The first metal acts always to "harden" the rays, but with increasing thickness the effect appears to approach a limiting value. Rays so hardened gradually become softer as they pass through increased thicknesses of the second metal, and may even regain their initial penetrating power. The



effects are complicated by the heterogeneity of the rays used, which were a mixture of the  $\gamma$ -rays of radium-*B* and -*C* derived from a tube of radium emanation. F. S.

**Method for the Production of Preparations of Radium Emanation.** ERICH EBLER (D.R.-P. 270765).—The method consists in the adsorption of radium emanation by colloidal silicic acid, which, after removal from the emanation, shows the same period of decay as the emanation itself. F. S.

**The Activity of Freshly-formed Radium Emanation.** HORACE H. POOLE (*Phil. Mag.*, 1914, [vi], 27, 714–718).—A test of the activity of the radium emanation at different periods from the moment of its formation showed no variation with age. A steady blast of air was swept over a film of radium salt, deposited on a platinum ribbon maintained at a white heat, through a series of vessels. The radiation in two vessels, one at the beginning and one at the end of the series, was compared, the direction of the air current through the vessels reversed, and the measurements repeated. A difference of 5% in the activity would have been observed, but none was found. F. S.

**Determination of the Periods of Transformation of Thorium and Actinium Emanation.** P. B. PERKINS (*Phil. Mag.*, 1914, [vi], 27, 720–731).—In order to determine these constants more accurately, the ratio of the initial to the final activity, and the time of decay, were made greater by initially introducing capacities in parallel with the leaf-system, and cutting them out as the emanation decayed. Thus, for the actinium emanation, the decay was followed for forty-three seconds, in which time the activity fell to less than 1/2000th of the initial value. The half-value periods for thorium and actinium emanations were found by this method to be  $54.53 \pm 0.041$  and  $3.92 \pm 0.004$  seconds respectively, the corresponding values for the  $\lambda$ 's being 0.01271 and 0.1768/(sec.)<sup>-1</sup>. F. S.

**The Transformations in the Active Deposit of Actinium.** E. MARSDEN and P. B. PERKINS (*Phil. Mag.*, 1914, [vi], 27, 690–703).—A search was made for a small proportion of  $\alpha$ -rays of longer range than 5.4 cm. in the  $\alpha$ -radiation of actinium-*C*, which was covered with a standard thickness of mica of known stopping power and mounted at a fixed distance from a zinc sulphide screen in a vessel in which the pressure of air could be varied. The results indicated that about 0.15% of the particles penetrate much further than 5.4 cm. The effects observed were small, and difficult to measure accurately. The range of these long-range  $\alpha$ -rays is 6.4 cm. The effect was shown not to be due to radium-*C* or radiothorium by special experiments, and the conclusion is drawn that they were not due to recoiled actinium-*X*, although the range differs little from that of the  $\alpha$ -particles of actinium-*A*, on account of the nearly constant ratio obtained in the experiments and the rate of decay of the long-range  $\alpha$ -particles.

No evidence of this small proportion of long-range  $\alpha$ -particles can be obtained from a study of the range-ionisation curve, contrary to the earlier observations of Mlle. Blanquies (A., 1909, ii, 634). It was found that the curves for polonium, actinium-C, and thorium-C are not exactly superimposable, as might have been anticipated, although not previously observed, owing to the straggling of the longer range  $\alpha$ -rays and their becoming less homogeneous in their passage, some of the  $\alpha$ -particles suffering more severe atomic encounters than others. A scheme of transformation, analogous to that accepted for radium-C and thorium-C, is put forward, in which actinium-C suffers a dual transformation, 99.85% of the atoms expelling first an  $\alpha$ - and then a  $\beta$ -ray, the remainder expelling the rays in the inverse order. F. S.

**The Ionometer and its Application to the Measurement of Radium and Röntgen Rays.** H. GREINACHER (*Physikal. Zeitsch.*, 1914, 15, 410—415).—A simple and transportable form of direct-reading instrument is described, by means of which the ionisation in gases can be determined very conveniently. The construction is based on the same principle as that which has been adopted in the Bronson instrument. One of the most important differences between the two forms lies in the fact that no quadrant electrometer is required in connexion with the new type of ionometer.

It is shown that the apparatus may be employed for the measurement of radium and radium emanation, and also for the determination of the intensity and the hardness of Röntgen rays.

H. M. D.

**Origin of Thermal Ionisation from Carbon.** O. W. RICHARDSON (*Proc. Roy. Soc.*, 1914, A, 90, 174—179).—The conditions obtaining in the experiments made by Pring (A., 1913, ii, 1005) are discussed, and the author draws the conclusion that the experiments in question cannot be held to prove that the emission of electrons from heated carbon is a consequence of chemical action between the carbon and the surrounding gases, or to invalidate the theory which regards this effect as a fundamental property of the heated substance.

It is probable that in the experiments at the highest temperatures, none of the electrons emitted by the carbon would reach the collecting electrode, and in regard to the experiments at lower temperatures it cannot be said, with certainty, that the observed thermionic currents are smaller than those which would be expected on the basis of the thermionic theory.

The fact that the observed currents increase with increasing pressure of the surrounding gas is to be expected, on account of (a) the interference of the gas molecules with the motion of the electrons; (b) the combination of electrons with atoms and molecules of the gas. The large specific effects observed in certain cases would suggest that the combination factor is of special importance.

H. M. D.

**Thermionic Currents in High Vacuum. II. The Electron Emission from Tungsten and the Effect of Residual Gases.** IRVING LANGMUIR (*Physikal. Zeitsch.*, 1914, 15, 516—526).—In absence of gas, the current carried by the electrons from a hot cathode reaches a limiting value, but in the presence of gas, and with potentials above 40 volts, there is commonly a strong positive ionisation, which diminishes the electronic emission and permits the flow of a larger current through the gas. Contrary to the view generally held, the presence of gas diminishes the electronic emission at low temperatures, and the effect vanishes at high temperatures. The constant  $b$  of the equation  $i = a\sqrt{T}e^{-b/T}$ , expressing the relation between electronic emission and temperature for tungsten, is diminished by oxygen, nitrogen water vapour, carbon monoxide, or carbon dioxide, but argon, mercury vapour, and hydrogen have no effect. In a perfect vacuum,  $a = 23.6 \times 10^6$  and  $b = 52,500$ , corresponding with a current of 0.0042 ampere per  $\text{cm}^2$  at  $2000^\circ$ . The action of nitrogen, but not of oxygen, depends on the anode potential, and in many cases a feeblar current passes with 240 than with 120 volts.

The theory is proposed that the action of gases in altering the saturation current is due to the formation of compounds on the surface of the cathode, either by direct reaction (oxygen), or by reaction with positive ions (nitrogen), or by volatilisation in consequence of the bombardment of positive ions. The conclusion is reached that the electronic emission from a solid body at high temperature in a very high vacuum under proper conditions is an important specific property of the substance, and is not due to secondary causes.

F. S.

**Ionisation Produced by Certain Substances when Heated on a Nernst Filament.** FRANK HORTON (*Proc. Camb. Phil. Soc.*, 1914, 17, 414—424. Compare A., 1913, ii, 272).—Experiments have been made to determine whether the emission of negative electricity by calcium oxide, heated on a Nernst filament, is comparable with that obtained when the oxide is heated as a superficial layer on platinum, and, further, to ascertain whether the emission of positive electricity from a Nernst filament is increased by covering the filament with a layer of sodium phosphate.

The observations show that the negative emission from the glowing filament is enormously increased by a covering of calcium oxide, and is of the same order of magnitude as the negative emission from platinum covered with a thin layer of oxide. This result indicates that the emissive effect is in no way connected with the metal in contact with the calcium oxide.

The positive emission from the glowing filament is increased by a coating of sodium phosphate, the increase depending on the pressure of the surrounding gas. Curves showing the variation of the thermionic current with the pressure at  $1422^\circ$  are recorded, and from these it is apparent that the sodium phosphate exerts a considerable influence on the nature of the current-pressure curve. This influence is supposed to be due to the increased forma-

tion of positive ions, and to the change in the nature of the gaseous atmosphere in contact with the filament. H. M. D.

**The Ionisation of Water Vapour by the  $\alpha$ -Rays of Polonium.** B. BIANU (*Le Radium*, 1914, 11, 65—69).—A special apparatus for the determination of the Bragg ionisation-distance curve in water vapour at temperatures up to  $100^{\circ}$  was constructed, which was airtight and insulated by amber, which was not affected by the high temperature and the water vapour so long as it did not condense. The range of the  $\alpha$ -particle of polonium was determined in water vapour at temperatures between  $75^{\circ}$  and  $100^{\circ}$ . At the last temperature it was 6.2 cm., whereas in air at  $100^{\circ}$ , calculated from its density, it should be 5.08. The ratio 0.819 is only 3.5% different from that calculated from the square root of the atomic-weight law. The Bragg curve in water vapour at  $83^{\circ}$ , using a tension of 580 volts per cm., was compared with that in dry air at 26.3 cm. pressure, the range of the  $\alpha$ -particle in the two cases being the same. The water-vapour curve departed from the air curve in the same sense as Taylor found for hydrogen; but the areas of the surfaces of the two curves were the same, showing that the total ionisation in water vapour is sensibly the same as that in air.

The ionisation curve as a function of the potential (saturation curve) in water vapour at  $83^{\circ}$  showed that the third part of the curve, due to ionisation by collision, began at 750 to 800 volts per cm. A comparison of the curve with the theory of Townsend showed great divergences at higher pressures. F. S.

**Method for the Preparation of Therapeutically Useful Compounds of Radium.** E. MERCK and WILH. EICHHOLZ (Austrian Patent 63166).—The method is characterised by the feature that the solution of the radium salt is precipitated by solutions of selenites, selenates, tellurites, or tellurates of the alkalis or alkaline earths, and the precipitation completed with alcohol. The selenium or tellurium is employed, not as the healing agent, as in Wassermann's method, but as transporting agent to carry the radium into the diseased tissue when the compound is administered intravenously or subcutaneously. F. S.

**Method for the Separation of Mesothorium and Radium in the Manufacture of Thorium from Thorium-containing Minerals.** KARL SCHWAB (D.R.P. 269541).—In this method the water used for diluting the product obtained by heating the monazite with sulphuric acid is saturated with barium sulphate before use by the addition of from one-third to two-thirds of the quantity of barium, mixed with the monazite initially. The product, diluted with two or three times its volume of water, is separated from the heavy, unattacked constituents of the sand, and the muddy liquid poured into thirty to sixty times as much water, containing barium, as the quantity of the sulphuric acid product used, when the mesothorium-radium-sulphate is completely precipitated with the crude thorium phosphate. F. S.

**The Distinguishing Between Radium Preparations and Between Mesothorium Preparations of Unequal Age by means of their Radiation.** OTTO HAHN (*Le Radium*, 1914, 11, 71—74).—Five different preparations were used, consisting of: (1) pure radium bromide; (2) freshly prepared commercial mesothorium bromide; (3) ditto, two years old; (4) new bromide of mesothorium free from radium; (5) radiothorium, separated from mesothorium a long time ago, and purified by precipitation. The absorption curves of the  $\gamma$ -radiations in lead were determined in the same electroscope, of lead 3.3 mm. thick, and showed that it was possible to distinguish certainly between all the preparations. The activity of mesothorium is measured commercially through 5 mm. of lead. Calling the radiation at this thickness 100, the following table shows the radiations unabsorbed by further thicknesses of lead for the five preparations above. In the first column the thickness of the lead electroscope is included:

Mm. of lead.	(1)	(2)	(3)	(4)	(5)
5	100	100	100	100	100
10	68.1	70.0	70.3	69.7	74.7
15	49.7	60.07	32.15	49.4	54.2
20	37.3	37.0	38.8	36.1	42.3
25	28.65	27.3	29.5	26.1	33.5
30	22.0	20.4	22.7	19.14	26.8
35	16.92	15.45	17.65	13.97	21.65
40	13.38	11.42	13.8	10.54	17.6
45	10.63	8.65	10.65	7.75	14.27

The old mesothorium and the radium have initially and finally the same ratio, but may be distinguished at the intermediate thicknesses 10 and 20 mm. In the last line, if the value for radium is made 100, the values for the other preparations are: (2) 81.4; (3) 100.2; (4) 73.3; (5) 134.3 (compare Russell and Soddy, A., 1911, ii, 88). F. S.

**Range of  $\alpha$ -Particles in Air at Different Temperatures.** A. F. KOVARIK (*Le Radium*, 1914, 11, 69—71).—The range of  $\alpha$ -particles from polonium has been determined in an apparatus, similar to that of Geiger and Nuttall, at temperatures between 90° and 362° A. (−183° and 89°). It was found that the range divided by the absolute temperature was constant, except for liquid-air temperature, but the difference is probably not greater than the experimental error at this temperature. From 90° to 362° A. the range increases from 1.13 to 4.73 cm. F. S.

**The Influence of the Presence of Other Substances on the Adsorption of Uranium- $X_1$ .** (On the Question of "Identical" Radio-elements.) H. FREUNDLICH, W. NEUMANN, and H. KAEMPFER (*Physikal. Zeitsch.*, 1914, 15, 537—542).—The observation of Ritzel on the prevention of the adsorption of uranium- $X_1$  by blood-charcoal by traces of thorium has been repeated and extended, and the explanation of Soddy that the effect is connected with the isotopism of the two elements has been found not to hold good. In absence of thorium, the  $\beta$ -activity of the uranium- $X_1$  in 11 c.c. of 0.55*N*-uranyl nitrate, shaken 230 hours

with 20 mg. of charcoal, was reduced from 154 to 26.8. In presence of 4 millimols per litre of thorium nitrate, the adsorption is completely prevented, and 0.0004 millimol. (1 mg. in 5 litres) has a clearly perceptible effect. But that this is not a specific action of isotropic thorium atoms is shown by other substances, zirconium salts, and even benzoic acid, producing a similar effect, the latter clearly perceptible at 0.006 millimol. per litre. The effect is explained as due to the substance in greater concentration driving out the first from the surface (*verdrängende Adsorption*). Any other substance, not a radio-element, adsorbed by charcoal is driven out by thorium nitrate. The adsorption of the copper ion was measured in very small concentration by its catalytic action on persulphate and iodine ions in presence of ferro-salts. A solution of a little copper nitrate and much sodium nitrate was mixed with water or equal volumes of thorium nitrate solution and 100 mg. of charcoal, and shaken sixty hours. The concentration of the copper ion in the solution fell from 0.0472 millimol. per litre in presence of 0.39 (millimol. per litre) of thorium nitrate to 0.0106 in absence of thorium, 0.004 of thorium nitrate producing a detectable effect. Further, it was shown that uranium- $X_1$  adsorbed in charcoal was driven out by subsequent addition of thorium nitrate to the solution.

No grounds are held to exist for the view that isotopic elements are more nearly related than the members of the rare earths. "Chemical mimicry" is often favoured by small concentration, and may be expected to be strongly shown by isotopic elements, and it is not wonderful that their behaviour is what it is. An observation of Ritzel that thorium emanation prevents the adsorption of uranium- $X$  by charcoal was shown to be due to traces of thorium nitrate carried over in the stream of emanation. F. S.

**The Action of Colloids on Radioactive Products in Solution.** T. GODLEWSKI (*Phil. Mag.*, 1914, [vi], 27, 618—632).—To account for the fact that radium- $C$  in pure water is deposited equally well at the cathode as at the anode, whereas radium- $A$  is deposited only on the anode and radium- $B$  only on the cathode, the hypothesis is advanced that in the  $\alpha$ -ray change of radium- $A$ , the radium- $B$  atom produced is expelled from the colloidal aggregate, whereas in the  $\beta$ -ray change of radium- $B$ , the radium- $C$  atom produced is not expelled. Hence the aggregate moves to the cathode when it contains an excess of radium- $B$  atoms, and to the anode when most of these have disintegrated and produced radium- $C$ .

The effect of various colloids, both negative and positive, on the products of the radium emanation in solution were tried. Arsenious sulphide, colloidal platinum, and other negative colloids make the products depositing at the cathode diminish in amount, and ultimately disappear. With increasing concentrations they are then deposited on the anode. Positive colloids, such as ferric oxide, act exactly oppositely. The radioactive colloids are first precipitated by addition of a colloid of opposite sign, which at higher concentrations adsorbs them and inverts their sign. The

compound hydrosols containing both radium-*B* and -*C*, which have a smaller positive charge than the initial ones containing radium-*B* only, are first precipitated, so that at a certain concentration pure radium-*B* is deposited at the cathode. If the colloid added is precipitated by addition of a suitable precipitant, such as aluminium sulphate solution, all the radioactive products are found in the precipitate. It is thus easy to concentrate a powerfully radioactive substance on a few milligrams of precipitated hydrosol, such as gold or platinum.

The precipitation on the filter-paper of radioactive products during filtration is shown to be connected with the known fact that negative colloids rise with the water when filter-paper is immersed in the solution, but positive hydrosols are precipitated in the immersed part of the paper. Aluminium sulphate and dilute hydrochloric acid added to a solution of emanation in water increase the amount of active deposit left on the paper on filtration. With stronger acid, the filter is inactive. If all the radioactive colloids are transformed into negative colloids by addition of a citrate, the activity of the filter may be greatly reduced.

A sheet of filter-paper was partly immersed in water containing emanation. In the immersed part, radium-*B* and -*C* are in the same relative amount as in the solution, but in the higher levels only pure radium-*C* is noticeable. Only the negative hydrosols and radium-*A* and -*C* can ascend the paper, and the former can travel only for a short distance, for on transformation into the *B*-member it is stopped. These results afford new and simple methods of concentrating radioactive products by filtration and burning the paper, which are applicable to all products forming positive hydrosols. It has been employed to remove uranium-*X* from uranium at a strength of 10 grams of uranyl nitrate to the litre, and is no doubt widely applicable. F. S.

### The Radioactivity of Some Type Soils of the United States.

RICHARD B. MOORE (*J. Ind. Eng. Chem.*, 1914, 6, 370—374).—The samples of soil used in this investigation were obtained by sieving through a sieve of six meshes to the linear inch, and grinding to an impalpable powder. Strutt's method (*A.*, 1906, ii, 411, 716) of getting the material into solution was used. The radium content was determined by introducing the emanation from the solution into an electroscope of the C. T. R. Wilson type, as modified by Boltwood (*A.*, 1904, ii, 666), the standard used being that also suggested by Boltwood (*loc. cit.*).

The average activity of the fourteen soils investigated is  $1.97 \times 10^{-12}$  grams of radium per gram of soil, that of the sub-soils being  $1.52 \times 10^{-12}$ . In the majority of cases, the soil or sub-soil which has the highest activity also has the largest amount of barium plus strontium. The amount of rare earths present in the soils was so small that no conclusion can be drawn as to the relation between the rare-earth content and the activity.

The thorium content of five soils was determined, using the method employed by Joly in determining the thorium content of

rocks and minerals. The average content, namely, about  $4 \times 10^{-5}$  gram per gram of soil, is much higher than Joly's average,  $1.58 \times 10^{-5}$ , for rocks, and much higher than the results obtained by Blanc for Roman soils (A., 1909, ii, 366, 459). T. S. P.

**The Measurement of the Radioactivity of Springs.** C. ENGLER, H. SIEVEKING, and A. KOENIG (*Chem. Zeit.*, 1914, **38**, 425—427 and 446—450).—This paper contains details of the measurement of the radioactivity of natural waters by means of the "fontaktoscope," tables in connexion with it, the drawing and transport of the water, the sources of error, and improved forms of the measuring instruments employed. F. S.

**Determination of the Electric Elementary Quantum by Thermo-mechanical Methods.** FRIEDRICH WÄCHTER (*Ann. Physik*, 1914, [iv], **44**, 127—144).—The author criticises the modern theory of electricity, and maintains that the elementary quantum cannot be regarded as an ultimate and fundamental constant of nature. The electrons are supposed to represent the smallest units of matter which owe their electrical charge to their kinetic energy. If the mechanical view is admitted as a working hypothesis, the so-called elementary quantum may be deduced from: (1) the kinetic energy of gas molecules; (2) the specific heat of solid substances; (3) the specific heat of liquid substances; (4) the specific heat of gases at constant volume. The agreement between the values obtained by these different methods is practically as good as that shown by the values obtained by methods which are based on the generally accepted modern views. H. M. D.

**[Electrical] Resistance of some Iron Nickel Alloys.** A. P. SCHLEICHER and W. GUERTLER (*Zeitsch. Elektrochem.*, 1914, **20**, 237—252).—Measurements of the electrical resistance have been made with wires of iron-nickel alloys containing respectively 35.25% Ni, 30.6% Ni, and 25.2% Ni. The measurements were made at temperatures from 0° to about 1000° in a vacuum. The object of the experiments was to determine the position of the equilibrium curve for the reversible and irreversible iron-nickel alloys. A number of curves are given, and from those obtained from the most trustworthy experiments, it is seen that a perfect parallelism exists, from which the conclusion is drawn that all three lie in a homogeneous field of the condition diagram, which extends for 25% nickel alloy upwards to 900°, for 30% nickel alloy up to 700°, and for 35% nickel alloy upwards to 420°. It is held that a second homogeneous field lies above this, and the transition curve probably lies between them. J. F. S.

**Electrical Conductivity and Pressure of Flow of Alloys of Potassium and Rubidium.** N. S. KURNAKOV and A. I. NIKITINSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 360—371).—The composition-electrical conductivity curve for mixtures of metals forming isomorphous mixtures in all proportions is a continuous curve exhibiting a minimum, the corresponding curve connecting the



composition with the temperature-coefficient of resistance being symbatic in form. Consequently, at low temperatures the minimal conductivity for such mixtures should become more pronounced, and at high temperatures less so. The measurement of conductivity at high temperatures is, however, accompanied by considerable difficulty, and few results have been obtained in this direction. This difficulty is avoided in the authors' measurements on alloys of potassium and rubidium, which fuse at low temperatures. The conductivity was measured at various temperatures from  $0^{\circ}$  to  $100^{\circ}$  with both liquid and solid alloys of different compositions. The alloys were prepared, and the measurements made in an atmosphere of nitrogen in special forms of apparatus.

At  $0^{\circ}$  and at  $25^{\circ}$  the conductivity curves show very flat minima at 73.11 and 80.57 atom % rubidium respectively, rise of temperature thus displacing the minimum towards the conductivity of the component with the lesser conductivity. The curves at  $50$ — $100^{\circ}$  for the liquid alloys possess no minima, the conductivity increasing continuously from that of rubidium to that of potassium. The curves for the solid alloys resemble those usually obtained for liquid solutions, owing to the slight lowering in the conductivity produced by adding potassium to rubidium, 19.43 atom % of the former metal changing  $k_0 \times 10^4$  only from 8.86 to 8.6. The temperature-coefficient of resistance curves are similar to those of conductivity.

Addition of rubidium to potassium is accompanied by a sharp rise in the pressure of flow at  $22^{\circ}$  from 0.09 to a maximum of 0.28 kilos. per sq. mm. with 14.29 atom % rubidium, after which a continuous fall takes place to the value 0.08 for the latter metal. The curve is thus antibatic to those of conductivity and temperature-coefficient of resistance. It is evident that the pressure of flow is more sensitive than the electrical conductivity as an indicator of those changes which accompany the formation of isomorphous mixtures of plastic substances.

T. H. P.

**Relation between Ionic Mobility and Ionic Volume.** G. R. MINES (*Kolloid-Zeitsch.*, 1914, **14**, 168—170).—The electrical conductivity of solutions of  $\text{CeCl}_3$  and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  has been measured at concentrations varying from 1/20 to 1/2560 molar. The conductivity of the simple salt is somewhat smaller in the more concentrated solutions, and a little greater in the more dilute solutions, but the differences are always small. The two salts have also been compared in respect of the rate at which they diffuse into gelatin which was placed in contact with 0.1 molar solutions of the salts. The observations show that the complex salt diffuses appreciably faster than the simple salt. It seems necessary to assume, therefore, that the simple metallic cation carries a much larger water envelope than the complex cation, and the author considers that the extent to which hydration of the ions occurs is determined by the size of the ion. In the case of a small ion, which is characterised by a large surface density of the electrical charge, the forces brought into play will be such as to bring a

relatively large number of water molecules into close association with the ions. The larger the volume of the free ion and the smaller the electrical density, the smaller will be the number of water molecules which are affected. These views are applied to the consideration of the relations subsisting between the mobilities and volumes of the alkali metal ions.

H. M. D.

**The Action of Electrolytes on the Dissociating Power of Solvents. I.** A. SACHANOV (*Zeitsch. physikal. Chem.*, 1914, **87**, 441—448).—A series of electro-conductivity measurements have been made with mixtures of electrolytes in solvents of low dielectric constant; these include mixtures of potassium formate and pyridine, pyridine acetate and aniline acetate in acetic acid (DC 6·5); mixtures of tetraethylammonium iodide and aniline hydrobromide, tetraethylammonium iodide and ammonium iodide in aniline (DC 6·8); mixtures of pyridine hydrobromide and diethylamine hydrobromide, pyridine hydrobromide and pyridine hydrochloride in chloroform (DC 4·7). Comparative measurements were made in aqueous solutions of binary mixtures of potassium chloride with succinic acid and tartaric acid, and of sodium chloride with the same acids. The specific conductivity measured in the case of the aqueous solutions is always smaller than that calculated from the single conductivity values, whereas the specific conductivity in the other cases is always larger than the calculated values, in some cases being six times as large. The increase in the conductivity is greater the smaller the dielectric constant of the solvent, and the presence of two salts with a common ion in these solvents also shows an increased conductivity. The conclusion is therefore drawn that in solvents of small dielectric constants, electrolytes exert a dissociating action on one another.

J. F. S.

**Distribution of Solvent between Solutes. II. Electrical Conductivity of Mixtures of Salts of the Alkaline-earth and Alkali Metals.** A. G. DOROSCHEVSKI and S. V. DVORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 371—379).—The measurements now described were made at  $18^{\circ} \pm 0.02^{\circ}$  under the same conditions as those made previously (A., 1913, ii, 1014). For the separate salts of the alkaline-earth metals, the conductivities, within the limits of dilution,  $v=10-100$ , are found to be in good agreement with the formula  $\lambda = A - a/\sqrt[4]{v}$ , the constants  $A$  and  $a$ , calculated from Kohlrausch's results, being respectively 122.77 and 61.852 for  $\frac{1}{2}\text{CaCl}_2$ , 121.32 and 69.269 for  $\frac{1}{2}\text{Ca}(\text{NO}_3)_2$ , 126.98 and 64.774 for  $\frac{1}{2}\text{BaCl}_2$ , 124.45 and 89.74 for  $\frac{1}{2}\text{Ba}(\text{NO}_3)_2$ , and 116.93 and 59.809 for  $\frac{1}{2}\text{MgCl}_2$ . For potassium iodide, the formula  $\lambda = 131.50 - 38.082/\sqrt[3]{v}$  holds, and for  $\frac{1}{2}\text{K}_2\text{SO}_4$  and  $\frac{1}{2}\text{Na}_2\text{SO}_4$  the formula  $\lambda = A - a/\sqrt[3]{v}$ ,  $A$  and  $a$  being 178.37 and 111.625 in the former and 151.90 and 98.10 in the latter case.

The results obtained with mixtures, each containing the chlorides of one alkaline-earth and one alkali metal, show that solutions

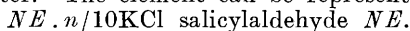
of salts of these two types of metals are isohydric at equivalent concentrations. This conclusion embraces salts the conductivities of which are expressed by the formulæ containing either  $\sqrt[3]{v}$  or  $\sqrt[4]{v}$  or  $\sqrt[5]{v}$ , and is hence of wider application than Barmwater's formula for the conductivity of mixtures (A., 1899, ii, 274, 396), as this is valid only when the conductivity of the salts is given by  $\lambda = A - a/\sqrt[3]{v}$ .

With mixtures of salts containing different negative ions, the calculated values of the conductivities are arrived at by assuming that the above condition of isohydry persists with the four salts formed from a binary mixture. Comparison of these calculated values with the experimental data shows, however, that the latter are in some cases lower, and in others higher, than the former. "Depression" of the conductivity occurs with  $\text{KNO}_3 + \frac{1}{2}\text{BaCl}_2$ ,  $\frac{1}{2}\text{K}_2\text{SO}_4 + \frac{1}{2}\text{MgCl}_2$ ,  $\text{KNO}_3 + \frac{1}{2}\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3 + \frac{1}{2}\text{BaCl}_2$ ,  $\text{NaNO}_3 + \frac{1}{2}\text{CaCl}_2$ , and  $\frac{1}{2}\text{Na}_2\text{SO}_4 + \frac{1}{2}\text{MgCl}_2$ , whilst "exaltation" takes place with mixtures in which the negative ions are interchanged. The conditions governing the magnitude of the "depression" or "exaltation" are being investigated. T. H. P.

**New Electric Crucible Furnace for Laboratory Use.** PAUL ASKENASY (*Zeitsch. Elektrochem.*, 1914, 20, 253).—An electrical crucible furnace is described in which the usual platinum resistance is replaced by a common metal. This is prevented from oxidising by a packing of powdered charcoal, which is placed in the space between the actual furnace and the outer casing. The furnace is 50 mm. diameter and 80 mm. deep, and can be connected directly with the lighting circuit without any resistance in series. The efficiency of the furnace is high, and a temperature of  $800^\circ$  can be obtained in ten minutes, and one of  $1100^\circ$  in thirty minutes. The highest temperature obtainable in this furnace is  $1100^\circ$ . J. F. S.

**Allotropy and Electromotive Equilibrium.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam.*, 1914, 16, 1002—1005).—A reply to Cohen's claim for priority (this vol., ii, 332) in respect of the accelerating influence of salt solutions on the attainment of equilibrium in metals. It is pointed out that the author's theory has reference to the equilibrium between different kinds of molecules in a metal, whilst Cohen's observations refer to the transformation of one polymorphic modification into another. H. M. D.

**Further Investigations on the Electrode-like Behaviour of Organic Substances which are Insoluble in Water.** R. BEUTNER (*Zeitsch. physikal. Chem.*, 1914, 87, 385—408. Compare A., 1913, ii, 468, 469, 662).—A continuation of the work previously published; the present paper deals with the measurement of the *E.M.F.* of galvanic elements composed of two conducting electrodes ( $\text{Hg}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $n\text{KCl}$ ), solution of a salt, and an organic substance insoluble in water. The element can be represented by



*N*/10-solutions of  $\text{NH}_4\text{Cl}$ ,  $\text{BaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$  were substi-

tuted for the potassium chloride in the element given above. By this arrangement, the *E.M.F.* at the surface of the solution and the salicylaldehyde is measured. Measurements are also given of elements in which salicylaldehyde has been replaced by guaiacol, acetophenone, benzyl alcohol, benzaldehyde, anisaldehyde, cinnamaldehyde, and ethyl acetoacetate, and in which the hydrochlorides of aniline, benzylamine, methylaniline, and dimethylaniline have been substituted for the metallic chlorides. It is shown that in elements where the hydrochloride of an organic base is measured against a solution of sodium chloride through an organic liquid, namely, aniline hydrochloride | salicylaldehyde | *N*/10-sodium chloride, the organic hydrochloride solution is always negative. This is in agreement with the theory previously put forward (*loc. cit.*), since it can be assumed that the partition-coefficient of the organic hydrochloride between water and the organic liquid is greater than that of sodium chloride between the same solvents. In elements where the sodium salt of an organic acid is measured against sodium chloride, the first-named solution is always positive. Substances with a relatively high partition-coefficient show an irreversibility of the potential difference. In binary salt solutions, the *E.M.F.* does not change in a linear manner with the composition. Addition of salts of large partition-coefficient influences the potential difference more than that of salts of low partition-coefficient. From the above-mentioned results, the author draws the conclusion that an *E.M.F.* is set up by two equally concentrated electrolytes, separated by a conducting organic liquid, insoluble in water, which is dependent on the partition-coefficients of the two salts between water and the organic liquid. It is shown that the idea of an adsorption potential (Baur, *Zeitsch. Elektrochem.*, 1913, **19**, 590) is unnecessary for the explanation of these potential differences on the basis of thermodynamic laws.

J. F. S.

**Influence of the Superposition of Alternating Current on Direct Current in Electrolysis.** O. REITLINGER (*Zeitsch. Elektrochem.*, 1914, **20**, 261—269).—In the electrolysis of many substances the overvoltage is responsible for the nature of the product, and as in many cases the same overvoltage, which is advantageous for the product of the reaction, also works disadvantageously toward certain intermediate products. The superposition of an alternating current on a direct current has the effect of reducing the overvoltage, and with the object of seeing whether such a current would give a yield of the intermediate product instead of the usual product, electrolyses were carried out. Thus, in the electrolysis of sulphuric acid, instead of persulphuric acid, ozone was obtained. In the electrolysis of ethyl and propyl alcohols, acetaldehyde and propaldehyde were obtained instead of the corresponding acids, as is usual. This result confirms the experiments of Dony-Hénault (*A.*, 1900, ii, 644), which show that when the potential of the anode is kept low enough, aldehydes are formed from alcohols, but at higher potentials acids are produced. A pulsating negative direct current opposed to the ordinary current reduces

the anode potential, and an increased yield of ozone is obtained. If the alternating current has a high frequency, its depolarising action is weaker, and this is shown to be due to the strong phase displacement brought about by the high capacity of the electrode. Experiments were also made on the oxidation of ammonia in sodium hydroxide solution in the presence of copper as catalyst. In this case a yield of 40.2% of the theoretical amount of nitrous acid was produced without any nitric acid. Benzoic acid and benzaldehyde were obtained from toluene suspended in sulphuric acid (D 1.22), using lead peroxide anodes, and *p*-benzaldehyde-sulphonic acid was obtained from the sodium salt of *p*-toluene-sulphonic acid dissolved in dilute sulphuric acid, using lead peroxide anodes.

J. F. S.

**Electrolysis of Mixtures of Molten Potassium and Sodium Salts.** BERNHARD NEUMANN and EINAR BERGVE (*Zeitsch. Elektrochem.*, 1914, **20**, 271—275).—Castner has shown in the preparation of sodium from fused sodium hydroxide that the yield of metal is better the lower the temperature of electrolysis. The present paper deals with attempts to lower the melting point of molten sodium hydroxide by the addition of salts of sodium and potassium, and from the mixtures of low melting point to obtain pure sodium by electrolysis. The first part of the paper deals with determinations of the melting point of sodium hydroxide to which various quantities of potassium hydroxide, sodium carbonate, a mixture of 48.5% sodium carbonate and 51.5% potassium carbonate, and a mixture of potassium hydroxide and sodium carbonate have been added. Complete melting-point curves are given for the above-mentioned mixtures, and minima are indicated as follows: 41.6% NaOH + 58.4% KOH, m. p. 167°; 17% Na<sub>2</sub>CO<sub>3</sub> + 83% NaOH, 280°; 79.3% NaOH + 20.7% (Na<sub>2</sub>CO<sub>3</sub> + K<sub>2</sub>CO<sub>3</sub> as above), 265°. The lowerings of the melting point of sodium hydroxide have been controlled by calculations based on the Raoult law of proportionality of the lowering of the freezing point, and the calculated figures agree well with those determined experimentally. These various more fusible mixtures have been electrolysed, and in every case an alloy of sodium and potassium was obtained. The electrolysis was effected in a nickel crucible, using an annular nickel anode, and a nickel rod as cathode, with an *E.M.F.* of 3.9 volts and 1 ampere per sq. cm. of anode as the current density. Using a constant current for electrolysis, the content of the metal deposited on potassium increased with increasing concentration of potassium in the melt. With the mixture 60% NaOH 40% KOH, the metal deposited had the composition 60% Na 40% K. On increasing the current density, the alloy increased its percentage of potassium; these same effects were also observed in the melts containing carbonate.

J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. II. Deposition of Copper-Tin Bronzes.** R. KREMANN, C. TH. SUCHY, J. LORBER, and R. MAAS (*Monatsh.*, 1914, **35**, 219—288).—The experiments were

conducted on the same lines as those described in the previous investigation (this vol., ii, 96), potential measurements being first carried out in order to determine with what concentrations and under what conditions the deposition potentials of the two metals were close together. Baths made up from copper sulphate, stannous chloride, and ammonia solutions, with or without the addition of sodium hydroxide and ammonium chloride, did not give satisfactory results, but bronze could be deposited either from tartrate or cyanide baths, a necessary condition for a good deposit in sheet form being a high content of free alkali hydroxide. As the content of alkali increases, the deposits become more elastic, and contain less hydrogen and cuprous oxide. With high concentrations of alkali hydroxide, however, the copper anode becomes passive, and accompanying this passivification, especially in tartrate baths, decomposition of the electrolyte takes place, thus limiting the length of time the bath may be used to a few days. There is an optimum alkali concentration which gives the best results. The decomposition in the tartrate baths is due to oxidation of the tartaric acid and subsequent reduction of the copper salt.

Investigation of the microscopic structure, of the *E.M.F.*, and of the sclerometric hardness of the deposits, showed that the bronzes obtained from the cyanide baths were more uniform in structure than those from the tartrate baths.

Technically, owing to the decomposition of the tartrate baths and the less uniform structure of the deposits, the cyanide baths are to be preferred.

T. S. P.

**Electro deposition of Nickel.** C. W. BENNETT, H. C. KENNY, and R. P. DUGLISS (*J. Physical Chem.* 1914, **18**, 373—384).—Experiments have been made to ascertain the conditions which affect the electro-deposition of nickel from a solution of nickel ammonium sulphate. This solution contained 80 grams of the double sulphate and 10 grams of nickel chloride per litre, and nickel anodes, containing 7.6% of iron, were used.

A good deposit of nickel may be obtained if the solution at the surface of the cathode is kept alkaline. The efficiency of the process depends on the alkalinity of the cathode solution, and diminishes if the alkalinity is reduced by vigorous stirring of the solution.

The iron content of the deposit formed on a rotating cathode is found to be greater than that of the deposit on a stationary cathode. The efficiency is not materially affected by the iron content of the anode.

H. M. D.

**The Interpretation of the Magnetic Properties of Mixtures of Oxygen and Nitrogen.** ALBERT PERRIER and H. KAMERLINGH ONNES (*Compt. rend.*, 1914, **158**, 1074—1076).—A theoretical discussion of results already obtained on the effect of diluting oxygen with nitrogen, the coefficient of magnetisation of the first element increasing towards the value which satisfies Curie's law.

The variation in density of oxygen only modifies its specific magnetisation, without varying its Curie constant. The molecular field varies practically with the density, although for large dilutions the variation is apparently slightly more rapid. W. G.

**The Magneton Theory.** R. GANS (*Ber. Deut. physikal. Ges.*, 1914, **16**, 367—368).—A reply to Heydweiller's criticism (this vol., ii, 24). H. M. D.

**The Magneto-chemistry of Nickel Compounds and the Theory of the Magneton.** B. CABRERA, E. MOLES, and J. GUZMAN (*Arch. Sci. phys. nat.*, 1914, [iv], **37**, 324—334; *Anal. Fis. Quim.*, 1914, **12**, 131—142).—Using the method previously described (this vol., ii, 24), the authors have determined the magnetic susceptibility of solutions of varying concentrations of nickel sulphate, nickel chloride, and nickel nitrate. The number of magnetons for nickel is found to be 16; it is independent of the concentration, and of the temperature between 14° and 25°. In the case of an almost saturated solution of potassium nickelocyanide at 15°, the magnetic susceptibility is found to be  $-1.77 \times 10^{-4}$ , the salt being diamagnetic. T. S. P.

**Influence of Molecular Constitution and Temperature on Magnetic Susceptibility.** A. E. OXLEY (*Phil. Trans.*, 1914, **A**, **214**, 109—146).—Measurements have been made of the magnetic susceptibility of a number of organic compounds, with special reference to the change in this property which accompanies the transition from the liquid to the solid state. The substances investigated were toluene, *o*-xylene, cymene, nitrobenzene, chlorobenzene, bromobenzene, aniline, benzyl chloride, benzoyl chloride, benzaldehyde, benzene, pyridine, phenylhydrazine, acetophenone, benzophenone, naphthalene,  $\alpha$ -bromonaphthalene, and  $\alpha$ -naphthylamine.

In most cases it has been found that the substance is more diamagnetic in the liquid than in the crystalline form. The behaviour of benzoyl chloride and phenylhydrazine is exceptional, and this abnormal change in the susceptibility was also found in the liquid crystalline compounds cholesteryl chloride and *p*-azoxyanisole. Nearly all the benzene derivatives show a change in the susceptibility of the order of 5% on solidification.

The observations are discussed in terms of the view which has been referred to in a previous paper (*A.*, 1912, ii, 325).

H. M. D.

**The Differential Scale of Temperatures.** THADÉE PECZALSKI (*Compt. rend.*, 1914, **158**, 1164—1166).—The author has developed an exponential scale of temperatures expressed by  $T = T_0 e^{\int_{t_0}^{adt}$  where  $a$  is a constant, which possesses the essential properties of differential temperatures, and he quotes several properties of this scale bearing upon the physical properties of substances. W. G.

**Expansion of Liquid Mixtures and Solutions on Heating.** W. HERZ (*Zeitsch. physikal. Chem.*, 1914, **87**, 63—68. Compare this vol., ii, 25).—The author has applied the Mendeléev equation on the thermal expansion of liquids to mixtures of liquids and solutions. Binary mixtures of benzene, toluene, aniline, and nitrobenzene have been prepared, and their densities have been measured by means of an Ostwald-Sprengel pyknometer at temperatures from 25—90°. The value for  $k$  has been determined and used for calculating the density in each case. There is a remarkably good agreement between the experimentally determined value and the calculated value. A number of solutions—diphenylamine in aniline, iodine in benzene, benzoic acid in benzene, and iodine in toluene—have been treated in the same way, with results which are equally good. It has been previously shown (*loc. cit.*) that water does not obey the Mendeléev law, but a series of aqueous solutions treated in the same way as the substances mentioned above give good agreement at temperatures above that of the maximum density of water and in the case of concentrated solutions. Experiments were made with aqueous solutions of sodium chloride, sodium hydroxide, sulphuric acid, acetic acid, and sucrose. In the case of sodium hydroxide, a 5% solution gave a  $k$  value which differed from the mean by 20·5%, whereas a 50% solution only differed 1·8%.  
J. F. S.

**Theoretical Treatment of the Phenomena in Dilute Gases.** B. BAULE (*Ann. Physik*, 1914, [iv], **44**, 145—176).—A mathematical paper in which the thermal conductivity and viscosity of gases at very low pressures are discussed.  
H. M. D.

**Ratio of the Specific Heats of Air, Hydrogen, Carbon Dioxide, and Nitrous Oxide.** H. N. MERCER (*Proc. Physical Soc. London*, 1914, **26**, 155—163).—The cooling effect of adiabatic expansion has been made use of to determine the specific heat ratio. The change in the temperature was measured by the alteration in the resistance of a very fine platinum wire. The resistance thermometer was compensated for conduction along the leads, and by the employment of an automatic contact which closes the galvanometer circuit at the right moment, it has been found possible to obtain measurements of considerable accuracy with a vessel of only 300 c.c. capacity. The values obtained for the specific heat ratio are: air, 1·400; hydrogen, 1·398; carbon dioxide, 1·292; nitrous oxide, 1·261. The values of  $c_p$ , calculated from these ratios, are: air, 0·2403; hydrogen, 3·4704; carbon dioxide, 0·2000; nitrous oxide, 0·2185. These numbers are in good agreement with the directly determined values of  $c_p$ .  
H. M. D.

**Specific Heat of Liquids at Constant Volume and the Difference between the Specific Heats at Constant Volume and at Constant Pressure.** DANIEL TYRER (*Zeitsch. physikal. Chem.*, 1914, **87**, 169—181).—The author has calculated the values of the



specific heat at constant volume ( $c_v$ ), the difference between the two specific heats ( $c_v - c_p$ ), and the ratio of the two specific heats,  $c_p/c_v$ , for a series of liquids from a series of previously published (T., 1913, **103**, 1675) compressibility determinations. A comparison of the  $c_v$  values for the liquid and vapour shows that the liquid value is considerably higher than that of the vapour. The hypothesis of de Heen on the change of ( $c_p - c_v$ ) with temperature is discussed, and it is shown that when the molecular attraction is expressed by the function  $a/v^2$  of the van der Waals equation, the de Heen hypothesis does not hold. The expression  $(c_p - c_v)v^2/(dv/dt) = \text{const.}$  is deduced on the assumption that the pressure of attraction is given by  $a/v^2$ ; this expression holds for normal liquids within the experimental error. The product of the molecular weight and the factor ( $c_p - c_v$ ) is approximately constant for normal liquids at the same temperature. The equation  $l.(dv/dt)/v(c_p - c_v) = 1$ , in which  $l$  is the latent heat, is deduced and found to be approximately correct. A table is given of the values  $c_p$ ,  $c_v$ , and the ratio  $c_p/c_v$  at a series of temperatures for the liquids benzene, toluene, chloroform, carbon tetrachloride, ether, chlorobenzene, carbon disulphide, ethyl alcohol, and water.

J. F. S.

**The Pyrophoric Phenomenon in Metals.** A. SMITS, A. KETTNER, and A. L. W. DE GEE (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 999—1001).—Dilatometric experiments have shown that the conversion of pyrophoric into non-pyrophoric iron is accompanied by an appreciable increase in volume. The transformation is completed in about forty-eight hours at 310—320°. The observed change in volume affords support for the theory that the pyrophoric modification consists of a mixture of different kinds of molecules which are not in a state of equilibrium (compare this vol., ii, 165).

H. M. D.

**Reheating and Annealing after Tempering of Copper-Tin and Copper-Zinc Alloys.** A. PORTEVIN (*Compt. rend.*, 1914, **158**, 1174—1177. Compare Grenet, A., 1911, ii, 42).—Alloys of copper-tin and copper-zinc behave in the same way as alloys of copper-aluminium (compare Portevin and Arnou, A., 1912, ii, 352) on reheating and annealing after tempering. The pro-eutectoid constituent, which had dissolved entirely or in part during tempering, separates out in such a way as to give the alloy the Widmanstaetten structure, visible under a microscope. Further, the commencement of reheating is accompanied by an increase in the hardness of the alloy.

W. G.

**Thermolysis The Ludwig-Soret Phenomenon in Solids.** HERMANN WESSELS (*Zeitsch. physikal. Chem.*, 1914, **87**, 215—252).—The author has investigated the manner in which the composition of solid mixtures changes when subjected to a gradation of temperature. The mixtures examined were: hydrated silica, borax glasses containing metal oxides (namely, CoO), silicate glasses coloured by

metal oxides, a solution of benzene in caoutchouc, and a 2% mixture of azobenzene in dibenzyl. It is shown that in the case of solids containing water, the water diffuses to the colder regions of the substance; the same observation is made in the benzene-caoutchouc mixture, namely, that the volatile constituent passes to the colder regions. In the cases of coloured glass, it is shown that the dissolved metal oxides pass to the colder regions of the mixture, but in the mixed crystals of azobenzene and dibenzyl the azobenzene diffuses to the warmer side.

J. F. S.

**Heats of Cooling of Aluminium, Iron, Antimony, and Nickel.** P. N. LASCHTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 311—333).—The amounts of heat developed by these metals during cooling were measured in the manner previously described (A., 1913, ii, 671).

The aluminium used contained 0.31% Si and 0.63% Fe, but was free from copper and lead. The curve connecting the amount of heat developed by 1 gram of aluminium in cooling from any given temperature to 23—24° with this temperature is continuous to 580°, and is somewhat convex towards the temperature axis. Between 580° and 590° a marked change in direction of the curve occurs, and at 670—650° a sudden increase in the amount of heat, owing to fusion of the metal. The heat of fusion is found to be 71 cal. per gram. Even when the metal is melted and heated at 700—720° it exerts no action on the quartz tube, and only at 750° does the formation of silicon occur.

In the experiments with iron, the metal used was free from pearlite, and contained only minimal inclusions of slag. The heat of cooling curve shows two marked changes in direction, at 730° ( $\alpha\text{-Fe} \rightleftharpoons \beta\text{-Fe}$ ) and 895° ( $\beta\text{-Fe} \rightleftharpoons \gamma\text{-Fe}$ ) respectively, and beyond 900°, when the iron is in the  $\gamma$ -form, the specific heat increases rapidly with rise of temperature. Measurement of the heat of cooling of electrolytic iron confirms the temperature 730° for the change of  $\alpha$ - into  $\beta$ -iron. The conversion of the  $\beta$ - into the  $\alpha$ -modification is accompanied by the development of 5 cal. per gram or 0.28 Cal. per gram-atom, and that of  $\gamma$ - into  $\beta$ -iron by about 6.1 cal. per gram or 0.38 Cal. per gram-atom.

The nickel employed was of 99.89% purity. The heat of cooling curve shows a break at 355—365°, in complete agreement with previous observations, and indicates, further, the existence of a third modification of nickel stable above 700°. This indication is confirmed by the change of the metal at high temperatures into a brittle form with a coarsely crystalline structure (compare Cohen, *Zeitsch. Elektrochem.*, 1909, **15**, 686). The first transformation, at 363°, is accompanied by the development of about 3.11 Cal. per gram-atom.

Antimony was investigated at temperatures ranging from 200° to 680°, and within these limits the heat of cooling curve is quite continuous. This metal melts at 630°, and the latent heat is 4.85 Cal. per gram-atom.

T. H. P.

**Application of Cryoscopy to the Determination of Double Salts in Aqueous Solution.** E. CORNEC and G. URBAIN (*Compt. rend.*, 1914, 158, 1118—1121).—A determination of the lowering of the freezing point of solutions of one compound in aqueous solutions of another gives an indication of the formation of a double salt. If a difference is found between the values observed and calculated, it is an indication of the existence of a double salt in solution, this difference being at its maximum when the two substances are in the molecular proportions corresponding with that of the double salt. The cases studied were cadmium iodide and alkali iodides, cadmium bromide and alkali bromides, and cadmium chloride and alkali chlorides. The results obtained were in agreement with the known constitution of the solid double salts in these cases. W. G.

**Differentiation of Racemic and Pseudo-racemic Substances.** G. TAMMANN (*Zeitsch. physikal. Chem.*, 1914, 87, 357—365).—A method of molecular-weight determination is developed for deciding whether an inactive substance is made up of mixed crystals of the *d* and *l* kinds, or whether it is a true racemic compound. The method is based on the entropy change in melting. It is shown that for the melting of a gram-molecule of a substance the entropy change is given by the equation

$$Mr_p/T_s \pm \Delta\alpha W/T_s = 10 \text{ to } 16 \text{ cal.},$$

in which  $r_p M$  is the molecular heat of fusion,  $T_s$  the melting point in degrees absolute,  $\Delta\alpha$  is the change in molecular concentration in fractions of a gram-molecule, and  $W$  the heat change due to the change of concentration in melting. The factor  $\Delta\alpha=0$  for normal liquids, consequently  $Mr_p/T_s=10-16$  cal. in these cases. This rule can also hold for abnormal liquids when  $W=0$ . Four cases are worked out for racemic substances and applied to the cases of carvoxime and methyl tartrate. The latent heat of fusion for 1 gram of the *d*-, *l*-, and *i*-forms of these substances was determined, and in the case of the three carvoximes the value of  $Mr_p/T_s$  is 11.2, which indicates that there is no change of molecular weight, and that the inactive carvoxime is not a true racemic compound, but presents a case of a pseudo-racemic substance. The inactive tartaric ester has a value of 17.4, whilst the *d*-ester has a normal value 11.9. From these figures and other considerations the conclusion is drawn that here a case of a true racemic compound is presented. J. F. S.

**Determination of the Critical Temperature of Some Mercury Haloids.** LÉON ROTINJANZ and WLADIMIR SUCHODSKI (*Zeitsch. physikal. Chem.*, 1914, 87, 253—256).—The critical temperature of mercuric chloride, bromide, and iodide have been determined. The substances were sublimed in a vacuum into small quartz tubes 1 mm. internal diameter and 15 mm. long. The tubes were sealed off and bound to the junction of a platinum-rhodium platinum couple, and heated in a small electric furnace. The critical temperatures were obtained from both sides, and did not differ

more than  $1^\circ$  in the various determinations. The following values in degrees absolute were obtained:  $\text{HgCl}_2$ ,  $976^\circ$ ;  $\text{HgBr}_2$ ,  $1011^\circ$ ;  $\text{HgI}_2$ ,  $1072^\circ$ . It is shown that the value  $T_s/T_k$ , where  $T_s$  is the boiling point at atmospheric pressure and  $T_k$  is the critical temperature, is equal to 0.59, a value much lower than that demanded by the formula  $T_s/T_k = 0.67$ . Using the expression

$$T_k = T_s \cdot v_s - 273/2(v_s - 1)$$

(Thorpe and Rucker, T., 1884, **45**, 143), in which  $v_s$  is the volume at the boiling point in relation to that at zero, and using the density values of Prideaux (T., 1910, **97**, 2032), the critical temperatures of the three substances are calculated to  $\text{HgCl}_2$ ,  $1268^\circ$ ,  $\text{HgBr}_2$ ,  $1013^\circ$ , and  $\text{HgI}_2$ ,  $1077^\circ$ , from which it will be seen that the values for the bromide and iodide agree well with the experimental value, whilst that for the chloride is widely divergent.

J. F. S.

**An Application of Nernst's Approximation [Vapour Pressure] Formula.** P. WINTERNITZ (*Physikal. Zeitsch.*, 1914, **15**, 397—399).—Whereas, according to the Trouton and the Le Chatelier-Forcrand rules, the ratio  $Q/T$  should be constant, where  $Q$  is the molecular heat of vaporisation or dissociation, and  $T$  is the temperature at which the vapour pressure or dissociation pressure becomes equal to that of the atmosphere, Nernst's formula indicates that this relation cannot hold at very high or very low temperatures. By reference to the data for tungsten and hydrogen, it is found that the conclusion drawn from Nernst's formula is in agreement with experiment. According to experiment,  $Q/T = 15.0$  for hydrogen and  $41.0$  for tungsten, and the values obtained from Nernst's formula are respectively  $17.0$  and  $42.2$ .

H. M. D.

**The Chemical Constant of Hydrogen.** VON KOHNER and P. WINTERNITZ (*Physikal. Zeitsch.*, 1914, **15**, 393—397).—The so-called "chemical constant" which appears as an integration constant in Nernst's vapour-pressure formula has been calculated for hydrogen by making use of Brönsted's data for the affinity of the reaction  $\text{H}_2 + \text{HgO} = \text{Hg} + \text{H}_2\text{O}$  (A., 1909, ii, 10, 369). The value thus obtained is  $C = -1.303$ .

H. M. D.

**The Atomic Character of Chemical Change in Gaseous Systems.** E. BRINER (*J. Chim. Phys.*, 1914, **12**, 109—132).—From the values calculated for the heats of formation of the molecules of iodine, bromine, chlorine, sulphur, and hydrogen, it seems probable that all chemical compounds are exothermic if the energy content of the compound is compared with that of the component elements in the atomic condition. This view is applied to the consideration of the equilibrium in gaseous mixtures at high temperatures, and it is shown that the concentration of so-called endothermic compounds should pass through a maximum as the temperature increases, afterwards falling as the temperature continues to rise. The influence of temperature on the proportion of

nitric oxide which is present in a mixture of nitrogen and oxygen is discussed as a special case.

On the assumption that the formation of compounds in gaseous systems is due to the reactivity of the elementary atoms, it is possible to give a satisfactory explanation of the phenomena of "false equilibrium," and also of various catalytic effects. The assumption also affords a basis for the deduction of the relationship between the reaction velocity and the temperature of gaseous systems.

H. M. D.

**The Gas Equation at Low Temperatures.** O. SACKUR (*Ber.*, 1914, **47**, 1318—1323).—Basing his considerations on the quantum hypothesis, and on Planck's theory, which is based on the assumption that the kinetic energy of a substance at the absolute zero has a definite value, the author puts forward the following gas equation for low temperatures (compare A., 1913, ii, 128):

$$PV = RT \left[ 1 + \frac{1}{RT} \left( b - \frac{a}{RT} \right) P + \frac{1}{12M} \cdot \frac{P^{2/3}}{T^{5/3}} + \frac{1}{10} \left( \frac{A}{M} \right)^{3/4} \cdot \frac{P^{1/2}}{T^{5/4}} \right],$$

where  $a$  and  $b$  are the van der Waals' constants,  $M$  is the molecular weight of the gas, and  $A$  is a universal constant for all gases, the value of which can be calculated by the quantum theory.

According to this equation, the curve showing the relation between the pressure and the product  $PV$  should be concave towards the axis of pressure. Experiments show that this is the case for hydrogen and helium at the temperature of boiling hydrogen ( $-253^\circ$ ) and pressures below one atmosphere. It can also be shown that a similar result holds at  $-196^\circ$  and  $-183^\circ$ , although the effect is not so marked.

T. S. P.

**Equation of Condition.** A. WOHL (*Zeitsch. physikal. Chem.*, 1914, **87**, 1—39).—The author has deduced an equation of condition of the form  $p = RT/(v-b) - a/v(v-b) + cv^3$ , in which  $a$  and  $b$  are constants having the same values as in the van der Waals' equation, and  $c$  is a constant which is a function of the temperature. The equation has been tested by means of the data collected for fluorobenzene, *n*-pentane,  $\beta$ -methylbutane, ethyl alcohol, carbon dioxide, argon, oxygen, helium, and hydrogen. It is shown that in all cases that the isothermals and vapour-pressure curves can be reproduced with sufficient exactitude by means of this equation, and their constants can all be obtained from the three values  $R$ ,  $T_\kappa$ , and  $p_\kappa$ . The dependence of the attraction factor on temperature is given by  $a/\theta$ , that of the repulsion factor is given by  $c/\theta$  above  $T_\kappa$  and  $c/\theta^2$  below  $T_\kappa$ . In the case of carbon dioxide between pressures of 100—1000 atmos.,  $b = v_\kappa/(\delta + \epsilon\pi)$ , in which  $\delta$  is approximately equal to 4. For pressures below  $p_\kappa$ ,  $b$  is constant. A number of equations of condition of variously second-, third-, and fifth-order equations of  $v$  are discussed and compared with the present equation, and it is shown the author's equation represents the actual facts better than any of them; it is also shown that a cubic equation with  $R$  and  $(v-b)$  in the numerator

cannot represent the actual conditions if the critical region is to be included in the range of the equation. J. F. S.

**Some Relationships between the Compressibility and other Physical Properties of Liquids together with Remarks on the Values of  $a$  and  $b$  in the van der Waals' Equation for the Liquid Condition.** DANIEL TYRER (*Zeitsch. physikal. Chem.*, 1914, **87**, 182—195).—Making use of compressibility data previously determined by the author (T., 1913, **103**, 1675), the expression  $\beta = T(dv/dt) \cdot v/c$ , where  $\beta$  is the isothermal compressibility, is confirmed. The relationship  $\beta\gamma^{4/3} = \text{constant} = 0.00253$ , deduced and applied by Richards and Matthews (A., 1908, ii, 158) to measurements at high pressures, is applied to the author's measurements at 1.5 atmospheres' pressure. It is shown that with increasing temperature the value increases, except in the case of water, whilst for the same temperature the value is approximately constant for all liquids except carbon disulphide, ethyl alcohol, and water. It is shown that the expression  $\beta\gamma^{4/3}/T^{1/3} = k$ , where  $\gamma$  is the surface tension and  $T$  the absolute temperature. A number of other relationships are also considered and tested on the same data. The value of  $b$  of the van der Waals equation is determined for a number of liquids (see this vol., ii, 425) from the compressibility data. It is shown that  $b$  is approximately equal to  $V^{2/3} \cdot V_0^{1/3}$ , where  $V_0$  and  $V$  respectively represent the molecular volume at the absolute zero and at the experimental temperature. The value of  $a$  is obtained by substituting that of  $b$  in the van der Waals equation, and it is shown that for temperatures below that of the critical point the value of  $a$  is approximately constant.

J. F. S.

**Surface Tension at the Surface of Separation of Two Solvents.** OSKAR LÓRÁNT (*Pflüger's Archiv*, 1914, **157**, 211—250).—The surface tension at the surface separating water or an aqueous solution from various other liquids has been measured by the method of capillary rise, and also by the method which involves the determination of the weight of the drop which is formed at the end of a capillary tube immersed in the second liquid. In general, the results indicate that there is no simple relation connecting the tensions observed at an air and at a water surface in the case of the liquids which have been examined.

From experiments with aqueous solutions of different electrolytes in contact with ethyl ether, nitrobenzene, chloroform, and carbon tetrachloride, it has been found that the surface tension depends on the nature of the ions and on the concentration of the solution. The influence of the anions is of greater importance than that of the cations. From the observations with 1*N*-solutions of potassium salts, it is found that the anions arrange themselves in the order Cl, SO<sub>4</sub>, Br, I, SCN in the case of ethyl ether and nitrobenzene. Chloroform and carbon tetrachloride give a somewhat different series.

Sodium oleate in 0.1*N*-solution reduces the surface tension at

all four surfaces to a small fraction ( $1/10$  to  $1/26$ ) of the value for pure water. Ethyl alcohol and chloral hydrate have a similar, but smaller, influence on the surface tension. A solution of egg-albumin has a smaller surface tension than water, and the influence of the albumin is much greater for a liquid-liquid surface than for a liquid-air surface.

Blood serum has also a smaller tension than water at the surface of each of the four liquids investigated. H. M. D.

**Work Done in the Formation of a Surface Transition Layer of a Liquid Mixture of Substances.** R. D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1914, 17, 409—413).—In a previous paper (A., 1913, ii, 26) a formula was deduced for the surface tension of a liquid on the assumption that no transition layer is formed at the surface. This formula is now extended to binary mixtures and values obtained for the surface tension of mixtures of benzene and carbon tetrachloride and of chloroform and carbon disulphide. The results show that the theoretical surface tension ( $\lambda_2$ ) for mixtures of benzene and carbon tetrachloride is practically independent of the relative proportions of the constituents in the mixture. A similar relation is exhibited by the observed values of the surface tension ( $\lambda_1$ ).

The difference  $\lambda_2 - \lambda_1$  represents the external work done in the formation of the transition layer. For pure liquids,  $\lambda_2 - \lambda_1$  is practically independent of the temperature, but for mixtures this difference increases with rise of temperature. H. M. D.

**The Viscosity of Rubber Solutions.** R. GAUNT (*J. Soc. Chem. Ind.*, 1914, 33, 446—452).—The method of procedure adopted in the determination of the viscosity of rubber solutions was practically identical with that suggested by Fol (A., 1913, ii, 301). The majority of the experiments were made with the following different kinds of rubber: (a) a pale, thin plantation crêpe Hevea, coagulated by means of acetic acid; (b) fine, hard Para; (c) Castilloa, prepared by centrifugalisation; (d) Funtumia sheet; (e) Ceara biscuits. The solvents, which were specially purified, with the exception of commercial xylene, were benzene, ether, light petroleum distilling below  $50^\circ$ , toluene, chloroform, and commercial xylene. The viscosities were measured at  $20^\circ$  with an Ostwald viscometer.

The Castilloa and Funtumia rubbers mix with the solvents in all proportions, whereas the Para and Ceara rubbers are only partly soluble; in the latter cases the greater the proportion of rubber to a given quantity of solvent, the more rubber dissolves, the dissolved rubber causing a partial solution of the insoluble constituent; moreover, crêping the Para rubber for forty-five minutes in cold water increases the solubility.

The relation between the viscosity ( $\eta$ ) of the rubber solutions in all the various solvents and the concentration ( $x$ ) is given by the formula  $\eta = \kappa x$ , where  $\kappa$  is a constant. The inclination of the straight lines obtained by plotting  $\log \eta$  against  $x$ , towards the

axis of  $x$ , gives the best method of comparing the viscosity of rubber solutions (compare Schidrowitz and Goldsbrough, A., 1913, ii, 760).

Rubber solutions diminish in viscosity on keeping, and heat, as well as light, increases the rate of diminution in viscosity. At high temperatures the effect of light is less marked than that of heat. Such diminution takes place in the absence of air, and cannot be ascribed to oxidation; probably the dissolved rubber undergoes a physical change, the so-called "depolymerisation." The change in viscosity follows the law:  $x = a + b \log t$ , where  $x$  is the diminution in viscosity in the time  $t$ ,  $a$  is the diminution in the first unit of time, and  $b$  the increment of diminution with time. The greater the concentration of the solution the more rapid is the diminution in viscosity.

The results of experiments are also detailed, in which the change of viscosity (1) of the same rubber in different solvents, and (2) of different rubbers in the same solvent, was investigated. The presence of xylene or higher hydrocarbons in commercial benzene affects the viscosity, and hence the necessity of using pure solvents (compare Schidrowitz, *loc. cit.*).  
T. S. P.

**Connexion between the Adsorption Isotherm and the Laws of Proust and Henry.** W. P. A. JONKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 970—974).—If a substance is in distribution equilibrium with respect to two immiscible media, then at a given temperature and pressure the three-component system is characterised by one degree of freedom. It follows that the concentration of the third substance in the one medium must be a function of its concentration in the second medium.

It is shown that the formation of a definite compound by combination of the third substance with one of the immiscible media and the distribution of the substance in a constant ratio may be regarded as special cases of the general law of adsorption.

H. M. D.

**Theory of Adsorption.** A. EUCKEN (*Ber. Deut. physikal. Ges.*, 1914, 16, 345—362).—The nature of adsorption is discussed in reference to the special case of the adsorption of a gas by a chemically indifferent solid substance. On the assumption that the adsorption is due to the formation of a highly compressed layer of gas under the influence of the molecular attractive forces, formulæ are deduced for the adsorption of (1) an ideal gas, (2) an actual gas above its critical temperature, (3) a vapour. In agreement with experiments, these formulæ indicate that at low pressures and high temperatures the quantity of gas adsorbed is proportional to the pressure of the gas. The dependence of the adsorption on the temperature observed by Homfray (A., 1910, ii, 771) and Titov (A., 1910, ii, 1041) is also shown to be in general agreement with the requirements of the author's formulæ. These also lead to values for the heat of adsorption which agree with the observed heat changes.

In consequence of the diminution of the compressibility which

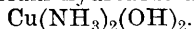


is shown by all gases as the density increases, the adsorption approximates to a maximum with increasing pressure. The surface saturation which corresponds with the attainment of this maximum can only be reached in the case of vapours if the adsorption takes place at a rough surface. H. M. D.

**Adsorption. X. Adsorption by Starch in Aqueous Ammoniacal Solutions of Cupric Hydroxide.** A. V. RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 246—258. Compare A., 1913, ii, 303).—The preparation of large quantities of pure cupric hydroxide is somewhat difficult. If copper sulphate solution is precipitated by sodium or potassium hydroxide, not taken in excess, the precipitate contains a considerable proportion of  $\text{SO}_4$ , which has a marked influence on the adsorbing properties of the hydroxide. If, on the other hand, the alkali hydroxide is added in excess, and especially if it is used in dilute solution (0.5%) to wash the precipitate, the latter readily changes, even below  $15^\circ$ , into cupric oxide, which is but sparingly soluble in aqueous ammonia. The best method to overcome these difficulties is to precipitate and wash the hydroxide with aqueous ammonia, which dissolves only very little of the cupric hydroxide gel.

In the present experiments, potato starch alone has been used. It has been found previously (A., 1913, ii, 302) that strongly dissociated alkalis are adsorbed in considerable proportions by starch, whereas the adsorption of the feebly dissociated ammonia is slight, and falls virtually to zero in presence of the strongly dissociated barium hydroxide. The base  $\text{Cu}(\text{NH}_3)_n(\text{OH})_2$  is a strong alkali, and may be expected to behave similarly to barium hydroxide as regards the adsorption of ammonium hydroxide by starch. The diminution in the concentration of the ammonia accompanying adsorption of aqueous ammoniacal cupric hydroxide solution may thus be taken to correspond with that entering into the composition of the complex alkali. Consequently, if the adsorbed copper and ammonia are determined simultaneously, the value of  $n$  in the formula  $\text{Cu}(\text{NH}_3)_n(\text{OH})_2$  will be obtained. A number of such determinations, made with ammonia solutions varying in concentration from 1.7 to 11.5*N*, gave values of  $n$  ranging from 1.89 to 2.07, the mean being 1.96. Under these conditions, therefore, a base of the composition  $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$  is always adsorbed.

Measurements of the velocity of adsorption show that the adsorption of  $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$  resembles that of barium hydroxide in so far as it is a complex process, the second stage of which proceeds very slowly, but differs from it in the diminution of the adsorption during this second stage. The cause of this complexity lies in an irreversible change of the starch resulting from the adsorption, the starch gelatinising and gradually passing into solution with formation of a product or products with adsorbing properties, which differ from those of the starch granule and are greater in the case of barium hydroxide and less with



Over their whole range the adsorption isotherms are expressed

neither by the equation  $C_2 = \beta C_1^{1/2}$ , nor by the equation for hydrolysis. The latter is applicable or inapplicable according as the concentration of the alkali is such that the volume of the deposited starch does not or does change considerably (by more than 100%).

T. H. P.

**Physico-chemical Force of Attraction.** L. GURVITSCH (*Zeitsch. physikal. Chem.*, 1914, **87**, 323—332).—Cases of irreversible adsorption have been examined, in which a chemical change or a change in the adsorbed substance is impossible. Such cases are found when the gently heated mineral floridin (a hydrated silicate of aluminium, magnesium, and calcium containing on the average 56.5%  $\text{SiO}_2$ , 11.6%  $\text{Al}_2\text{O}_3$ , 6.3%  $\text{MgO}$ , 3.3%  $\text{CaO}$ , and 18%  $\text{H}_2\text{O}$ ) is used as the absorbent for solutions of naphthenic acids, benzoic acid, or valeric acid. It is shown that floridin adsorbs 6% of the naphthenic acids which cannot be extracted by light petroleum, but can be removed by ether. A series of adsorption experiments were made with solutions of benzoic acid in benzene, benzoic acid in light petroleum, and valeric acid in light petroleum. These solutions were all shaken with floridin. The results are calculated by means of the Freundlich formula,  $y = ax^n$ , and it is shown that the values found experimentally do not agree with those calculated, the difference between the calculated and experimental results increasing with increasing concentration. A formula of the type  $y = A + Kx^n$ , however, gives values which agree well with the experimental values. A series of partition experiments on valeric acid in the binary mixtures, benzene-sulphuric acid and light petroleum-sulphuric acid, were also carried out. It is shown that the amount of valeric acid taken up by the sulphuric acid as calculated by the Nernst partition formula does not agree with the experimental results, the divergence increasing with decreasing concentration. A good agreement between calculated and experimental quantities taken up by the sulphuric acid can be got by a formula of the type  $y = A + f(x)$ , in which  $x$  is the amount of dissolved acid originally present in the other solvent. As a result of these experiments, the author specifies the characteristic properties of the three forces, (a) physical attraction, (b) chemical attraction (affinity), (c) physico-chemical attraction. Physical attraction is not specific; it has an unbounded sphere of action; its action on a given mass is independent of the presence of other masses; its action is not atomic, that is, it acts as a whole from a given surface, and not along separate lines. Chemical attraction is specific; its sphere of action is limited, probably to atomic distances; its action on a given mass is conditioned by its "saturation" with other masses; its action is atomic, that is, it acts along a small number of lines and is discontinuous. Physico-chemical attraction is specific; its sphere of action limited, probably to molecular distances; its influence on a given mass is unaffected by the simultaneous presence of other masses; it is not atomic, that is, it acts as a whole, and not along separate lines. The force, therefore, which comes into action in the processes of solution and adsorption is intermediary between

the chemical and physical forces; it is more related to the chemical force, but differs quantitatively from this in its smaller intensity and wider range of action, and qualitatively in not being atomic.

J. F. S.

**The Adsorption Capacity of Kaolin.** PAUL ROHLAND (*Kolloid. Zeitsch.*, 1914, **14**, 193—195).—According to Carli (A., 1913, ii, 1029), kaolin does not adsorb colloidal ferric hydroxide to any appreciable extent. The author considers that this behaviour is conditioned by the special character of the kaolin which was used in Carli's experiment. In view of the general adsorbing capacity which kaolin has been shown to exhibit, it is to be expected that colloidal ferric hydroxide would also be adsorbed, and experiments made with kaolin from Hohburg in Saxony show that this is the case. This kaolin was found to contain 95.89% kaolin, 1.06% feldspar, and 3.05% quartz. On heating to redness there was a loss of 12.67%, and it is supposed that this high value of the loss on heating is connected with the presence of organic colloids (humus substances).

H. M. D.

**Adsorption by Filter Paper.** M. A. GORDON (*J. Physical Chem.*, 1914, **18**, 337—354).—Experiments have been made on the behaviour of the constituents of an aqueous solution when strips of filter paper are immersed in the solution (compare Bayley, T., 1878, **33**, 304). The rise of the solution in the filter paper is accompanied by changes in concentration in consequence of selective adsorption. If the solute is adsorbed relatively more quickly than the water, the outer zone will be less concentrated than the original solution, but more concentrated if the water is more rapidly adsorbed. The capillary distribution not only depends on the nature of the solute, but also on the concentration of the solution under examination. From experiments with solutions of copper and cadmium sulphate it is found that cadmium sulphate diffuses more rapidly than copper sulphate if the concentration is less than 0.1 molar. This observation is in accord with Bayley's statement (*loc. cit.*) that cadmium can be detected in presence of copper in virtue of the difference which the sulphates show in regard to capillary rise in filter paper.

The adsorption effects diminish with rise of temperature, and certain foreign substances have a similar influence. The adsorption effects observed in the case of hydrolysable salts have no quantitative connexion with the degree of hydrolysis.

H. M. D.

**The Sorption Theory. A New Theory of Dyeing.** G. VON GEORGIEVICS (*Chem. Zeit.*, 1914, **38**, 445—446).—A restatement of the author's views on the nature of the process by which acids and dyes are removed from aqueous solution by animal fibres (compare A., 1913, ii, 561, 562).

H. M. D.

**Theory of Dyeing. III.** WILDER D. BANCROFT (*J. Physical Chem.*, 1914, **18**, 385—437. Compare this vol., ii, 178, 250).—Further extracts from the literature have been collected together,

more particularly with reference to the nature of mordants and mordanting. These are discussed in terms of the author's adsorption theory.

According to this theory, a mordant is a substance which is adsorbed strongly by the fibre and at the same time is capable of readily adsorbing the dye. There is no evidence that definite compounds are formed when the mordants are taken up by wool, silk, or cotton. The difference between the behaviour of wool and cotton is merely a difference in degree determined by the magnitude of the adsorption-coefficients.

The metallic mordants are in all probability hydroxides, and not basic salts, and the mordanting process is said to be influenced to a greater extent by the rate of coagulation of the hydroxide than by the degree of hydrolysis of the corresponding salt. These views are examined in some detail with reference to the mordanting action of aluminium salt solutions, the phenomena observed with aluminium hydroxide being regarded as typical of basic mordants.

H. M. D.

**The Changing Over of an Adsorption Reaction into a Diffusion Reaction.** M. TRAUTZ (*Verh. Ges. deut. Naturforsch. Aerzte*, 1914, **11**, 314—317).—The author shows, theoretically, how a gas reaction may be changed from an adsorption reaction into a diffusion reaction, by varying the temperature at which the reaction occurs, the volume of the gas, and the surface of the containing vessel. All the predictions of the theory have been verified by experiments on the reaction between oxygen and hydrogen iodide at temperatures between 100° and 230°.

T. S. P.

**The Rate of Dissociation of Nitrogen Peroxide.** W. L. ARGO (*J. Physical Chem.*, 1914, **18**, 438—450).—From measurements of the wave-length of stationary waves in nitrogen peroxide and air, it has been found that the value of  $d\rho/dp$ , where  $\rho$  is the density and  $p$  the pressure of the gas, is in agreement with the assumption that the dissociation equilibrium responds to the rapid changes of pressure which occur during the passage of the sound waves. This high velocity of the opposed reactions was found in the case of nitrogen peroxide which had been dried over phosphoric oxide, and of nitrogen peroxide which contained 0.32% by volume of water vapour.

The measurement of the velocity of sound in nitrogen peroxide cannot be used for determining the value of the specific heat ratio  $c_p/c_v$ .

H. M. D.

**Diffusion of Some Dyes.** R. O. HERZOG and A. POLOTZKY (*Zeitsch. physikal. Chem.*, 1914, **87**, 449—489).—A number of dyes in 0.25% aqueous solution have been allowed to diffuse in Öholm's apparatus (*ibid.*, 1904, **50**, 309) into pure water, and at stated intervals of time the concentration of the dye at various heights in the water layer was determined colorimetrically. Parallel with the foregoing experiments, 5% gelatin

solutions of the same dye were allowed to diffuse into 5% gelatin, and the concentration at various heights at stated intervals determined colorimetrically. A very voluminous series of tables of results is given for some twenty-six dyes, and from it the following general conclusions are drawn. The retarding influence of gelatin on the diffusion is noticeable in all cases, and in the case of rhodamine it is shown that the difference between the diffusion in 15% and 10% gelatin is much less than the difference between that in 10% and 5% gelatin. A small addition of sodium hydroxide or hydrochloric acid to solutions of Capri-blue and rhodamine is without influence on the coefficient of diffusion; traces of impurities have a marked influence on the diffusion-coefficient, as is shown by the influence of dialysis on primulin. The partition of the dye in the different layers in many cases corresponds with the Stefan formula, and in others it does not hold in the sense that the higher layers contain too much dye in relation to the lower layers. This is explained on the assumption that in those cases where the formula does not hold the dye is made up of particles of different sizes, of which the smaller diffuse more quickly. In gelatin solutions the divergence from the Stefan formula is still greater, which is to be explained by the fact that the larger particles will be relatively more retarded than the smaller, and also by the adsorption of gelatin by the particles. Biltz (*van Bemmelen-Gedenboek*, 1904, 112) has shown that in dialysis dye molecules of less than 45 atoms in the molecule dialyse quickly, those with 55—70 atoms dialyse slowly or not at all, and those with more than 70 atoms do not dialyse at all. A similar condition is found here for the diffusion into water; dyes containing up to 50 atoms in the molecule have a diffusion-coefficient which lies near, but above, 0.2, with a larger number of atoms the diffusion-coefficient is less than 0.2. If the Stefan formula does not hold, the above regularity also does not hold. In general, a parallelism exists between dialysis and diffusion. There is no regularity observed between the diffusion-coefficient in water and in gelatin, the ratio between the two values fluctuating between 2 and 10. The experiments lead the authors to the conclusion that diffusion is an additive constitutive property, in which the relationship between the solvent and the dissolved substance plays an important part. J. F. S.

**Osmotic Compressibility of Emulsions Considered as Fluids with Visible Molecules.** JEAN PERRIN (*Compt. rend.*, 1914, 158, 1168—1171).—A theoretical discussion of the experimental work of Costantin (compare following abstract). By the application of van der Waals' equation to very dilute emulsions it is possible to find the molecular weight of a fluid compressed to invisible molecules, thus giving an emulsion, and also to determine Avogadro's number, the value  $60 \times 10^{22}$  being obtained. W. G.

**Experimental Study of the Osmotic Compressibility of Emulsions.** RENÉ COSTANTIN (*Compt. rend.*, 1914, 158, 1171—1173. Compare Perrin, preceding abstract).—A study of the variations

of the osmotic pressure with concentration, by means of microphotographs, the number of uniform grains present in horizontal strips being counted for different emulsions. The law governing the results is markedly different, at a concentration of 1%, from van't Hoff's exponential. The results indicate the existence of a term of negative internal pressure, and the curve plotted from these figures indicates that for concentrations greater than 2–4% this internal pressure diminishes in absolute value. W. G.

**Changes of Volume Occurring in the Dissolution of Certain Solids.** A. CAVAZZI (*Gazzetta*, 1914, **44**, i, 448–468).—The author has measured the changes in volume occurring when a number of salts and acids and sucrose are dissolved in water, and when crystalline copper sulphate is dissolved in ammonia solution, sulphur or iodine in carbon disulphide, or iodine in ether. The measurements were made at 15°, and the numerical results, which are given in full, lead to the following conclusions.

The specific gravity of substances in solution gradually diminishes as the concentration increases, and this happens also with anhydrous salts, especially when the concentrations giving diminutions in volume are surpassed, that is, when the specific gravities of the solutes assume positive values. The predominating cause of this variation of the specific gravity of solutes, particularly with substances which under ordinary conditions separate from solution in an anhydrous state, is the dissociation, but the specific gravities of sucrose in water and of sulphur in carbon disulphide are sensibly greater in dilute than in concentrated solutions.

Of all the compounds examined, ammonium chloride is the only one which has the same specific gravity in very dilute solution, as in the solid state, but here, too, diminution accompanies increasing concentration.

Substances which dissociate in water and are readily soluble and crystalline in the anhydrous form, produce, when dissolved in their concentrated solutions, increases of volume corresponding exactly or nearly so with the ordinary specific gravities; the same is the case when boric acid is added to its nearly saturated solution at 15°, but oxalic acid behaves differently.

Of all the compounds containing water of crystallisation, oxalic acid alone has a specific gravity less than the normal value in both concentrated and dilute solutions.

Selenite exhibits in solution a high specific gravity, which is otherwise found only with anhydrous salts which become hydrated in contact with water. It would appear then that, when dissolved in water at 15°, selenite forms a stable hydrate more complex than  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and less complex than that obtained by shaking an excess of powdered selenite which has been moderately heated with water at a low temperature.

That potassium fluoride, like anhydrous calcium, barium, and strontium chlorides, undergoes hydration when dissolved in water is shown by its very high specific gravity in comparison with those of potassium and sodium chlorides, and is confirmed by the deposi-

tion of anhydrous crystals at  $40^{\circ}$  and of crystals containing  $2\text{H}_2\text{O}$  by evaporation in the cold or by addition of alcohol.

The contraction in the volume of the solvent produced by dissolution of anhydrous sodium carbonate and by magnesium, zinc and copper sulphates is undoubtedly due principally to the hydration of the salts.

T. H. P.

**Influence of Neutral Salts on the Condition of Ions in Solution.** I. G. POMA and A. PATRONI (*Zeitsch. physikal. Chem.*, 1914, **87**, 196—214).—The authors have determined the concentration of copper ions in solutions of copper nitrate and copper sulphate of various concentrations to which neutral salts of the same anion had been added in a series of different concentrations. In the case of copper sulphate, magnesium sulphate was added up to a concentration of  $4.8N$ , and in the case of copper nitrate the nitrates of rubidium, potassium, sodium, lithium, strontium, calcium, and magnesium were added; a series of determinations was also made with a solution of copper nitrate to which alcohol in concentrations up to 72% had been added. The measurements were all made by means of *E.M.F.* determinations. From the results, the authors have calculated the factor  $\text{Cu}_0^{++}/\text{Cu}^{++}$ , in which  $\text{Cu}_0^{++}$  is the concentration of the copper ion in a solution to which no neutral salt has been added, and  $\text{Cu}^{++}$  the concentration in the same solution to which a neutral salt has been added. The results obtained with copper sulphate show that this ratio is always greater than unity, and increases with increasing concentration of the neutral salt, which points to a decreased ion concentration in the solutions to which the neutral salt has been added. In the case of copper nitrate, with the addition of rubidium and potassium nitrates, the ratio also increases in the same way, but in the cases of the addition of the other nitrates and of alcohol, the value either falls at once below unity and steadily decreases with increasing concentration of the neutral salt, or, at first (namely, with the lowest concentration of neutral salt), rises above unity and then steadily decreases until it is less than unity, this pointing to an increased ionisation, or at least an increased copper ion concentration which increases with increasing concentration of neutral salt or of alcohol. The order of the influence is seen from the values of  $\text{Cu}_0^{++}/\text{Cu}^{++}$  for a  $0.008N$ -solution of copper nitrate to which  $2N$ -solutions of the nitrates of other metals have been added: Rb, 1.44; K, 1.67; Na, 1.14; Li, 0.75; Sr, 0.97; Ca, 0.89; and Mg, 0.81; with 72% alcohol the value falls to 0.2. These results are explained on the hypothesis that in the solution an equilibrium  $\text{Cu}(\text{H}_2\text{O})_n^{++} \rightleftharpoons \text{Cu}^{++} + n\text{H}_2\text{O}$  exists, and of the two ions, the non-hydrated ion alone reacts with the electrode. When a neutral salt is added, there is a competition between it and the hydrated ion for the water with which it is combined, and if the neutral salt forms hydrated salts, it will take some of this water, more the greater the avidity with which it takes up water, and consequently the equilibrium expressed above will be displaced toward the right.

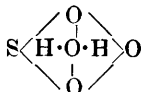
J. F. S.

**Processes Operative in Solutions. XXXI. Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents. A Discussion of the Constitution of Sulphuric and other Polybasic Acids and of the Nature of Acids.** HENRY E. ARMSTRONG and F. P. WORLEY (*Proc. Roy. Soc.*, 1914, [A], 90, 73—100. Compare A., 1913, i, 1116).—A comparative study has been made of a number of sulphonic acids when used as catalysts in the hydrolysis of sucrose at 25°. In most cases, the molar ratio of sucrose to acid was kept constant (0.25 : 1), whilst the ratio of acid to water was varied.

The relative values obtained for the velocity-coefficient from experiments on solutions containing the acid and water in the molar ratio 1 : 100 are as follows: sulphuric, 256; benzenesulphonic, 220; *p*-toluenesulphonic, 217.4; mesitylenesulphonic, 203; *p*-chlorobenzenesulphonic, 216; *p*-bromobenzenesulphonic, 208; *p*-iodobenzenesulphonic, 214;  $\alpha$ -bromocamphor- $\beta$ -sulphonic, 201.3; *p*-dichlorobenzenesulphonic, 209; *p*-dibromobenzene-sulphonic, 212; *p*-di-iodobenzenesulphonic, 223; benzene-*o*-disulphonic, 452; benzene-*p*-disulphonic, 522; benzene-*m*-disulphonic, 533; benzene-1 : 3 : 5-trisulphonic, 982; toluene-2 : 4 : 6-trisulphonic, 950.

These numbers show that the substitution of hydrogen in benzenesulphonic acid by halogens or by methyl groups has very little influence on the hydrolytic activity of the acid. The disulphonic acids show very markedly the influence of the relative position of the sulphonic groups, in that the ortho-acid is very much weaker than the other two isomerides, whilst the para-acid is somewhat less active than the meta-acid. The molecular hydrolytic activity of benzene-*m*-disulphonic acid is much more than twice, and that of benzene-1 : 3 : 5-trisulphonic acid much more than three times, as great as the activity of benzenesulphonic acid. If, however, the three acids are compared when the concentrations are equivalent instead of equimolecular, it is found that the activities are equal. In other words, the  $\text{SO}_3\text{H}$  group has the same value in each of the three acids when the amount of water present is proportional to the number of the sulphonic groups.

The properties of sulphuric acid, and in particular its activity as a hydrolyst, are considered to afford evidence that sulphuric acid is a strong monobasic acid, for which the formula



is suggested. On the assumption that the valency volume of sulphur, like that of oxygen, is twice that of hydrogen, a model has been constructed which shows the spacial relations between the atoms in the molecule.

Similar considerations are applicable to other inorganic acids, such as carbonic, silicic, phosphoric, and arsenic acids. In all cases these are to be regarded as compounds of the anhydrides with hydrone rather than as hydroxyl derivatives, and, like sulphuric, they are all essentially monobasic.



In discussing the nature of acidity, it is maintained that this property is a function of the acid molecule as a whole, and that this reacts with water, giving rise to two compounds,  $\text{HX} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$  and  $\text{H}_2\text{O} < \begin{smallmatrix} \text{H} \\ \text{X} \end{smallmatrix}$ . The proportions in which these are present will depend on the concentration of the solution. The lack of agreement between the results obtained by the hydrolytic and electrolytic methods of comparing acids may possibly be explained from this point of view.

H. M. D.

**Processes Operative in Solutions. XXXII. The Influence of Sulphonates on the Hydrolytic Activity of Sulphonic Acids. A Contribution to the Discussion on the Influence of Neutral Salts.** HENRY E. ARMSTRONG and F. P. WORLEY (*Proc. Roy. Soc.*, 1914, [A], 90, 101—111).—The influence of potassium, calcium, strontium, barium, zinc, and cadmium *p*-toluenesulphonates on the activity of *p*-toluenesulphonic acid has been examined by experiments on the rate of inversion of sucrose at 25°. The effects produced by equivalent amounts of the various salts are not very different, the velocity-coefficients varying from 235 for a solution containing the barium salt to 245 for the zinc salt, the corresponding number obtained with the acid alone being  $217 \times 10^{-5}$ .

From experiments in which the ratio of sucrose to water was kept constant, whilst the concentration of the acid was varied, it has been found that the relative effect of the addition of a gram molecule of the potassium salt increases as the proportion of acid in the solution decreases.

The data are applied in the calculation of "apparent hydration values." For solutions which contain the acid, sucrose and water in the molar ratio 1:0.5:100, together with one equivalent of salt, these values vary from 7.5 for the potassium salt to 10 for the zinc and cadmium salts.

The later part of the paper is devoted to a discussion of the association hypothesis, with special reference to the recently expressed view that chemical activity is conjointly determined by the action of ions and undissociated molecules.

H. M. D.

**Ideal Concentrated Solutions.** J. N. BRÖNSTED (*Zeitsch. Elektrochem.*, 1914, 20, 278—279).—Polemical. An answer to Nernst's criticism (this vol., ii, 251) on the author's treatment of concentrated solutions (this vol., ii, 251).

J. F. S.

**Is the Continuous Passage from the Liquid Condition to the Crystalline Possible and Can Critical Points Appear?** LÉON SCHAMES (*Zeitsch. physikal. Chem.*, 1914, 87, 369—378).—A theoretical paper in which the titular questions are discussed; it is shown that, contrary to the Tammann closed curve, one with two critical points is possible. These points lie, however, at  $p=0$ ,  $T=0$ , and  $p=\sigma$ ,  $T=T_k$ , so that in reality a continuous change from the crystalline to the liquid condition is not possible. The

condition surface obtained on these conditions for normal and abnormal liquids is discussed, and it is shown from the measurements of Bridgman (A., 1913, ii, 39) that the second critical temperature for water is probably identical with the usual critical temperature (liquid-vapour). Since water is to be regarded as a normal liquid at such high pressures, this conclusion is to be made also in the case of other normal liquids. In the abnormal region of water, at the absolute zero of pressure and temperature, the identity of liquid water and ice I is regarded as certain, and the identity of liquid water and the other varieties of ice as very probable. J. F. S.

**Application of E. S. Fedorov's Crystallo-chemical Method in Scientific Investigations.** B. ORELKIN and G. FIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 227—234).—The authors emphasise the value of crystallographic measurements in the identification of compounds, and, consequently, in following chemical changes. Several examples are given. T. H. P.

**The Mobility of the Molecules in a Solid Crystal.** FRED WALLERANT (*Compt. rend.*, 1914, 158, 1143).—As a result of experiments on fused, crystalline potassium nitrate, the author has been led to modify his views on the polymorphism of camphor, and he now considers it to be trimorphic, and not quadrimorphic (compare this vol., i, 420).

A crystal of potassium nitrate is fused and allowed to crystallise between two glass plates, and is then heated to a temperature well below its melting point. On applying pressure at one point of the top plate, one or more new crystals appear at the point of compression, and grow at the expense of the original crystal. There is, however, no relation of orientation between the new and the original crystals. W. G.

**Microscopical Metallography in Three Dimensions.** A. PORTEVIN (*Intern. Zeitsch. Metallographie*, 1914, 6, 58—71. Compare Oknov, A., 1911, ii, 495, 986).—A device is described for holding specimens in such a way that successive layers may be removed by grinding, and the same area brought repeatedly into the field of the microscope. In this way, the form of a crystal may be reconstructed from successive serial sections. The method is applied to crystals of the compounds SbSn and CuSn. C. H. D.

**Morphological Studies of Benzene Derivatives. V. The Correlation of Crystalline Form with Molecular Structure. A Verification of the Barlow-Pope Conception of "Valency-Volume."** HENRY E. ARMSTRONG, R. T. COLGATE, and E. H. RODD (*Proc. Roy. Soc.*, 1914, [A], 90, 111—173. Compare T., 1910, 1578; A., 1912, i, 756).—From an examination of the crystalline form of a large number of compounds of the type  $C_6H_3R_1R_2 \cdot SO_2X$ , in which  $R_1$ ,  $R_2$ , and X represent either chlorine or bromine, evidence has been obtained which is said to furnish a conclusive proof of the

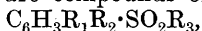
validity of the postulates on which the Barlow-Pope method of correlating crystalline form with internal molecular structure is based, and also of the general accuracy of the conclusions to which the application of this method leads.

For thirty-one compounds of the above type, including fourteen examples of disubstituted sulphonyl chlorides and bromides of the para-series, six of the meta- and eight of the ortho-series, together with three monosubstituted derivatives, the mean values of the equivalence parameters are  $x:y:z=3.904:3.360:2.772$ , the extremes being  $3.806:3.222:2.680$  and  $4.040:3.419:2.865$ . For benzene itself, the equivalence parameters assigned by Barlow and Pope are  $3.101:3.480:2.780$ . It is to be noted that the  $y$  and  $z$  parameters are practically the same for the thirty-one compounds investigated as for benzene. The difference in the  $x$  parameter corresponds with the change brought about by the introduction of the  $\text{SO}_2\text{X}$  group. This difference ( $3.904-3.101=0.803$ ) is practically equal to that deduced from the molecular models, constructed on the assumption that the valency volume of sulphur and oxygen is twice that of hydrogen, whilst that of the halogens is equal to the volume of hydrogen.

From a consideration of compounds in which complex radicles of equal valency volume, such as  $\text{SO}_2\text{Cl}$ ,  $\text{NO}_2$ ,  $\text{CH}_3$ , and  $\text{CH}_2\text{Br}$ , are present, it is found that these have practically the same influence on the crystalline structure. The small differences are no doubt connected with the fact that groups containing two large atoms cannot be "packed" quite in the same way as those which contain a larger number of smaller atoms.

From the same point of view, the authors have compared the crystalline forms of benzenesulphanilide and its derivatives, of acetanilide and a number of allied compounds, and find that in these cases, also, the crystalline form can be correlated with the molecular structure on the basis of the Barlow-Pope theory.

A number of benzene derivatives which have been examined cannot, however, as yet be interpreted in accordance with the authors' method. Such are compounds of the type



which crystallise in anorthic, pseudotetragonal, or pseudocubic forms.

The paper concludes with a detailed record of the crystallographic measurements made for each of the substances investigated.

H. M. D.

**Atomic Theory. III. The Preparation of Colloidal Solutions by [Electric] Disintegration.** D. ZAVRIEV (*Zeitsch. physikal. Chem.*, 1914, 87, 507—510. Compare this vol., ii, 451).

—The Bredig method for the preparation of colloidal solutions of metals can only be applied to the noble metals. The present paper deals with a modification of Svedberg's method for the production of colloidal solutions of metals other than the noble metals. Two electrodes made of the metal to be disintegrated are placed 1/10 mm. apart in a vessel of water, and a current is passed from

an induction coil, fed by 15—20 amperes at 120 volts, and having a spark 20 cm. long, and bound with a large condenser. In this way it is possible to obtain colloidal solutions of practically all the metals. An iron solution prepared in this way could be kept for a month, magnesium for two days, copper and aluminium for somewhat less than a month. Cobalt, zinc, and nickel could only be got to give poor solutions by this arrangement, but by replacing the coil by a large Holtz influence machine, they could readily be disintegrated when a spark-gap was connected in parallel with the metal electrodes.

J. F. S.

**Fluctuations of Concentration in a Colloidal Emulsion.** RENÉ COSTANTIN (*Compt. rend.*, 1914, 158, 1341—1343).—A mathematical paper in which the author shows that his results on the compressibility of a colloidal emulsion (compare this vol., ii, 438) verify Smoluchowski's theory on the fluctuations in density produced by molecular agitation (compare *Bull. Acad. Sci. Cracow*, 1907, December).

W. G.

**Significance of Ionic Volume for the Action of Electrolytes on Colloidal Systems.** G. R. MINES (*Kolloid-Zeitsch.*, 1914, 14, 167—168).—The observed differences in the activity of simple and complex cations towards colloidal substances are attributed partly to differences in ionic volume which give rise to variations in the surface density of the electric charge; and partly to variations in the specific inductivity capacity of the colloidal particles.

The volumes of the  $\text{La}^{+++}$  and  $\text{Co}(\text{NH}_3)_6^{+++}$  ions are approximately in the ratio 1:13, and in view of this difference in ionic size, it is not surprising to find that these ions exhibit considerable differences in their behaviour towards colloidal substances. In equivalent solutions, it is to be expected that the complex ion will exert an influence on a much larger number of colloidal particles, and if the ion serves as nucleus in the coagulation of the colloid, it may be anticipated that the complex will tend to form larger molecular aggregates.

H. M. D.

**Measurement of the Tyndall Effect in Colloidal Solutions.** WERNER MECKLENBURG (*Kolloid-Zeitsch.*, 1914, 14, 172—181).—A photometric apparatus is described which has been designed for the production and measurement of the intensity of the Tyndall effect in colloidal solutions. The intensity of the light emitted from the Tyndall beam in a direction perpendicular to the beam itself is compared with the intensity of the incident light by reflecting a portion of this and reducing its intensity by an arrangement of Nicol prisms until it becomes equal to that of the light emitted by the Tyndall beam. The intensity of the Tyndall beam diminishes as the length of its path in the colloidal solution increases, but by taking a series of observations at different points in the path of the beam, it is possible to obtain the intensity of the light emitted by the Tyndall beam at the point at which the light enters the solution. The graphically extrapolated intensity

is found to be characteristic of a given solution, and for one and the same substance is proportional to the number of colloidal particles in unit volume.

The Tyndallmeter, as the instrument is called, may be used in the comparison of different solutions of the same colloidal substance, in the investigation of the processes which occur during coagulation, and in the examination of polluted waters. H. M. D.

**New Determination of the Avogadro Constant from the Brownian Movement of Small Mercury Particles Suspended in Water.** IVAR NORDLUND (*Zeitsch. physikal. Chem.*, 1914, 87, 40—62).—The Avogadro constant has been determined from the Brownian movement of submicroscopic mercury particles. The particles were produced by electric disintegration, and the movement, as well as the rate of fall through the liquid medium, were determined photographically at intervals of one-sixtieth of a second, which were automatically made. The temperature of the experiments was carefully regulated, and did not vary more than  $3/100^\circ$  in any series of measurements. The measurements were made in narrow quartz glass cells, and the retarding influence of the walls on the Brownian movement and on the velocity of deposition of the particles was compensated by multiplying the viscosity  $\eta$  of the dispersion medium by the factor  $1/n$ , where 
$$n = 1 - \{9P^2(16A + 9P)/16(A - 2P)(8A + 9P)\} \cdot \log_e(16A - 7P)/25P,$$
  $P$  being the radius of the particles and  $A$  the distance apart of the walls of the cell. The value  $N = 5.91 \times 10^{23}$  is obtained as a mean of twelve determinations which lie between  $4.57 \times 10^{23}$  and  $7.00 \times 10^{23}$ , the most generally accepted value for  $N$  being  $6.06 \times 10^{23}$  (Millikan). The law  $(\text{displacement})^2 = \text{time} \times \text{constant}$  is confirmed in many cases. J. F. S.

**The Vertical Partition of Particles in the Brownian Movement.** B. ILJIN (*Zeitsch. physikal. Chem.*, 1914, 87, 366—368).—The partition of particles in emulsions of gamboge in water and gum arabic in castor oil and water, with respect to their vertical concentration, has been investigated. It is shown that the partition of the particles with the height follows the theoretical law of Perrin within the experimental error (Perrin, A., 1910, ii, 493). J. F. S.

**The Mechanism of the Chemical Reaction.** GEORGES BAUME (*Compt. rend.*, 1914, 158, 1177—1179).—A theoretical paper in which the author further develops the theory of "quanta" already put forward by him (compare A., 1913, ii, 1038). W. G.

**Reaction Velocity and Activation.** M. TRAUTZ (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), 11, 310—314).—A theoretical paper, in which the author shows that there is a general relation between the absolute value of the chemical reaction velocity and the temperature quotient. T. S. P.

**Retardation of the Decomposition of Hydrogen Peroxide in Presence of Colloidal Platinum by Indifferent Narcotics.** OTTO MEYERHOF (*Pflüger's Archiv*, 1914, 157, 307—325. Compare this vol., ii, 450).—Experiments have been made to determine the influence of various narcotics (alcohols, ketones, urethanes) on the rate of decomposition of hydrogen peroxide in presence of colloidal platinum. In general, the results show that the activity of members of homologous series increases with the molecular weight, and it would seem, therefore, that the retardation effects are similar to those which have been observed in the inversion of sucrose by invertase, and also in connexion with respiration. The most clearly marked influence of homology on the retardation is found in the case of the aliphatic alcohols.

According to ultramicroscopic observations, the retarding influence of narcotics is not determined by a reduction in the number of the colloidal particles of the catalyst. There was also no evidence that the colloidal solution became less stable after the addition of the narcotic.

H. M. D.

**Action of Light on Chlorine Water.** ALFRED BENRATH and HERBERT TUCHEL (*Zeitsch. wiss. Photochem.*, 1914, 13, 383—398).—The rate at which chlorine water is decomposed under the influence of light has been investigated in a series of experiments, in which the effect of the addition of hydrochloric acid and of various metallic chlorides was also examined. The source of light was a quartz mercury lamp, and during the period of insolation the solution was subjected to a continuous rotary movement in order to eliminate disturbances from any inequalities in the concentration which might be set up in consequence of the greater amount of decomposition in the outer layers of the solution. The progress of the reaction was followed by measurement of the electrical conductivity by means of two electrodes inserted in the insolation tube.

On the assumption that the change in conductivity is proportional to the change in the concentration of the chlorine, it is found that the data agree with the unimolecular formula  $k=1/t \cdot \log a/(a-x)$ . In the case of pure chlorine water, the whole of the chlorine disappears in the photochemical change, but in solutions which contain hydrochloric acid or metallic chlorides, the reaction comes to an end before the whole of the chlorine has been decomposed. When the reaction is incomplete, the value of  $a$  is given by the concentration of the decomposable chlorine, and not by the total chlorine in the original solution.

If the concentration of the added hydrochloric acid is greater than about 0.5*N*, no decomposition is observed on exposure to light. In the less concentrated acid solutions, the observed rate of decomposition indicates that  $k$  is practically unaffected by the acid present. On the other hand, the coefficient has a higher value in presence of certain chlorides. According to the data for 1*N*-solutions, sodium, potassium, and calcium chloride have a greater influence on the reaction velocity than the chlorides of barium,

magnesium, and strontium. The greater the influence of a salt on the proportion of chlorine which remains undecomposed, the less is its influence on the reaction velocity. This is clearly shown by the data for the alkaline earth metal chlorides.

From experiments at 5° and 30°, it is found that the reaction velocity increases in the ratio 1:1.395 for a rise of 10°.

H. M. D.

**The Temperature-coefficient of Chemical Reactions.** A. SKRABAL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), ii, 306—309).—Mainly a theoretical paper, in which the author shows that it is possible to have reactions for which the temperature quotients are very large. Such reactions generally proceed with extremely small velocity, which is usually incapable of measurement.

The author has succeeded in carrying out measurements on the reaction  $3\text{I}_2 + 6\text{OH}' = 3\text{H}_2\text{O} + 5\text{I}' + \text{IO}_3'$ , and shows that the results are in accordance with his theory.

The relations holding between the temperature and the temperature quotient are also discussed.

T. S. P.

**Dynamics of the Time Reaction between Aqueous Carbonic Acid and Bases.** A. THIEL and R. STROHECKER (*Ber.*, 1914, 47, 1061—1068).—In a previous communication (A., 1913, ii, 396) it has been shown that the slow neutralisation of an aqueous solution of carbonic acid by bases is probably dependent on the reaction represented by the equation  $\text{CO}_2 + \text{OH}' \rightarrow \text{HCO}_3'$ , and is not conditioned by the rate of hydration of carbon dioxide to carbonic acid. The reaction should therefore be bimolecular.

The authors have succeeded in measuring the velocity of reaction, using a colorimetric method with  $\alpha$ -naphtholphthalein as indicator, and find that it is really proportional to the concentrations of the free carbon dioxide and of the hydroxide ion, but also inversely proportional to the concentration of the hydrogen carbonate ion, the proportionality factor being 0.38 at 4°.

The bases used in the investigation were sodium hydroxide, potassium hydroxide, and tetraethylammonium hydroxide.

T. S. P.

**Kinetics of the Change of Halogen-alkylamines into Heterocyclic Compounds. III. The Change  $\beta$ -Bromoethylamine into Dimethyleneimine Hydrobromide.** H. FREUNDLICH and W. NEUMANN (*Zeitsch. physikal. Chem.*, 1914, 87, 69—86. Compare also Freundlich and Krestovnikov, A., 1911, ii, 266, and Freundlich and Richards, A., 1912, ii, 633).—The transformation of  $\beta$ -bromoethylamine into dimethyleneimine hydrobromide has been carried out in the presence of sodium hydroxide solution, and the velocity of the reaction determined. It is shown that the reaction is unimolecular, and that the temperature-coefficient is 4.9 for 10° over the range 0—10°. Measurements were made at 0°, 15.65°,

and  $26^{\circ}$ . The reverse reaction was carried out in hydrogen bromide solution at  $25^{\circ}$ . This reaction is bimolecular, but is complicated by the formation of piperazine to a small extent, consequently the reaction constant is somewhat uncertain. The temperature-coefficient of this reaction is less than that of the preceding reaction. The equilibrium between dimethyleneimine hydrobromide and  $\beta$ -bromoethylamine was determined from both sides, but the value of  $k$  obtained (3.95) does not agree with that calculated from the two velocity constants (0.1). J. F. S.

**The Equilibrium and the Velocity of Transformation of Fumaric and Maleic Acids under the Influence of the Light from a Quartz Mercury Lamp.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1914, 87, 333—356. Compare Ciamician and Silber, A., 1904, i, 161; Stoermer, A., 1911, i, 295).—It has previously been shown that fumaric acid is converted into maleic acid by ultra-violet light (*loc. cit.*). The present investigation has as its object the determination of the equilibrium which exists between the two acids and the velocity of transformation in either direction. The transformation was carried out in aqueous solutions of the acids of  $0.084N$ ; these were subjected to the action of the light from a quartz mercury lamp in vessels of glass and of quartz. Other experiments were carried out with the solid acids. The method of analysis of the acids depended on the measurement of the molecular conductivity, and by means of empirical extrapolation formulæ the content of the solution on both acids could be calculated. In the solid condition fumaric acid is not converted into maleic acid by ultraviolet light, whilst maleic acid is converted into fumaric acid only to the very slightest extent. In aqueous solution equally, whether the solution was contained in glass or in quartz vessels, an equilibrium between the two acids could be reached from either side. The equilibrium was displaced somewhat toward the maleic acid side with increasing concentration; thus at  $45$ — $50^{\circ}$  with  $1/10N$ -solution the equilibrium mixture contained 75% of maleic acid and in  $2/5N$ -solution 79% of maleic acid. The velocity of transformation was much greater in quartz vessels than in glass vessels, whilst the position of the equilibrium is uninfluenced; warming of the material before subjecting it to the light has no influence on the velocity of transformation. It is shown in an empirical manner that, under the present experimental conditions, between the concentrations  $0.02N$  to  $0.08N$  the velocity of transformation of fumaric acid into maleic acid increases as the  $2/5$  power of the concentration of the fumaric acid, and the opposite reaction as the  $7/20$  power of the maleic acid. An empirical formula is given, which allows the velocity to be expressed as a function of the excess of one of the acids above that required for equilibrium. It is shown that the decomposition of maleic and fumaric acids with the loss of carbon dioxide, as shown by Berthelot and Gaudechon (A., 1911, ii, 170), does not take place under the present conditions to a measurable amount in forty-eight hours.

J. F. S.



**Retardation of Ferment Reactions by Indifferent Narcotic Substances.** OTTO MEYERHOF (*Pflüger's Archiv*, 1914, 157, 251—306).—The retarding influence of indifferent narcotics on the rate of inversion of sucrose by invertase has been examined, with the result that the members of homologous series are found to arrange themselves in the same order as that which has been previously observed in the retardation of respiration and alcoholic fermentation. In the homologous series of the aliphatic alcohols, ketones and urethanes, the retarding influence increases with increasing molecular weight.

In respect of the action of invertase, it has been found that the retardation effect increases with decreasing sucrose concentration for most of the substances investigated. Purification of the invertase or addition of egg albumin has no appreciable influence on the retardation. If the invertase is adsorbed by colloidal ferric hydroxide and the precipitate distributed through the sucrose solution, inversion takes place at the same rate as if the invertase were added to the solution in the ordinary way. In general, the retardation effects observed with adsorbed invertase are the same as those found for the unadsorbed ferment.

Other experiments indicate that the degree of dispersity of egg-albumin solutions is not appreciably affected by the addition of narcotics.

From observations on the retardation of respiration in sea urchin's eggs, and of the rate at which oxygen is absorbed by mechanically disintegrated eggs, it has been found that higher concentrations of the various narcotics are required to produce a given retardation in the second process. Since acetone egg powder is affected to a still smaller extent, it would seem that the narcotic influence is largely determined by the vitality of the cells.

H. M. D.

**Forces between Atoms and Chemical Affinity.** SIR J. J. THOMSON (*Phil. Mag.*, 1914, [vi], 27, 757—789).—On the assumption that the forces exerted by an atom are the same as those which may be brought into play if each atom contains an electrical doublet, the moment of which is characteristic of the atom, the author shows that chemical compounds may be divided into two classes. In the one class, the component atoms are electrically neutral, whilst in the other they are either positively or negatively charged. The properties are strikingly different according to whether a compound forms a member of the one or of the other class. This difference is to be expected in view of the circumstance that the poles of the doublets are more widely separated in the case of compounds of the second class.

The above views are applied to the consideration of the chemical effects which are produced by the electric fields, of the number of molecules which may enter into combination, and of the conditions which determine the existence of a chemical compound and give rise to the effect of valency.

H. M. D.

**The Atomic Theory. I. The Partition of the Particles in a Kinetic Field.** RICHARD LORENZ and W. EITEL (*Zeitsch. physikal. Chem.*, 1914, **87**, 293—304. Compare Smoluchowski, *Boltzmann Festschrift*, 1904, 626).—A mathematical paper in which the formula of Smoluchowski, giving the probability of a given volume  $v$  in a large volume  $V$  containing  $n$  molecules out of  $N$  contained in the whole volume, is developed, without the use of simplifying assumptions.  
J. F. S.

**The Atomic Theory. II. The General Formulæ for the Partition of Particles in a Kinetic Field.** RICHARD LORENZ and W. EITEL (*Zeitsch. physikal. Chem.*, 1914, **87**, 434—440. Compare preceding abstract).—The formulæ for the partition of particles deduced by the authors (*loc. cit.*) and Smoluchowski (*Boltzmann Festschrift*, 1904, 626) have been applied by Svedberg (A., 1910, ii, 772) to observations in the kinetic field of colloidal systems, and found not to be applicable. He uses, therefore, modified formulæ, which the authors deduce mathematically in the present paper.  
J. F. S.

**Electron Conception of Valence.** STUART J. BATES (*J. Amer. Chem. Soc.*, 1914, **36**, 789—793).—A series of objections is raised to the electron theory of valence. The author acknowledges that the theory has been of value for the classification and relation of compounds and of reactions (compare Nelson, Beans, and Falk, this vol., ii, 44), but points out that the actual movement of the electron is not necessarily involved in the conclusions drawn, and suggests that some other assumption might lead to a similar classification.  
E. G.

**Flask with Ground-in Distilling Arrangement (Still-head).** GEORG WEMPE (*Zeitsch. angew. Chem.*, 1914, **27**, 240).—Ground into the neck of a conical flask is a still-head, which consists essentially of a bulb, from the top of which passes a tube bent in such a way that it can be fitted into a condenser. It can be used for separating a solvent and solute in organic work, the solute remaining in the flask without being contaminated, as it would be if a cork or bung were used to fit in the still-head.  
T. S. P.

**The Relation of Pulsation to Filtration.** ROBERT A. GESELL (*Amer. J. Physiol.*, 1914, **34**, 186—202).—Solutions were filtered through various membranes under constant and pulsatile pressure. Pulsation favours filtration, and so also does stirring. The composition of the filtrate is not influenced, except when colloids (globulins) are used; more globulin passed the membrane during periods of constant than during periods of pulsatile pressure.  
W. D. H.

**A Durable Gas Generator.** U. KREUSLER (*Zeitsch. anal. Chem.*, 1914, **53**, 234—241).—A somewhat complicated form of gas generator is described, which has been found to give satisfactory results

in the generation of hydrogen sulphide, hydrogen, and carbon dioxide for general laboratory work. The acid is admitted to the vessel in which the gas is generated through an adjustable conical glass valve, and the regulation of the gas pressure as well as the removal of the waste liquor is effected by means of a Liebig condenser, the inner tube of which terminates within the outer tube. The side-tube at the lower end of this outer tube is connected laterally with a flask which communicates with the lower end of the gas generating cylinder.

H. M. D.

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## Inorganic Chemistry.

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**Rate of Solution of Hydrogen by Palladium.** ALFRED HOLT (*Proc. Roy. Soc.*, 1914, [A], 90, 226—237. Compare A, 1913, ii, 330, 839).—Further experiments have been made to ascertain the connexion between the rate of solution of hydrogen in palladium at constant pressure and the concentration of the gas in the metal. The curves, which are obtained by plotting the rate of solution as a function of the quantity of gas which has been occluded by the metal, consist of two portions, which indicate the occurrence of two distinct processes. It is supposed that the platinum consists of two modifications of the element, which differ very considerably in respect of their activity towards hydrogen. The first portion of the velocity-concentration curve is probably determined by the dissolution of the hydrogen in the active or  $\alpha$ -form, whilst the second part of the curve has reference to the dissolution of the gas in the inactive or  $\beta$ -modification. The fact that a smooth curve is obtained when platinum-black is used as the absorbing medium is supposed to show that this consists almost entirely of the active modification.

The phenomena observed when the heated metal is allowed to cool in contact with an atmosphere of hydrogen are shown to be capable of interpretation on the basis of the theory put forward.

H. M. D.

**Partial and Intermittent Combustion of Gas.** E. E. SOMERMEIER (*J. Ind. Eng. Chem.*, 1914, 6, 374—378).—The author has investigated the influence of the volume of gas, of the method of ignition, and of the shape of the container, on the combustion of mixtures of hydrogen and air, and of natural gas and air.

With a high initial ignition temperature a reaction may start in a gas mixture which, as a whole, is incombustible, that is, the heat of combustion is insufficient to maintain the temperature at the kindling point. When the combustion is started from a source of very high temperature, more gas is burned in a large volume

of mixture than in a small volume, but the greater percentage of gas is burned in the mixture of smaller volume.

With a continuous source of high temperature, as with a white-hot wire, a lamp flame, or a running electric spark, the reaction produced may be intermittent. The gas immediately round the point of ignition burns and expands, combustion then ceasing until the expanded gas and products of combustion are replaced by another portion of the mixture of gas and air.

Full details are given of the way in which the limits of appreciable ignition or combustion vary with the volume of gas used, the source of ignition, and the shape of the container. The results indicate that a comparatively small excess of hydrogen above the theoretical requirement (compare this vol., ii, 356) is necessary to produce a vigorous reaction. Natural gas, or methane, on the other hand, ignites with such difficulty that, with ordinary methods of ignition, an appreciable reaction does not occur unless a very large excess of gas is present above that required by the thermal calculation.

T. S. P.

**Preparation of Hydrogen Peroxide.** HENCKELL & Co. (Swiss Patent 63359, 63360).—(I) A 1% solution of sulphuric acid is saturated with oxygen under a pressure of 100 atmospheres and electrolysed with the use of an amalgamated gold cathode. Solutions of hydrogen peroxide up to 3% concentration are obtained in this way. (II) Hydrogen peroxide is obtained by the action of oxygen under pressure in the presence of water on hydrogen passing through a porous tube impregnated with a catalyst such as palladium.

J. C. C.

**Process for Increasing the Stability of Hydrogen Peroxide in Neutral Carriers of this Substance.** E. MERCK (Swiss Patent 63361).—The stability of hydrogen peroxide can be greatly increased by the addition of acyl esters of aminohydroxycarboxylic acids; for example, (1) 1 part of  $\beta$ -dimethylamino- $\alpha$ -benzoyloxyisobutyric acid is added to 1000 parts of 3–30% hydrogen peroxide. (2) 600 parts of carbamide, 2500 parts of a 15% hydrogen peroxide solution, and 1 part of benzoyleneguanine are evaporated in a vacuum. The product (940 parts) contains about 36% of hydrogen peroxide; (3) 60 parts of ammonium sulphate and 75 parts of 30% hydrogen peroxide are stirred together, cooled, and the crystalline mass is separated, mixed with 0.05 part of  $\alpha$ -benzoyl- $\beta$ -piperidylpropionic acid, and dried in a vacuum. The product contains 20–22.2% of hydrogen peroxide.

J. C. C.

**The Influence of Ocean Spindrift and Blown Spray on the Chlorine Content of Inland Waters.** WILLIAM BARR (*J. Hygiene*, 1914, 14, 119–128).—Chlorine in inland ground waters, except where beds of salt occur, is derived from the sea through the ocean spindrift and blown spray; the amount diminishes with the distance from the seaboard, but is affected by the configuration of the land, being greater where the land is continuously low, and

by the direction of prevailing winds. These statements are illustrated by charts of certain districts in Scotland, constructed from the analyses of the inland waters there. W. D. H.

**Revision of the Density of Oxygen.** ALBERT F. O. GERMANN (*J. Chim. Phys.*, 1914, 12, 66—108).—The methods employed in the determination of the density of the air at Geneva (A., 1912, ii, 636) have been applied to oxygen. In order to obtain greater accuracy in the measurement of the pressure of the gas at the moment when the containing vessels (capacity 250 to 850 c.c.) were closed, readings were taken on four barometers. The oxygen was obtained by heating potassium permanganate, and afterwards purified by fractional distillation.

The mean of fifteen determinations of the weight of a normal litre (0°, 760 mm., sea-level, and a latitude of 45°) is 1·42906 gram. In combination with the values obtained by Morley and Rayleigh, the most probable value is considered to be 1·42905 grams.

Two separate measurements made by the author gave for the density of air 1·2927 and 1·2932. H. M. D.

**Occurrence of Ozone in the Upper Atmosphere.** J. N. PRING (*Proc. Roy. Soc.*, 1914, [A], 90, 204—219. Compare T., 1910, 97, 868).—It has been found that an aqueous solution of potassium iodide may be used for the estimation of ozone in the air at temperatures down to -60°. Below -24°, the reaction gives rise to iodate, whatever the ozone concentration, but at higher temperatures and at high dilutions (1:100,000) the products formed are hypoiodite and free iodine. Since the oxides of nitrogen give the iodate at all concentrations, and hydrogen peroxide can be distinguished by the titanium test, it has been found possible to differentiate between these various substances, with the result that atmospheric air has been found to contain definite quantities of ozone, but no detectable quantities of hydrogen peroxide or the oxides of nitrogen.

Observations made in this country indicate that the average amount of ozone is 2·5 volumes per million volumes of air, and that this amount varies very little with the altitude between 5 and 20 kilometres. In the Alps, a mean value of 2·5 volumes was obtained at 2100 metres, and 4·7 volumes at 3580 metres. From colorimetric observations, it would seem that ozone must be regarded as a contributing factor in determining the blue colour of the sky.

According to experiments on the action of ultra-violet light on air, ozone is formed to a limited extent. The rate of formation of the gas is only slightly diminished in the presence of water vapour, but decreases rapidly with falling pressure. H. M. D.

**Boiling Point of Sulphur on the Thermodynamic Scale.** N. EUMORFOPOULOS (*Proc. Roy. Soc.*, 1914, [A], 90, 189—203).—The results obtained in previous experiments (A., 1908, ii, 1029) could

not be regarded as final on account of the change in the volume of the glass bulb of the constant-pressure gas thermometer. In the experiments now described, the glass bulb was replaced by a bulb of fused silica. The new observations lead to  $444.61^{\circ}$  as the boiling point of sulphur on the thermodynamic scale, and to  $273.13^{\circ}$  as the melting point of ice.

H. M. D.

**The Reducing Power of Sulphurous Acid. I. Action of Sodium Hyposulphite on Tellurium and Selenium.** L. TSCHUGAEV and W. CHLOPIN (*Ber.*, 1914, **47**, 1269—1275).—Using an apparatus in which reactions can be carried out in an atmosphere of hydrogen, all oxygen being rigorously excluded, the authors find that tellurium (0.3—0.5 gram) dissolves in 10% sodium hydroxide (12—20 c.c.) containing sodium hyposulphite (1.2—2 grams) when the mixture is heated on the water-bath. The solution is at first violet, and then grows colourless; on cooling, colourless crystals separate, in which the ratio of sodium to tellurium agrees with that of a *sodium telluride*,  $\text{Na}_2\text{Te}$ ; they are hydrated, but could not be obtained dry owing to their ready decomposition with separation of tellurium. The sodium telluride was further characterised by the formation from it of *benzyl telluride*,  $(\text{C}_6\text{H}_5\cdot\text{CH}_2)_2\text{Te}$ , by heating it in aqueous alcoholic solution with benzyl chloride, or in aqueous solution with phenylbenzyl-dimethylammonium chloride (leucotrope), which also acts as a benzylating agent. Benzyl telluride crystallises in pale yellow needles, m. p.  $53\text{—}53.5^{\circ}$ , which readily decompose in the air, with separation of tellurium.

The mother liquor from the preparation of the sodium telluride contains chiefly sodium sulphite, together with varying quantities of sodium sulphide. The reaction is probably expressed by the equation:  $\text{Na}_2\text{S}_2\text{O}_4 + \text{Na}_2\text{Te}_2 + 4\text{NaOH} = 2\text{Na}_2\text{SO}_3 + 2\text{Na}_2\text{Te} + 2\text{H}_2\text{O}$ , the sodium telluride resulting from the tellurium and the sodium hydroxide. The sodium sulphide results from a secondary reaction between the sodium hyposulphite and the sodium hydroxide.

Sodium telluride is much more readily obtained when rongalite is used in place of sodium hyposulphite, formaldehyde being liberated; no sodium sulphide is formed. Sodium selenide can be obtained similarly from selenium, although the reaction does not go so readily; sulphur is attacked only to a very slight extent under the same conditions.

T. S. P.

**The Sulphuric Acid Chamber Process.** WALTHER HEMPEL (*Zeitsch. angew. Chem.*, 1914, **27**, 218—223).—An arrangement is described by means of which a mixture of sulphur dioxide, oxygen, and water vapour, in the proportions necessary to form sulphuric acid, could be introduced into a glass vessel containing nitrogen, oxygen, and oxides of nitrogen in known amounts. The mixture containing the sulphur dioxide was made by decomposing sulphuric acid by contact with a hot surface electrically heated. The glass vessel, which could be heated in a water-bath, contained a central

tube, through which a stream of cold water could be passed; there was also an exit tube for the sulphuric acid formed.

A prolonged series of experiments showed that the best yield of sulphuric acid was obtained when the gaseous mixture was obtained by the decomposition of sulphuric acid of D 1.5297, the glass vessel was heated at 60°, and cold water was run through the inner tube. Unless a temperature difference was maintained in the glass vessel, the yield of sulphuric acid was very small. Nitrous oxide was formed during the reaction in quantities greater than those observed in the manufacture by the chamber process. Further experiments also showed that when a mixture of nitric oxide, oxygen, and sulphur dioxide is absorbed by concentrated sulphuric acid, some nitrous oxide is formed.

The results obtained in the analyses of the chamber gases, etc., from various plants are given, and compared with those of Inglis (A., 1906, ii, 226; 1907, ii, 613).

By means of an appropriate arrangement, the velocity with which sulphur dioxide, oxygen, water vapour, and the various oxides of nitrogen react at different temperatures was determined. It was found that the velocity of formation of sulphuric acid is somewhat greater when nitrogen trioxide is used than with nitrogen tetroxide, this being in agreement with the formation of an intermediate product. The reaction proceeds best the more water and oxides of nitrogen there are present. With very high concentrations of oxides of nitrogen, the best temperature is 70°.

In the presence of a large excess of sulphurous acid and water, nitric oxide is almost completely reduced to nitrous oxide, only very small quantities of nitrogen being formed. T. S. P.

**Preparation of Persulphates from Sulphates or Bisulphates Without the Use of a Diaphragm.** *FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 271642).*—The electrolytic preparation of persulphates can be carried out without the addition of electrolytes or the use of a diaphragm if tin or aluminium cathodes are employed. J. C. C.

**The Formation of Dithionic Acid during the Preparation of Cuprous Sulphites.** *HENRY BAUBIGNY (Ann. Chim., 1914, [ix], 1, 201—239).*—In the first part of the paper the author gives a brief review of the earlier work done on the formation of cuprous sulphites. The second part of the paper is a résumé of work already published (compare A., 1912, ii, 351, 447, 647). W. G.

**Hydrogen Telluride and the Atomic Weight of Tellurium.** *L. M. DENNIS and R. P. ANDERSON (J. Amer. Chem. Soc., 1914, 36, 882—909).*—The work described in this paper was undertaken in order to determine the atomic weight of tellurium, and obtain evidence with regard to its alleged complexity.

Magnesium and aluminium tellurides were prepared, and hydrogen telluride was obtained by decomposing the latter compound with hydrochloric acid. The hydrogen telluride thus pre-



pared was fractionally distilled, and the atomic weight of tellurium in the fractions was determined by means of the ratio  $\text{Te}:\text{TeO}_2$ . As this method of preparing hydrogen telluride was not altogether satisfactory, a further quantity was obtained by electrolysis, using a tellurium cathode, a platinum anode, and a 50% solution of phosphoric acid as the electrolyte. The product was fractionally distilled, the twenty-one fractions were decomposed by passing the gas into nitric acid, and the solutions of tellurium dioxide and nitric acid thus obtained were evaporated to dryness, and the residues fused. The atomic weight of the tellurium in the various fractions was determined by titrating the resulting tellurium dioxide with potassium permanganate. The results support the view that tellurium is not complex, and that the atomic weight, 127.5, now assigned to it is the correct value.

Solid hydrogen telluride forms white crystals, and melts at  $-57^\circ$  to a very pale yellow liquid. Liquid hydrogen telluride boils at  $0^\circ$ , and when freshly distilled is almost colourless; when left, however, the colour gradually becomes darker, owing to the presence of dissolved tellurium formed by decomposition. When hydrogen telluride is left in sealed tubes, it slowly dissociates, tellurium being deposited on the walls; this change seems to take place as rapidly in the dark as in the light.

E. G.

**The Active Modification of Nitrogen.** II. H. B. BAKER and R. J. STRUTT (*Ber.*, 1914, **47**, 1049—1055. Compare this vol., ii, 357).—A reply to the second communication of Tiede and Domcke (this vol., ii, 196), in which the authors maintain the correctness of Strutt's previous experiments. They have also repeated the experiments of Tiede and Domcke, but cannot confirm their results. Special reference is made to Strutt's spectrographic investigations (*A.*, 1912, ii, 214).

T. S. P.

**New Confirmation of the Nernst Theorem.** M. TRAUTZ (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), ii, 363—366).—Between the temperatures  $140^\circ$  and  $320^\circ$ , the extent to which combination takes place between nitric oxide and chlorine is almost independent of the temperature, in spite of the fact that the heat of formation of nitrosyl chloride is 14,400 cal. (compare Briner and Pylkov, *A.*, 1913, ii, 317). Also, the dissociation constants calculated from the equilibria obtained are less than those to be expected according to Nernst's theorem.

The above discrepancies are explained, according to the author, by the fact that the usually accepted equation,  $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$ , is wrong. The author's experiments show that between  $-72^\circ$  and  $+40^\circ$  nitric oxide and chlorine combine to a brown gas, which, at low temperatures, consists practically completely of  $\text{NOCl}$ . At higher temperatures it is mixed with a gas richer in nitric oxide, perhaps  $(\text{NO})_2\text{Cl}$  or  $(\text{NO})_3\text{Cl}$ , and may be also with a gas richer in chlorine, perhaps  $\text{NOCl}_2$ . Assuming the existence of these other gases, the results obtained are in agreement with Nernst's theorem.

T. S. P.

**Synthesis of Hydroxylamineisomonosulphonic (Amidopersulphuric) Acid.** FRITZ SOMMER and HANS GEORG TEMPLIN (*Ber.*, 1914, **47**, 1221—1229).—*Hydroxylamineisomonosulphonic acid*,  $\text{NH}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ , the existence of which was first indicated by Raschig (*Annalen*, 1887, **241**, 161) in the product formed by hydrolysing hydroxylamineisodisulphonic acid with hydrochloric acid, has now been obtained in almost pure condition by the action of chlorosulphonic acid on hydroxylamine hydrochloride at the ordinary temperature. It separates from a mixture of ether and methyl alcohol in the form of a microcrystalline powder, liberates iodine from potassium iodide, and is hydrolysed in acid solution to hydroxylamine.

A solution of the acid is also obtained by gently warming hydroxylamine sulphate with fuming sulphuric acid. F. B.

**The Formation of Red Phosphorus by the Oxidation of Phosphorus Vapour.** V. KOHLSCHÜTTER and A. FRUMKIN (*Ber.*, 1914, **47**, 1088—1100. Compare this vol., ii, 267).—By means of an appropriate apparatus, the authors have been able to study the oxidation of phosphorus vapour at ordinary temperatures, oxygen being allowed to mix, in small portions at a time, with saturated phosphorus vapour. A dark red, homogeneous, and transparent product is formed, in which the ratio of phosphorus to oxygen increases as the rate of addition of oxygen to the vapour decreases. Within the limits of the experiments done, the increase does not stop at any simple atomic ratio of the elements. Nevertheless, the authors consider that the product is a definite compound, containing the ready-formed molecule of red phosphorus,  $(\text{P}_2)_x(\text{P}_4)_y$  (compare Stock, A., 1913, ii, 1051), together with another part containing oxygen and phosphorus; by the splitting off of the latter part, red phosphorus is produced. The authors adduce evidence in support of their theory, the red product above-mentioned being considered to be analogous to the intermediate products which are formed in the transformation of white into red phosphorus by the catalytic action of phosphorus iodide and bromide. The analogy is not complete, however, and the differences are discussed in detail.

The authors' experiments again open the question of the existence of phosphorus suboxide, since their product cannot be a mixture of finely divided red phosphorus and solid phosphorus hydride, the presence of hydrogen being excluded by their method of experiment. T. S. P.

**Reductions and Reactions in Reversed Flames. II. Reduction of the Liquid, Anhydrous Chlorides of Groups 3—5 of the Periodic System, in the Reversed Chlorine-Hydrogen Flame.** FRIEDRICH MEYER and HANS KERSTEIN (*Ber.*, 1914, **47**, 1036—1049).—The apparatus previously described (A., 1912, ii, 1051) for the study of reactions in reversed flames has been considerably improved by the authors, and a full description is given of the new apparatus.

The following are the results of experiments on the reduction of

various anhydrous chlorides in the reversed chlorine-hydrogen flame: boron trichloride and silicon tetrachloride are not affected. Carbon tetrachloride is reduced to finely divided, very voluminous carbon, which, however, still retains some hydrogen and chlorine; on oxidation with fuming nitric acid the carbon gives mellitic acid.

Titanium tetrachloride is readily reduced to the trichloride in the new apparatus, a yield of 70% being easily obtained. Since the reaction is reversible, the yield is improved by increasing the velocity of the current of hydrogen used. Stannic chloride gives a quantitative yield of stannous chloride (compare A., 1913, ii, 969).

Phosphorus pentachloride gives a red product, which is very similar to Schenk's phosphorus, and contains 92—94% of phosphorus, together with some of the chloride. Arsenic trichloride is reduced quantitatively to arsenic. Antimony pentachloride gives a greyish-black, loose powder, containing 93% of black antimony and 7% of antimony trichloride.

Vanadium tetrachloride gives a violet, very voluminous powder, consisting of 80% of the dichloride and 20% of the trichloride. If the velocity of reaction is increased by heating the tetrachloride more strongly, some of it is actually found in the reaction product. The relations are very complicated; in all probability the dichloride is first formed, and then combines to some extent with chlorine in the colder zone of the flame.

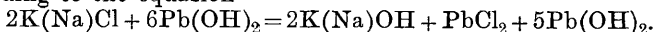
T. S. P.

#### Water of Crystallisation. Compounds with $2\text{H}_2\text{O}$ . I.

ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1914, **49**, 455—476).—The author's experiments show that it is not possible to state a dehydration temperature for a substance unless the conditions are specified. The dehydration should be effected in a thermostat in a dry atmosphere, or in a current of dry gas. The following dehydration temperatures were obtained for the salts mentioned under conditions of experiment described in the original:  $\text{CaSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , about  $180^\circ$  (?);  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $50^\circ$ ,  $55^\circ$ , and  $60^\circ$ ;  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $50^\circ$  and  $60^\circ$ ;  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $50^\circ$  and  $60^\circ$ ;  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $30^\circ$ . Of these, the barium chloride loses the two molecules of water separately, the tin salt and the two sodium salts lose the two molecules simultaneously, but at different rates. The work of Rosenstiehl (A., 1911, ii, 270, 386) is adversely criticised.

R. V. S.

**Preparation of Alkali Hydroxides.** JULIUS KERSTEN (Austrian Patent 62281).—Alkali hydroxides can be obtained in a quantitative yield by the action of lead hydroxide on alkali chlorides according to the equation



The lead hydroxide is suspended in a dilute, aqueous solution of the alkali chloride, and the mixture heated gradually to boiling. The basic lead chloride, after being separated from the alkali hydroxide, is dissolved in nitric acid, the solution evaporated to dryness, whereby the hydrogen chloride is evolved and is con-

densed, and the lead nitrate is dissolved in water and precipitated with ammonia.  
J. C. C.

**The Hydrothermal Formation of Silicates.** M. SCHLAEFFER and P. NIGGLI (*Zeitsch. anorg. Chem.*, 1914, **87**, 52—80. Compare Niggli and Morey, A., 1913, ii, 1054).—When calcium chloride is used, it is necessary to line the autoclave with silver in order to avoid the introduction of iron. Starting from amorphous materials,  $\alpha$ -quartz and tridymite have been identified, with corundum, orthoclase, and potassium-nepheline. Hieratite,  $K_2SiF_6$ , is identical with an artificially prepared mineral formerly wrongly identified as potassium-faujasite. Pyrophyllite, and a mineral resembling zunyite, are doubtful. The products from a large number of experiments are described.

Tridymite must be unstable. It is only obtained in the absence of alkali, and is then probably only converted into the stable quartz. In the system  $H_2O-Al_2O_3-K_2O-SiO_2$  at  $470^\circ$ , quartz, orthoclase, potassium-nepheline, corundum, and possibly pyrophyllite are probably stable phases, according to the composition. Systems containing lime have very little tendency to crystallise. Iron facilitates the formation of anorthite. When iron is added, iron olivine is formed, and crystallises well.  
C. H. D.

**The Action of Hydrogen Sulphide on Sodium Hyposulphite.** FRANK STURDY SINNATT (*J. Soc. Dyers*, 1914, **30**, 189—191).—Dry hydrogen sulphide has no action on dry sodium hyposulphite, but in the presence of water rapid reaction takes place quantitatively, according to the equation  $Na_2S_2O_4 + H_2S = Na_2S_2O_3 + H_2O + S$ . The sulphur is liberated in such a form that it can be readily collected and weighed, and the author suggests that the reaction may serve as a rapid method for the valuation of sodium hyposulphite.  
T. S. P.

**The Transformation Points of Sodium Tungstate.** H. S. VAN KLOOSTER and H. C. GERMS (*Zeitsch. anorg. Chem.*, 1914, **86**, 369—372).—In the thermal determination of transformation points (this vol., ii, 167), only a single point, at  $587^\circ$ , was found for sodium tungstate. A second point was observed on the cooling curves, but not on the heating curves. By using a differential method, with potassium metaphosphate as comparison substance, the two transformation points are found to be  $587^\circ$  and  $591^\circ$ , the thermal effect at the latter temperature being very small.  
C. H. D.

**Purity of Fused Lithium Perchlorate and its Bearing on the Atomic Weight of Silver.** THEODORE W. RICHARDS and MARSHALL W. COX (*J. Amer. Chem. Soc.*, 1914, **36**, 819—828).—Richards and Willard (A., 1910, ii, 292) have described a method for determining the atomic weight of silver which involved a study of the ratio  $LiCl:LiClO_4$ . An investigation has now been made with reference to the purity of the lithium perchlorate, and particularly as to its freedom from water.

In order to estimate traces of water in pure, fused lithium perchlorate, the salt may be decomposed, and the amount of water evolved with the products of decomposition determined. On decomposing the salt in this way, however, a portion of the solid in an exceedingly fine powder is carried along with the stream of gas. This source of error can be overcome by passing the gas through a porous porcelain dry filter or "dust-trap," the construction of which is fully described.

It has been found that lithium perchlorate, prepared entirely in contact with air filtered through the porcelain "dust-trap," is much less easily decomposed by heat than the salt which has been less carefully prepared. The purest lithium perchlorate decomposes slowly at 410–430°, and rapidly at 450°. The perchlorate, after being kept fused until of constant weight, does not yield a significant quantity of water even when the temperature is raised to 430° and most of the salt is decomposed.

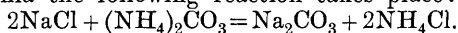
The results of this work tend to justify the use of lithium perchlorate as a basis for determining the ratio of oxygen to silver, and confirm the value  $Ag=107.81$  [ $O=16.000$ ] obtained by Richards and Willard (*loc. cit.*). E. G.

**Lithium Iridichloride and Iridochloride.** MARCEL DELÉPINE (*Compt. rend.*, 1914, 158, 1276–1278.\* Compare A., 1908, ii, 702, 765; 1910, ii, 34; and Antony, A., 1893, ii, 380).—The author has prepared lithium iridichloride and iridochloride, and examined their properties. The former is obtained by adding the theoretical quantity of lithium carbonate to a solution of chloroiridic acid and evaporating to dryness in the cold over sulphuric acid. On recrystallisation from chlorine water the salt is obtained in large, black, exceedingly deliquescent crystals,  $Li_2IrCl_6 \cdot 6H_2O$ . It is very soluble in both alcohol and water, and loses  $4H_2O$  in dry air at 100°. On boiling its solution with a little alcohol, it is reduced, giving *trilithium iridochloride* and chloroiridous acid. This iridochloride is best prepared by reducing lithium iridichloride in aqueous solution with lithium oxalate. It crystallises from water in large, black, deliquescent rhombohedra,  $Li_3IrCl_6 \cdot 12H_2O$ . It is very soluble in water and alcohol. A mixture of sodium and lithium iridichlorides left to crystallise deposits almost pure crystals of the former salt, containing only a trace of lithium. A solution of the iridochlorides at first also deposits the almost pure sodium salt, but on concentrating the solution further, hexagonal prisms of *disodium lithium iridochloride*,  $Na_2LiIrCl_6 \cdot 12H_2O$ , are formed, and then hexagonal needles of *sodium dilithium iridochloride*,  $NaLi_2IrCl_6 \cdot 12H_2O$ . These salts are only stable in solution in the presence of an excess of a salt richer in lithium. W. G.

**A New Theory of the Ammonia Soda Process.** WILLIAM MASON (*Chem. Zeit.*, 1914, 38, 513).—In the present-day ammonia soda process the ammoniacal sodium chloride is carbonated in two stages; in the first stage the treatment with carbon dioxide is continued until more than 80% of the ammonia has been transformed

\* and *Bull. Soc. chim.*, 1914, [iv], 15, 505–510.

into ammonium carbonate; in the second stage the solution from the first stage is further carbonated. At times the author has noticed a precipitate of sodium carbonate before all the ammonia has been changed into ammonium carbonate. From this and the results of various analyses of the products in the carbonating tower the author draws the conclusion that in the complete carbonation of the ammonia the following reaction takes place:



Part of the sodium carbonate precipitates as such, that remaining in solution being transformed into hydrogen carbonate and then precipitated.

The usual statement that the ammonia is first transformed into ammonium hydrogen carbonate, which then undergoes double decomposition with the sodium chloride, does not agree with the fact that ammonium hydrogen carbonate is just as insoluble as sodium hydrogen carbonate in the mother liquors; also such a reaction should be accompanied by absorption of heat, whereas actually heat is developed, in agreement with the known thermal effect of the action of carbon dioxide on a solution of sodium carbonate.

T. S. P.

**The Distribution and Fate of Colloidal Silver in the Mammalian Body. I. The Characters of Colloidal Silver.** J. VOIGT (*Biochem. Zeitsch.*, 1914, **62**, 280—294; **63**, 497).—An account is given of the ultramicroscopic analysis of various commercial preparations of colloidal silver, and the effect of different colloids in protecting them from aggregation on addition of salts. S. B. S.

**An Application of Calcium Carbide in the Formation of Alloys.** W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1914, **33**, 445—446).—A mixture of calcium carbide with borax or sodium chloride is a most efficient de-oxidising flux for copper and some copper alloys, such as bronzes, cupro-nickel, etc. A considerable number of metallic oxides are reduced to the metallic state by carbide, but unless the metal is very fusible, or a large amount of flux (borax, sodium, or magnesium or barium chloride) be employed, the infusible calcium oxide and any separated carbon or free carbide hold up the metal in shots or globules. Much more satisfactory results are obtained when the haloid salts of the metals are used, the calcium haloid formed during the reaction acting as a flux.

The following alloys have been obtained: copper-manganese, copper-nickel, nickel-manganese, cobalt-manganese, copper alloys with tantalum, titanium, zirconium, etc.; manganese alloys with tin, bismuth, antimony, and lead.

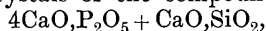
The manganese alloys with tin and bismuth, which contain more than 10% of manganese, show decided magnetic properties.

Where iron- and aluminium-free alloys are required, the carbide reduction is of value. Only in the cases of nickel, cobalt, and iron alloys with manganese does any carbon appear to be taken up.

A convenient method for obtaining metallic chlorides in the

molten, anhydrous state is to drop a mixture of the metallic oxide and ammonium chloride into a red-hot crucible, in small portions at a time, using a slight excess of ammonium chloride. T. S. P.

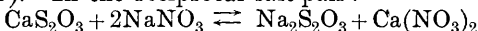
**Constitution of Thomas Slag.** H. BLOME (*Zeitsch. Kryst. Min.*, 1914, 53, 568; from *Diss. Tech. Hochschule Berlin*, 1910, 1—21).—Mixtures of lime, phosphoric oxide, and silica were fused, and the solubilities of the products determined in 2% citric acid. Tetra-calcium phosphate melts at 1870°. When quickly cooled, the binary system  $4\text{CaO}, \text{P}_2\text{O}_5 - 2\text{CaO}, \text{SiO}_2$  shows maxima at the molecular ratios 1:1 and 1:4. Slow cooling favours the crystallisation of a calcium silico-phosphate, which is readily soluble in citric acid, and the separation of free lime; the former is probably identical with the blue ortho-rhombic crystals of the compound



described by Stead and Ridsdale in 1887.

L. J. S.

**The Formation of a Triple Salt from Aqueous Solutions without the Simultaneous Formation of a Binary Double Salt.** ROBERT KREMANN and HANS RODEMUND (*Zeitsch. anorg. Chem.*, 1914, 86, 373—379).—In the reciprocal salt-pair:



a double salt is not formed, but a small region of stability exists for a triple salt,  $\text{NaNO}_3, \text{CaS}_2\text{O}_3, \text{Na}_2\text{S}_2\text{O}_3, 11\text{H}_2\text{O}$ , this region diminishing with rising temperature, but only single salts being formed. The invariant transformation point is found by solubility determinations to be 29°, and by thermal measurements to be 29.2°. The determinations are tabulated, and the region is represented graphically by Jänecke's method, in which a square diagram is used.

C. H. D.

**Fusions of Bisilicates with Sulphides and Haloids.** A. WOLOSOKOV (*Zeitsch. Kryst. Min.*, 1914, 53, 615; from *Ann. Inst. Polytechn. St. Pétersbourg*, 1911, 15, 421—442).—The systems  $\text{MnSiO}_3 + \text{MnS}$ ,  $\text{BaSiO}_3 + \text{BaS}$ , and  $\text{BaSiO}_3 + \text{BaCl}_2$  were investigated. Further, the solubilities of  $\text{MnS}$  and  $\text{FeS}$  in  $\text{BaSiO}_3$  were determined.

L. J. S.

**Corrosion of Zincs of Different Compositions.** EUG. PROST (*Bull. Soc. chim. Belg.*, 1914, 28, 94—99).—The author has studied the action of solutions of sulphuric acid (0.5%), hydrochloric acid (0.372%), and sodium chloride (5%) on specimens of commercial zinc containing known quantities of impurities. In the cases of the acid solutions, the zinc plate is allowed to remain in the solution at the ordinary temperature for seven and a-half hours. With the salt solutions the time of the experiment is prolonged to eighteen days, and the solution agitated by a current of air on the tenth and fifteenth day. In the latter case a white, flocculent precipitate which contains zinc is formed in the solution, and the plates are found to be covered with a greasy, adherent film of zinc hydroxide.

The author is led to the following conclusions: The presence in zinc of quantities of lead, cadmium, or iron greater than those

usually found in the refined product causes an increase in corrosion by acidic agents. Minute traces of arsenic, antimony, copper, or tin, in addition to the previously mentioned impurities, can considerably increase the tendency of zinc to corrode, and this influence is particularly marked in the cases of arsenic and antimony.

The action of sodium chloride solutions on zinc does not show any very striking features. The quantities of zinc dissolved are as great or even greater in the case of normal zincs as in that of zinc containing arsenic, antimony, copper, or tin. This result is possibly due to the protective action of the film of zinc hydroxide.

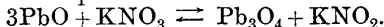
H. W.

**The Freezing-point Diagram of the Lead-Arsenic Alloys and the Melting Point of Arsenic.** W. HEIKE (*Intern. Zeitsch. Metallographie*, 1914, 6, 49—57. Compare Friedrich, A., 1906, ii, 230).—When lead and arsenic are fused together in a sealed porcelain tube and thoroughly mixed, complete miscibility is found to occur. The freezing-point curve consists of only two branches, meeting in a eutectic point at 288° and 8.25 atomic % of arsenic. The curve has only been determined as far as 82.3 atomic % As, but extrapolation of the eutectic time curve indicates that solid solutions are not formed. The melting point of arsenic is found by extrapolation to be 852° (compare Goubau, this vol., ii, 189).

C. H. D.

**Red Lead. The Preparation of Pure Lead Orthoplumbate.** JAROSLAV MILBAUER (*Chem. Zeit.*, 1914, 38, 477—479, 559—560, 566—567, 587—588).—The author has investigated the various methods which have been proposed for the preparation of pure red lead.

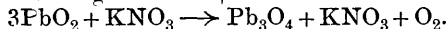
Oxidation of lead oxide with oxygen or air at 470° and extraction of the resulting mass with a 10% solution of lead acetate, gives a pure product, but the process is tedious. Johnson's method, according to which lead oxide is heated with potassium nitrate, simply leads to an equilibrium, depending on the temperature, in accordance with the equation:



If, however, the product is then extracted with a solution of lead acetate, as proposed by Dumas, the lead oxide dissolves, and pure red lead is left. Lead nitrate cannot be used in place of lead acetate, as proposed by Löwe, since an insoluble basic lead nitrate is formed.

Oxidation of lead oxide with potassium chlorate is not satisfactory, since lead dioxide may be formed in addition to red lead; potassium bromate acts similarly to the chlorate, but potassium iodate gives no red lead. Also, lead nitrate cannot be used as the oxidising agent.

A new method, which gives very satisfactory results, is to heat a mixture of lead dioxide and potassium nitrate at 470°, reaction taking place according to the equation:





The resulting mass is then extracted either with a very concentrated solution of potassium hydroxide or with a solution of lead acetate. Other solvents were tried, but gave unsatisfactory results.

Extraction of calcium orthoplumbate with potassium hydroxide, or with solutions of sucrose, does not give good results. Levöl's method (*Ann. Chim. Phys.*, 1854, **75**, 101), as given, is not satisfactory, as also that of Frémy (*ibid.*, 1840, **12**, 489), unless special precautions are taken. On the other hand, Brauner's method, in which the lead oxide of the composition  $\text{Pb}_5\text{O}_7 \cdot 3\text{H}_2\text{O}$  (compare Abegg's *Handb. anorg. Chem.*, Vol. III., Part 2, p. 570) is treated with concentrated potassium hydroxide, gives good results.

Investigation of the action of potassium hydroxide on lead dioxide and mixtures of lead oxide and lead dioxide, showed that a pure red lead is readily obtained by boiling a mixture of these oxides in the proportion of  $3\text{PbO} : 2\text{PbO}_2$  with a strong solution of potassium hydroxide (150—200 grams in 100 c.c. of water).

T. S. P.

**The Nature of Basic Lead Carbonate.** EDWIN EUSTON (*J. Ind. Eng. Chem.*, 1914, **6**, 382—383. Compare this vol., ii, 366).—The author finds that normal lead carbonate withdraws lead hydroxide from basic lead acetate solution, with the formation of basic lead carbonate. Basic zinc carbonate, precipitated calcium carbonate, precipitated barium sulphate, and precipitated barium carbonate act in a similar manner, giving substances corresponding with the formulæ  $\text{ZnCO}_3 \cdot \text{Zn}(\text{OH})_2 \cdot 3\text{Pb}(\text{OH})_2$ ;  $2\text{CaCO}_3 \cdot \text{Pb}(\text{OH})_2$ ;  $3\text{BaSO}_4 \cdot \text{Pb}(\text{OH})_2$ ; and  $3\text{BaCO}_3 \cdot 2\text{Pb}(\text{OH})_2$  respectively. The lead hydroxide portion of these compounds is soluble in ammonium chloride solution, but not in sucrose solution, as is also the case with basic lead carbonate. The barium carbonate and basic zinc carbonate compounds show the same characteristics as pigments as does white lead.

From the above results the author draws the conclusion that in basic lead carbonate the lead hydroxide is present neither in mechanical mixture nor in true chemical combination; basic lead carbonate is an adsorption compound of lead carbonate and lead hydroxide.

T. S. P.

**Action of Hydrogen Peroxide on Basic Lead Salts.** V. ZOTIER (*Bull. Soc. chim.*, 1914, [iv], **15**, 402—408. Compare A., 1913, ii, 216).—Hydrogen peroxide reacts with basic lead acetates in two stages. In the first colloidal lead peroxide is formed, and in the second the lead peroxide reacts with the hydrogen peroxide. At the end of the reaction the liquid always contains some lead peroxide in solution. Basic lead formates and nitrates react similarly, except for the fact that dilute solutions of these salts only give colloidal lead peroxide. The amount of residual lead peroxide is controlled by four factors. It is at its maximum when the hydrogen peroxide and the lead oxide of the basic salt are in equimolecular proportions. It diminishes with increase in the basicity of the lead salt,

and also with rise in temperature. For different basic acetates it is at its maximum when the salts have undergone the same molecular dilution.

The solution of lead peroxide obtained is exceedingly stable, being unaltered by prolonged boiling. On warming, the lead peroxide is reduced by formaldehyde, dextrose, and sulphites, but not by alcohol. In several of its reactions, such as the liberation of iodine from iodides, it resembles hydrogen peroxide. It presents the characteristic properties of colloidal suspensions. It has a distinct absorption spectrum, showing a broad band from the violet to the blue or green, according to the concentration and thickness of the liquid.

W. G.

**The Hardness of Metals.** J. H. ANDREW (*Intern. Zeitsch. Metallographie*, 1914, 6, 30—43).—Alloys of copper and aluminium containing 10—11% of aluminium are harder when quenched than when slowly cooled, but alloys containing 12—13% Al are much harder when slowly cooled. With a pure  $\beta$ -alloy containing 12.5% Al, the hardness is independent of the temperature of quenching, between 570° and 1100°. With copper-tin alloys containing 20—28% Sn, the hardness is greater in the slowly-cooled condition, the difference increasing with the proportion of tin. Little difference is observed in the copper-zinc series, in which resolution of the  $\beta$ -constituent only takes place very slowly.

The hardness of quenched steels is attributed to a partial resolution of austenite into its components in the formation of martensite.

C. H. D.

**Hardness and Modulus of Elasticity of Isomorphous Mixtures of Copper and Nickel.** N. KURNAKOV and J. RAPKE (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 380—394).—Maxwell's relaxation theory leads to the expression  $\eta = E \cdot T$ , where  $\eta$  is the coefficient of internal friction and is proportional to the pressure of flow (compare Kurnakov and Shemtschushni, A., 1913, ii, 929),  $E$  the modulus of elasticity, and  $T$  the time of relaxation. Further, it has been found experimentally that the hardness,  $H$ , determined by Brinel's method, and the pressure of flow, are proportional to one another, so that  $\eta$  and  $H$  should also exhibit proportionality.

The authors have determined the hardness and modulus of elasticity of a series of alloys of nickel and copper in various proportions. Addition of nickel to copper is accompanied by a gradual increase of the hardness from 32 kilos. per sq. mm. to a maximum of 81.3 kilos. per sq. mm. for 47—50% Ni, beyond which the hardness falls regularly to 62.8, the value for nickel. On the other hand, the modulus of elasticity, in kilos. per sq. mm., increases linearly from 11,110 for copper to 20,100 for nickel.

Hence, the increase in the hardness and in the coefficient of internal friction for solid solutions showing a maximum of hardness does not depend on increase of the modulus of elasticity in the equation,  $\eta = E \cdot T$ , but is related to increased time of relaxation. This conclusion is confirmed by observations made on a

number of solid solutions of copper and of iron, in which increased hardness corresponds with diminution of the modulus of elasticity; this is the case with brass, bronze, steel, and other alloys of technical importance. Further, it seems that alteration of "relaxation" hardness proceeds parallel with that of brittleness.

A second typical case, theoretically possible, is that in which increased hardness results from increase of the modulus of elasticity. Such substances would be of great industrial interest, as they would be very hard without exhibiting increased brittleness. Whether manganese, nickel, and other special steels belong to this class must be determined by further experiment. T. H. P.

**Action of Chloroform on the Metallic Sulphates. Method of Preparation of Anhydrous Chlorides.** AUGUSTE CONDUCHÉ (*Compt. rend.*, 1914, 158, 1180—1182).—Chloroform when passed over anhydrous copper sulphate at  $250^{\circ}$  gives a mixture of oxides and oxychlorides of carbon and sulphur. If the temperature rises to  $280$ — $300^{\circ}$  the copper sulphate is soon completely converted into anhydrous cupric chloride. The reaction is more rapid the higher the temperature, but at  $400^{\circ}$  cuprous chloride begins to be formed, and the proportion of it increases rapidly with further rise in temperature. In the case of iron, whether ferrous or ferric sulphate is used, a mixture of ferrous and ferric chlorides is always obtained, the one which predominates corresponding with the sulphate used. Numerous other sulphates have been tried, and the minimum temperature at which the conversion into chloride occurs is given, being in the case of barium, calcium, and sodium sulphates  $500^{\circ}$ . At temperatures between  $400^{\circ}$  and  $500^{\circ}$  the chloroform itself begins to decompose, giving a carbonaceous deposit in the hot parts of the tube, and a crystalline deposit of carbon hexachloride in the cool parts. W. G.

**Copper Peroxite.** L. MOSER (*Zeitsch. anorg. Chem.*, 1914, 86, 380—388).—The term "peroxite" has been proposed (Ebner and Krause, A., 1911, ii, 801) to denote the true salts of hydrogen peroxide. Copper peroxite, prepared from copper hydroxide and hydrogen peroxide (A., 1907, ii, 549), is always impure, owing to partial hydrolysis. By mixing solutions of cupric chloride and hydrogen peroxide, cooling to  $-40^{\circ}$  or  $-50^{\circ}$ , and adding alcoholic potash, the pure peroxite,  $\text{CuO}_2$ , is obtained, and may be washed at  $-50^{\circ}$  with alcohol and ether. Gas is not evolved. The same product is obtained by the action of hydrogen peroxide at low temperatures on an alcoholic suspension of copper hydroxide. The mean ratio Cu: active oxygen is 1.05:1. The peroxite may be obtained at about  $0^{\circ}$  by using ethereal hydrogen peroxide and very finely powdered copper hydroxide. The freshly prepared product may be almost quantitatively converted into hydrogen peroxide and a cupric salt by the action of dilute acids at about  $0^{\circ}$ .

Several other methods of preparation have been tried without success. C. H. D.

**Working Up Mercury Residues.** H. J. TAVERNE (*Chem. Weekblad*, 1914, **11**, 448).—The author recommends reduction of mercury residues to the metal by iron and hydrochloric acid, any nitric acid present being previously eliminated by heating. The precipitated mercury is filtered, and distilled in a vacuum.

A. J. W.

**Double Sulphites of the Alkalis and Mercury.** HENRY BAUBIGNY (*Ann. Chim.*, 1914, [ix], **1**, 332—341).—Fuller experimental details are given of work already published (compare A., 1912, ii, 1175).

W. G.

**Scandium Sulphate and Oxalate.** F. WIRTH (*Zeitsch. anorg. Chem.*, 1914, **87**, 9—12).—Scandium sulphate is the most soluble of the sulphates of the rare earths, 100 c.c. of water dissolving 54.61 grams of the pentahydrate at 25°. The oxalate is the least soluble of the rare-earth oxalates in sulphuric acid, approaching thorium oxalate. Its solubility in sulphuric acid is greatly lessened by the presence of an excess of oxalic acid.

C. H. D.

**Scandium Alkali Oxalates, Scandium-sulphuric Acid, and Scandium Sulphide.** FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1914, **87**, 1—6).—The following salts are described: *sodium scandium oxalate*,  $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{Na}_2\text{C}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ ; the *potassium* and *ammonium* salts have the corresponding compositions. All are readily soluble in hot solutions of the alkali oxalates, and crystallise well on cooling. One of the ammonium salts shows a slight solubility in a cold saturated solution of the alkali oxalate. Hydrochloric acid precipitates crystalline scandium oxalate from the hot solutions. The compounds are to be regarded as salts of a complex acid,  $[\text{Sc}(\text{C}_2\text{O}_4)_3]\text{H}_3$ .

Scandium sulphate,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , dissolves in sulphuric acid (D 1.6), and a *compound*,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{SO}_4$ , separates. This corresponds with similar compounds of the other rare earths.

Dry hydrogen sulphide converts the sulphate into *scandium sulphide*,  $\text{Sc}_2\text{S}_3$ , which is yellow, and stable in air at 100°.

C. H. D.

**Action of Magnesium Salts on Complexes of Aluminium, Iron, and Bismuth with Organic Substances.** A. QUARTAROLI (*Gazzetta*, 1914, **44**, i, 418—443).—The author has investigated the action of magnesium salts on ferric, aluminium, and bismuth hydroxides in absence and in presence of organic compounds, such as citric, tartaric, lactic, salicylic, and quinic acids, dextrose and mannitol, with which the above metals form complex compounds.

When ferric and aluminium hydroxides are precipitated in alkaline solution in presence of magnesium salts, the latter combine with the hydroxides to form insoluble ferrates and aluminates very rich in magnesium, five or six atoms of magnesium being sometimes present per atom of iron or aluminium. From solutions containing iron, aluminium or bismuth existing in combination with

hydroxy-acids or polyhydric alcohols in the form of complex ions, magnesium salts in moderate excess will precipitate these metals quantitatively. In some cases the precipitates consist of the same ferrates or aluminates as are formed in the absence of organic compounds, but in others the latter are also partly precipitated, probably owing to a molecular transformation of the complex salt into ordinary basic salt. Excess of the organic compound retards or limits the precipitation, unless a greatly increased proportion of magnesium salt is added. Deficit of the organic compound, if it is not such as to permit of immediate precipitation of ferric hydroxide by means of ammonia, causes the colloidal iron compounds generated to polymerise into so stable a form that they fix but little magnesium, and, unlike ferric hydroxide itself, retain their brick-red colour in presence of a very large excess of magnesium.

The author's results throw doubt on the trustworthiness of the method universally adopted as the official one for the estimation of phosphoric acid in superphosphates. It is found, indeed, that iron and aluminium retard the precipitation of magnesium ammonium phosphate in presence of ammonium citrate, and that, if filtration is protracted, precipitates of totally different character are obtained. This estimation is being investigated further.

The constitution of the complexes referred to above is discussed.

T. H. P.

**The Chemical or Physical Nature of Colloidal Hydrrous Aluminous Silicates.** GEORG WIEGNER (*Centr. Min.*, 1914, 262—272); R. GANS (*Centr. Min.*, 1914, 273—279, 299—306).—Further discussion and replies bearing mainly on the constitution of "permutite" (compare this vol., ii, 55, 208). L. J. S.

**Action of Salt Solutions on Aluminous Silicates.** HANS SCHNEIDERHÖHN (*Jahrb. Min.*, 1914, i, *Ref.* 204—206; from *Zeitsch. Deutsch. Geol. Ges.*, 1913, 65, *Monatsber.* 349—354).—During the years 1872—1888, J. Lemberg made numerous experiments with salt solutions, acting for a period of a few days to a year and a-half, at 100° or 200°, on various minerals. The data he obtained, including some 600 analyses, are now discussed. With aluminous silicates of all types, the end-product of the reaction has the composition  $R'O, Al_2O_3, nSiO_2, mH_2O$ . Here  $R'O$  represents the base of the salt solution which has replaced the base of the original mineral, this replacement being complete provided that the reaction has been continued for a sufficiently long period. When the solution contains an alkali hydroxide, carbonate, chloride, or sulphate, the silica molecules  $n=2$ , whilst with alkali silicate solutions  $n=5$ .

L. J. S.

**Action of Soluble Sulphates on Kaolin and Clays.** R. RIEKE (*Zeitsch. Kryst. Min.*, 1914, 53, 567—568; from *Sprechsaal für Keramik*, 1910, No. 48—51).—The addition of small amounts of soluble salts, particularly sulphates of calcium, zinc, copper, and

aluminium, to a paste of clay have the effect of increasing its toughness. With alkali sulphates, the effect is only noticeable when very small quantities of the salt are present. The sulphates are absorbed by the clay; and in the case of iron salts (the chloride as well as the sulphate) iron is extracted from the solution in the form of hydroxide.

L. J. S.

**A Compound of Manganese Tribromide with Ethyl Ether.** F. DUCELLIEZ and A. RAYNAUD (*Bull. Soc. chim.*, 1914, [iv], 15, 408—413).—Fuller details are given of work already published (compare this vol., ii, 273).

W. G.

**The Allotropic Transformations of Iron.** ALBERT SAUVEUR (*J. Inst. Metals*, 1913, 88, 171—190).—The view of Benedicks (A., 1913, ii, 599) that the  $Ar_2$  point is merely the termination of the  $Ar_3$  change is inconsistent with the facts that the points  $Ar_2$  and  $Ac_2$  are to be detected on the cooling and heating curves of electrolytic iron, that  $Ac_2$  is given by steels containing less than 0.6% of carbon, and that the principal magnetic change occurs between 780° and 800°, and not at  $Ac_3$ .

C. H. D.

**The Structural Changes of Iron during Annealing.** DONALD EWEN (*Intern. Zeitsch. Metallographie*, 1914, 6, 1—17. Compare Kroll, A., 1910, ii, 1070).—A Swedish wrought iron containing 0.007% of carbon is heated in a vacuum. Three distinct heat-relief patterns are obtained, corresponding with the original  $\alpha$ -iron,  $\gamma$ -iron structure, and final  $\alpha$ -iron structure. The development of the  $\alpha$ -iron relief on first heating is attributed to selective volatilisation at the crystal boundaries, whilst the subsequent reliefs are due to changes of volume accompanying allotropic transformations. At high temperatures, within the  $\gamma$ -range, pitting is produced, especially when the metal is heated by the direct passage of a current (compare Kaye and Ewen, A., 1913, ii, 830).

C. H. D.

**The Crystallising Properties of Electro-deposited Iron.** J. E. STEAD and H. C. H. CARPENTER (*J. Iron Steel Inst.*, 1913, 88, 119—170).—Specimens of electro-deposited iron, containing 0.008% of carbon, 0.009% of manganese, and 0.014% of silicon, in sheets 0.25 mm. thick, become very coarsely crystalline when heated above  $Ac_3$ , and then cooled below  $Ar_3$ . This is the range within which ordinary specimens of iron and steel become more finely crystalline, whilst annealing between 700° and 800°, which leads to the formation of coarse crystals in mild steel, is without influence on electro-deposited iron, even after cold-working. A few seconds above 920° suffice to produce the coarse crystals, but very prolonged heating above that temperature, followed by slow cooling, is without effect. The coarse structure, when once produced, is only destroyed by cold-working, by heating above  $Ac_3$  and quenching, or by heating for a long time above  $Ac_3$  and cooling slowly. The results accord best with the view that at  $Ar_3$  iron changes directly from the  $\gamma$ - to the  $\alpha$ -condition.

Thicker sheets of electro-deposited iron do not exhibit this behaviour, the upper limit of thickness being at about 0.26–0.30 mm., the most favourable thickness being 0.22–0.25 mm.

C. H. D.

**A. New Method for the Determination of the Critical Points  $A_{r1}$ ,  $A_{c1}$  [in Steel].** J. E. STEAD (*J. Iron Steel Inst.*, 1914, 88, 399–415).—The point  $A_{c1}$  in steel may be determined with an accuracy of  $3^\circ$  by quenching a rod in ice-cold water after heating in a muffle in such a way that the temperature gradient along the length of the rod is steady. The temperatures at different points are determined by inserting wires of silver, silver coated with sodium chloride, aluminium, and zinc, and measuring the lengths to which fusion takes place. The points  $960^\circ$ ,  $800^\circ$ ,  $655^\circ$ , and  $420^\circ$  are thus fixed, and intermediate temperatures are found by graphical interpolation. After quenching, the decarburised layer is removed from one surface of the bar by grinding, and the steel is then etched with dilute (20%) nitric acid. The boundary between the hardened portion (black) and the soft portion (grey) indicates the point  $A_{c1}$ , and is quite sharp.

C. H. D.

**Corrosion by Dissolved Oxygen.** J. W. COBB and G. DOUGILL (*J. Soc. Chem. Ind.*, 1914, 33, 403–407).—The object of the authors' investigations was to determine the extent to which dissolved gases are responsible for extensive rusting in hot-water pipe systems. A sloping iron pipe, 180 cm. long and 2.5 cm. in diameter, heated by a furnace at the lower end, was fed with water under a constant head of pressure; the gaseous contents of the water were estimated before and after passage through the pipe, and the gases evolved from the water after passing through the pipe were also analysed.

It was found that a very large proportion of the dissolved oxygen in the water supply was not present in the water or gas leaving the pipe, but had been absorbed in the pipe. On collecting the evolved gases, by means of a special arrangement, just above the furnace, it was found that about half the loss of oxygen occurred in the first 30 cm. length of the pipe, that is, in the heater. The further loss of oxygen occurred in the 150 cm. of pipe beyond the heated length, and could be prevented if the expelled gases were collected at the end of the heated length.

In small-scale experiments on the rusting of pure iron foil when immersed in water, it was found that the expulsion of dissolved gas from the water by previous boiling was an effective method of preventing rusting. The rusting could also be almost prevented by treating the cold, air-saturated water with the quantity of sodium hydroxide and ferrous sulphate necessary to take up the dissolved oxygen.

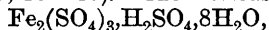
T. S. P.

**Glowing of Oxide Gels when Heated.** K. ENDELL and R. RIEKE (*Centr. Min.*, 1914, 246–249).—The fact that certain metallic hydroxides emit a sudden glow when heated has long been known. Plotting the rise in temperature against the time, the heating

curves show a break (exothermic effect) at a point corresponding with the glow. Titanium dioxide precipitated from a cold solution glows and shows such a break at  $670^{\circ}$ ; when, however, it is precipitated from a hot solution and dried at  $110^{\circ}$  (then containing 8.5%  $\text{H}_2\text{O}$ ), it shows the effect at about  $400\text{--}500^{\circ}$ . Ferric hydroxide precipitated from a hot solution of ferric chloride and dried at  $160^{\circ}$  (then containing 8%  $\text{H}_2\text{O}$ ) glows and shows a break in the curve at  $450^{\circ}$ ; but ferric oxide obtained by oxidising in the air the precipitate from a cold solution of a ferrous salt shows no such heating effect. Chromium oxide precipitated from a hot solution and dried at  $160^{\circ}$  (4.5%  $\text{H}_2\text{O}$ ) shows the effect at  $500\text{--}610^{\circ}$ . In each case heat is developed, and the process is not reversible. The effect is due to an increase in the size of the particles and the giving up of surface energy, and is perhaps accompanied by the incipient crystallisation of the material.

L. J. S.

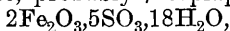
**The Ferric Sulphates.** F. WIRTH and BJARNE BAKKE (*Zeitsch. anorg. Chem.*, 1914, 87, 13—46).—The “tetrasulphate,”



is prepared by dissolving the anhydrous sulphate in 10*N*-sulphuric acid and drying the white, crystalline product. It loses  $5\text{H}_2\text{O}$  very slowly over sulphuric acid, rapidly at  $98^{\circ}$ . It is sparingly soluble in alcohol, and is hydrolysed by steam.

Coquimbite,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , loses  $5\text{H}_2\text{O}$  at  $98^{\circ}$ , and becomes anhydrous at  $175^{\circ}$ .

Yellow ferric sulphate, probably  $\beta$ -copiapite,



slowly breaks up in the solid state, yielding coquimbite.

The solubility relations in the system  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$  have been studied in detail at  $25^{\circ}$ , three to four weeks being allowed for the attainment of equilibrium. Crystallisation is very slow, and considerable supersaturation is necessary. Four solid phases are found: coquimbite,  $\alpha$ -copiapite,  $\beta$ -copiapite, and the tetrasulphate. The solubility curve of the tetrasulphate may be followed far into the metastable region.  $\alpha$ -Copiapite is  $3\text{Fe}_2\text{O}_3 \cdot 8\text{SO}_3 \cdot 27\text{H}_2\text{O}$ . The most concentrated solutions of ferric sulphate contain basic salts. The velocity of crystallisation increases with the acidity.

C. H. D.

**The Reciprocal Influence on Solubility of Ferric Sulphate and Aluminium Sulphate.** F. WIRTH and BJARNE BAKKE (*Zeitsch. anorg. Chem.*, 1914, 87, 47—51. Compare Wirth, A., 1913, ii, 221).—The solubility of either ferric or aluminium sulphates in water at  $25^{\circ}$  is lowered by the addition of the other salt, the solubility curves meeting at the ratio  $\text{Fe}:\text{Al}=1:0.3831$ . There is no evidence of the formation of a compound or of solid solutions.

C. H. D.

**Higher Oxides of Cobalt.** A. METZL (*Zeitsch. anorg. Chem.*, 1914, 86, 358—368).—Cobalt peroxide,  $\text{CoO}_2$ , may be prepared



from cobalt sulphate, iodine, and alkali, washing by decantation, and filtering through asbestos in order to avoid reduction by filter paper. The ratio of cobalt to oxygen is then determined. The same compound is obtained by using silver nitrate and potassium hydroxide as the oxidising agent. Silver, which is precipitated at the same time, is removed by washing with a solution of potassium permanganate and nitric acid.

Oxidation with hydrogen peroxide and sodium hydrogen carbonate yields a green precipitate, which, analysed in the moist state, has the composition  $\text{CoCoO}_3 \cdot \text{CoCO}_3$ , thus consisting of cobalt carbonate and cobalt cobaltite. It is partly decomposed on washing with alcohol and ether. Copper sulphate, when similarly treated, yields a product,  $\text{Cu}_2\text{CuO}_4 \cdot \text{CuCO}_3$ .  
C. H. D.

**Colour of Cobalt Salts in Solution.** J. E. MARSH (*Chem. News*, 1914, 109, 193. Compare this vol., ii, 373).—When a solution of sodium chloride (1 part by weight) and cobalt chloride hexahydrate (2 parts) in acetone (8 parts) and water (8 parts) is electrolysed, a light blue layer forms at the anode, the remainder of the solution retaining its pink colour. The experiment illustrates very well the electronegative character of the blue cobalt complex. In the absence of sodium chloride there is no separation into layers.  
T. S. P.

**Determination of the Atomic Weight of Nickel.** ECHSNER DE CONINCK and GÉRARD (*Compt. rend.*, 1914, 158, 1345—1346).—A determination of the atomic weight of nickel from the ratio nickel oxalate,  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ : Ni. The nickel oxalate was prepared pure as follows: An ingot of nickel was dissolved in nitric acid, hydrogen sulphide passed through, and then the iron oxidised and precipitated by ammonium hydroxide. The filtrate was treated with ammonium sulphide, the precipitate being washed with hydrochloric acid and then dissolved in aqua regia. The solution was evaporated to dryness, and the residue extracted with dilute hydrochloric acid. On addition of barium carbonate, followed by a current of chlorine, the cobalt was precipitated, and filtered off. The barium was precipitated, filtered off, and the filtrate evaporated to crystallisation. The crystals were dissolved in very dilute hydrochloric acid, and on the addition of a concentrated solution of oxalic acid the nickel was precipitated as nickel oxalate,  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , collected, washed and dried, and finally left over sulphuric acid for several weeks. A weighed quantity of the oxalate was heated in a current of hydrogen, the temperature being finally raised to 270—275°. The mean of five determinations gave the value 58.57 for the atomic weight.  
W. G.

**Preparation of Nitrogen Compounds of Molybdenum.** BADISCHE ANILIN- & SODA-FABRIK (Austrian Patent 62524. Compare A., 1912, ii, 946).—Pure precipitated molybdic acid is reduced by means of hydrogen at 700°, and nitrogen is then led over the product at the same temperature and under atmospheric pressure.

The temperature should not exceed  $1000^{\circ}$ , and molybdenum nitride is thus formed without operating under pressure, as in the process described previously (*loc. cit.*).  
J. C. C.

**Binary Eutectics of Tin, Zinc, and Cadmium.** A. M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 223—224).—The results obtained by Lorenz and Plumbridge (A., 1913, ii, 1056) confirm the law established by Flavicki (A., 1906, ii, 152) for eutectic alloys. For the zinc-tin eutectic,  $q/p=0.0892$ , and for the cadmium-zinc eutectic,  $q/r=0.2163$ . Hence, for the cadmium-tin eutectic, the value of  $r:p$  should be  $0.0892/0.2163=0.4123$ , the actual value obtained being 0.4124.  
T. H. P.

**Experiments at High Temperatures. II. Preparation of Refractory Objects of Zirconium Dioxide.** OTTO RUFF, H. SEIFERHELD, and O. BRUSCHKE (*Zeitsch. anorg. Chem.*, 1914, 86, 389—400. Compare A., 1913, ii, 690).—Crucibles of zirconia may be used in a carbon tube resistance furnace at temperatures up to  $2200^{\circ}$ . It is advisable to mix the oxide with 1% of dry starch, which gives great mechanical strength when dried at  $140^{\circ}$ , and 3% of magnesia. The addition of magnesia causes considerable shrinkage in the first firing at  $1450^{\circ}$ , and there is then very little shrinkage at higher temperatures. The zirconia powder used for the original mixture must not have been ignited at a higher temperature than  $1000^{\circ}$ . Clay and colloidal oxides have not been found useful as binding material. Borax yields porous crucibles.

The dry mixture is just moistened with water, shaped in a press, and removed. The crucibles are dried for one hour at  $100^{\circ}$  and for three hours at  $140^{\circ}$ , and are fired, first at  $1500^{\circ}$  and then at  $2200^{\circ}$ . Natural zirconia (83.5%, with 11.5%  $\text{SiO}_2$  and 4.7%  $\text{Fe}_2\text{O}_3$ ) is more easily manipulated than the pure dioxide. The crucibles are only slightly porous, but it has not yet been found practicable to glaze them.  
C. H. D.

**Extraction of Germanium from the Waters at Vichy.** JACQUES BARDET (*Compt. rend.*, 1914, 158, 1278—1280).—Germanium having been detected spectrographically in Vichy mineral waters (compare A., 1913, ii, 785) the author has extracted it in the form of its oxide, separating it from the other metals present by a process of fractional precipitation with hydrogen sulphide and solution in acid alternately. The starting material is the deposit obtained on boiling off the carbon dioxide from the waters. Germanium is present to the extent of 1 part in 40,000,000 parts of water.  
W. G.

**Extraction of Vanadium by Treating its Ores with Acids and Oxidising Agents.** BYRAMJI DORABJI SAKLATWALLA (D.R.-P. 270346).—The ore is boiled with dilute sulphuric acid (1:1), and to the solution is added ammonium persulphate. After prolonged boiling the vanadium separates as a red hydroxide, which on heating furnishes vanadium pentoxide in an almost pure condition.  
J. C. C.

**Chemical and Physico-chemical Observations in the Preparation of Colloidal Gold Solutions.** WALTER HALLE and ERNST PRIBRAM (*Ber.*, 1914, 47, 1398—1401).—Donau (*Vers. Deut. Naturforsch. Aerzte Wien.*, Sept. 1913) has shown that a colloidal solution of gold may be obtained by letting a hydrogen flame play on the surface of a very dilute solution of a gold salt, the formation of the colloidal solution being ascribed to the strong reducing action of the flame. The authors find, however, that such a solution contains nitrous acid, which is formed by the hydrogen flame burning in the air, and ascribe the formation of the colloidal gold to the reducing action of this acid. In confirmation of this they show that colloidal solutions are readily obtained by the action of nitrous acid (sodium nitrite and sulphuric acid) on a solution of gold chloride; as the concentration of the nitrous acid is reduced from 0·00075 to 0·000452%, the colour of the gold solution changes from blue, through violet, to red.

This method of preparing colloidal gold solutions is important, because the gold particles are of uniform size.

The most convenient method of testing whether a glass vessel is suitable for preparing or containing a colloidal solution is to put into it 10 c.c. of water containing 2 drops of a 0·2% alcoholic solution of methyl-red; if the colour changes to yellow within twenty-four hours, owing to alkali dissolving from the glass, the glass is not suitable.

T. S. P.

**Alloys of Gold and Arsenic.** A. P. SCHLEICHER (*Intern. Zeitsch. Metallographie*, 1914, 6, 18—22).—Alloys containing from 0 to 25 atomic % of arsenic have been investigated thermally by melting an alloy rich in arsenic with gold. The freezing-point curve indicates a eutectic point in the neighbourhood of 46 atomic % As, the eutectic temperature being 665°. Only two micrographic constituents are visible, gold and the eutectic. Arsenic is evolved suddenly at the eutectic temperature on cooling.

C. H. D.

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### Mineralogical Chemistry.

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**The Rôle of Water in Minerals.** W. W. COBLENTZ (*Zeitsch. Kryst. Min.*, 1914, 53, 623; from *J. Franklin Inst.*, 1911, 172, 309—355, etc.).—The absorption spectra of a large number of minerals and other compounds were examined for the bands characteristic of water ( $3\mu$ ,  $6\mu$ , and faintly at  $1.5\mu$ ,  $2\mu$ , and  $4.75\mu$ ) and of hydroxyl ( $3\mu$ ). The following show the presence of water (but whether this is as water of crystallisation, absorbed water, or water in solid solution cannot be distinguished): gypsum, opal, zeolites, mellite ( $\text{Al}_2\text{C}_{12}\text{O}_{12}, 18\text{H}_2\text{O}$ ), etc. Constitutional water (OH group) is present in micas and chlorites, serpentine, brucite,

diaspore, gibbsite, goethite, manganite, azurite, turquoise, datolite, tourmaline, etc. Talc shows the presence of neither water nor hydroxyl, being an acid metasilicate ( $\text{H}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$ ). L. J. S.

**Composition of Russian Minerals.** K. NENADKEVITSCH (*Zeitsch. Kryst. Min.*, 1914, 53, 609—610; from *Trav. Mus. Géol. Pierre le Grand, Acad. Sci. St. Pétersbourg*, 1911, 5, 37—56).—A soft, earthy, chocolate-coloured mineral occurring in cavities and crevices in calamine ores in the Olkusch zinc mine had the following composition.  $\text{D}^{15}$  (of material dried at  $100^\circ$ ) 4.63:

ZnO.	MnO <sub>2</sub> .	PbO <sub>2</sub> .	PbO.	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	Tl <sub>2</sub> O + K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
23.28	52.27	6.89	0.54	1.28	0.94	0.12	0.06	0.51	13.59	99.48

Traces of cobalt, barium, and copper are also present. The lead varies in amount in different samples, but the ratio of  $\text{MnO}_2:\text{ZnO}$  is constant; the formula is  $\text{ZnO}, 2\text{MnO}_2, 2\text{H}_2\text{O}$ . This is regarded as a salt of dimetamanganese acid, and is referred to as zinc dibraunite—braunites being salts of the meta-acid, and manganites the salts of the ortho-acid (for example, manganite and hausmannite).

Cupriferous gold from Mt. Karabasch in the Urals gave:

Au.	Ag.	Cu.	Insol.	Fe.	Total.	$\text{D}^{17}$ .
74.33	4.49	20.39	0.26	trace	99.47.	15.17

Powellite occurring as a pseudomorph after molybdenite from the Karysch mine, Minussinsk district, Yeniseisk, gave:  $\text{CaO}$  28.85,  $\text{MoO}_2$  71.14. L. J. S.

**Spinel-Magnetite Eutectic.** J. H. L. VOGT (*Zeitsch. Kryst. Min.*, 1914, 53, 592; from *Videnskabs-Selskabets Skrifter, Math.-Naturw. Klasse, Christiania*, for 1910, 1911, No. 5, 1—25).—The Norwegian and Swedish titanomagnetite-spinellites consist mainly of spinel (pleonaste) and titanomagnetite, the latter being a mechanical mixture of magnetite and ilmenite. The proportions are approximately: spinel, 6—14; magnetite, 47—72; and ilmenite, 19—35. The analyses of spinel show an unbroken series from  $\text{MgAl}_2\text{O}_4$  to  $\text{FeAl}_2\text{O}_4$ , but the series  $(\text{Mg}, \text{Fe})\text{Al}_2\text{O}_4\text{--FeFe}_2\text{O}_4$  is discontinuous. In the rocks the spinel occurs embedded in a eutectic consisting of spinel 3% and magnetite 97%. Spinel can hold about 10% of magnetite, but magnetite takes up very little of the spinel.

L. J. S.

**Some Native Iron-Manganese Oxides.** GUSTAV ROTHER (*Centr. Min.*, 1914, 223—224).—The minerals examined are from the mines at Hüttenberg, Carinthia. Analysis I is of a reddish-brown jelly intermixed with quartz grains and mica scales; II is of a dry, soft, friable, brown mass, containing much clayey material; and III is of a hard, compact, brown iron-ore. The materials analysed were dried at  $105^\circ$ , and the amounts of water lost, as

well as the hygroscopicity of the dried material are given in the last columns below:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	Loss on ignition.	Total.	H <sub>2</sub> O lost at 105°.	Hygros- copicity.
I.	36.62	8.67	19.81	18.70	10.00	99.73*	71.90%	16.67%
II.	52.49	10.75	15.78	13.55	7.26	99.83	2.61	9.97
III.	9.63	0.17	71.03	5.60	12.13	98.62	1.02	1.92

\* Including MgO 1.37, CaO 1.86, K<sub>2</sub>O 2.70.

The hygroscopicity of the first of these is comparable with that of freshly precipitated ferric hydroxide, whilst the third material possesses in only slight degree the nature of a gel. L. J. S.

**Some Calcites which are Very Phosphorescent under the Action of Heat.** F. PISANI (*Compt. rend.*, 1914, 158, 1121—1123. Compare Headden, A., 1906, ii, 680).—The author has found samples of calcite, from three localities only out of a large number, which exhibited phosphorescence on heating at a temperature between 150° and 165°. The light emitted during phosphorescence was reddish-yellow, and its duration varied with the size of the piece of calcite under examination. The phosphorescence does not appear to be due to the yellow colour or to the presence of oxides of metals of the yttrium group. W. G.

**Solid Solution in Minerals. V. The Isomorphism between Calcite and Dolomite.** H. W. FOOTE and W. M. BRADLEY (*Amer. J. Sci.*, 1914, [iv], 37, 339—345).—Analyses I—VI are of calcite occurring as crystals of various habits deposited on dolomite. The solutions from which they were deposited were therefore presumably saturated for dolomite. Except in No. VI, the average amount of magnesium carbonate present is approximately 1%, suggesting that calcite is saturated by this amount at the common temperature of crystallisation:

	CaCO <sub>3</sub> .	MgCO <sub>3</sub> .	MnCO <sub>3</sub> .	FeCO <sub>3</sub> .	Total.	Sp. gr.
I. Locality unknown...	99.07	1.03	0.11	—	100.21	2.713—2.722
II. Ouray, Colorado ...	96.59	0.80	2.93	—	100.32	—
III. Joplin, Missouri(?)	99.23	1.04	0.18	—	100.45	—
IV. Guanajuato, Mexico	93.15	1.09	5.75	—	99.99	2.741—2.769
V. Niagara .....	99.38	0.87	0.42	—	100.67	—
VI. Joplin, Missouri.....	99.65	0.44	0.22	—	100.31	—
VII. Guanajuato, Mexico	60.64	33.50	—	6.05	100.19	2.865—2.914
VIII. " "	60.71	31.48	—	8.46	100.65	2.891—2.907
IX. Ouray, Colorado ...	63.03	30.71	3.24	3.43	100.41	2.887—2.860
X. Joplin, Missouri.....	58.16	40.22	—	1.92	100.30	2.834—2.868

Analyses VII—IX are of dolomite crystals, which were deposited on calcite. Here the ratios of CaCO<sub>3</sub> : (Mg,Mn,Fe)CO<sub>3</sub> = 1.349, 1.361, and 1.492 respectively, showing a considerable excess over the normal dolomite ratio. This excess is, however, variable, suggesting that the degree of saturation of calcite in dolomite is largely influenced by the temperature of crystallisation. Anal. X is of dolomite which crystallised both before and after the calcite with which it is associated; here the ratio of CaCO<sub>3</sub> : (Mg,Mn,Fe)CO<sub>3</sub> = 1.176 : 1. L. J. S.

**Unusual Dolomites.** NICHOLAS KNIGHT (*Chem. News*, 1914, **109**, 193).—The following are analyses of: (1) a typical dolomite from the rock formation of North-east Iowa; (2), (3), and (4) different layers of the dolomite rock in Mount Vernon, Iowa, and vicinity:

	CaCO <sub>3</sub> .	MgCO <sub>3</sub> .	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	Total.
(1)	54·35	43·65	1·00	1·00	100·00
(2)	64·50	33·87	0·57	0·96	99·90
(3)	52·81	46·15	0·37	0·68	100·01
(4)	51·52	47·06	0·53	0·58	100·01

(1) corresponds with the formula CaCO<sub>3</sub>.MgCO<sub>3</sub>, and (2) with the formula 3CaCO<sub>3</sub>.2MgCO<sub>3</sub>; in this latter case ferric oxide, alumina, and silica replace the equivalent amount of magnesium carbonate.

T. S. P.

**Minerals [Lillianite, Wiikite, and Loranskite] from Finland.** LEON H. BORGSTRÖM (*Zeitsch. Kryst. Min.*, 1914, **53**, 593—595; from *Geol. För. Förh.*, 1911, **32**, 1525—1545).—Seleniferous lillianite occurs as irregular grains with galena, quartz, etc., at Ilijärvi. There are three rectangular cleavages, one less distinct than the other two, suggesting that the mineral is orthorhombic or tetragonal. D 7·22. Analysis I (the mean of two made on small amounts of material) agrees with the formula Pb<sub>3</sub>Bi<sub>2</sub>S<sub>6</sub> with all three elements in part replaced isomorphously:

	Pb.	Ag.	Cu.	Zn.	Fe.	Bi.	Sb.	S.	Se.	Total.
I.	43·83	0·88	2·65	0·49	1·23	26·43	5·30	15·93	2·97	99·71
II.	83·21	0·74	—	—	0·23	—	0·90	13·63	—	100·49*

\* Including gangue 1·78.

Galena from Uskela gave analysis II. Wiikite and loranskite, which have been described from the felspar quarries at Impilaks, are scarcely distinguishable from one another. Eight varieties are, however, recognised according to differences in colour (yellow to black), density (3·78—4·817), and water content (11·14—4·30), those lighter in colour being lower in density and containing more water. The material is optically isotropic. The roughly developed crystals are orthorhombic, with  $a:b:c=0·5317:1:0·5046$ , these elements being very close to those of samarskite. It is proposed to reserve the name wiikite for varieties rich in uranium (as in the following analysis of Holmquist), as well as for the whole group, and to apply the name loranskite to the yttrium-rich varieties, as that analysed by Crookes (A., 1908, ii, 695):

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Cb <sub>2</sub> O <sub>5</sub> .	(Ce,Y) <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	UO <sub>3</sub> .	UO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Mn <sub>3</sub> O <sub>4</sub> .	CaO.	Pptd. by H <sub>2</sub> S.	H <sub>2</sub> O.	Total.
8·75	29·58	23·67	4·06	7·51	7·37	1·86	0·74	1·28	4·86	1·06	11·06	101·80

L. J. S.

**Wolframite from New Brunswick.** T. L. WALKER (*Zeitsch. Kryst. Min.*, 1914, **53**, 637; from *Economic Geology*, 1911, **6**, 396—398).—Large wolframite crystals, from a newly-discovered deposit in quartz veins, gave:

FeO.	MnO.	WO <sub>3</sub> .	Total.	Sp. gr.
16·90	8·37	74·43	99·70	7·20

corresponding with 2FeWO<sub>4</sub>.MnWO<sub>4</sub>.

L. J. S.

**Crystallised Chrysocolla from Mackay, Idaho.** JOSEPH B. UMPLEBY (*J. Washington Acad. Sci.*, 1914, 4, 181—183).—The crystallised material forms bluish-green, mamillated crusts, and occurs as small, acicular crystals embedded in other copper minerals. It graduates into brown, ferruginous chrysocolla, which forms the common ore at the Empire copper mine, and is intermixed with malachite, etc. Under the microscope the fibres are seen to be optically uniaxial and positive, with refractive indices  $\omega=1.46$  and  $\epsilon=1.57$ . A partial analysis by R. C. WELLS shows that the massive material consists of chrysocolla (87.3%), intermixed with kaolinite (4.5%) and opal (8.2%):

SiO <sub>2</sub> .	CuO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	ZnO.	MgO.	H <sub>2</sub> O.	Total.	Sp. gr.
39.3	32.0	2.4	1.7	3.6	trace	18.7	97.7	2.4

L. J. S.

**Kaolimates and their Derivatives.** S. WEYBERG (*Zeitsch. Kryst. Min.*, 1914, 53, 610—615; from *Trav. Mus. Géol. Pierre le Grand, Acad. Sci. St. Pétersbourg*, 1911, 5, 57—215).—By fusing kaolin with various salts a large number of crystalline compounds were obtained; for example, lithium “kaolinate” ( $\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8$  and the basic salt  $\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 2\text{Li}_2\text{O}$ ), potassium “kaolinate,” sodium chromate sodalite ( $2\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{Na}_2\text{CrO}_4$ ), lithium bromide sodalite ( $7\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 2\text{LiBr}$ ), etc.

L. J. S.

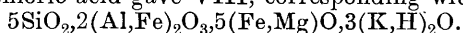
**Two Felspars from the Urals.** V. V. ARSCHINOV (*Zeitsch. Kryst. Min.*, 1914, 53, 603; from *Publication No. 2, Petrographical Institute “Lithogaea,” Moscow*, 1911, 1—12).—A potash-soda-felspar (microperthite) from pegmatite at the source of the Tscherschanka stream in the Ilmen Mountains, gave anal. I, corresponding with  $\text{Or}_{59}\text{Ab}_{40}\text{Ce}_1$ . Oligoclase-albite from a chlorite mica-schist from the village Kulachtinsky Otrjad in the southern Urals, gave II; optical examination gives the composition  $\text{Ab}_{75}\text{An}_{25}$  to  $\text{Ab}_{87}\text{An}_{13}$ :

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> (FeO).	BaO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	64.52	19.87	0.16	0.55	0.05*	4.46	9.89	0.49	99.99	2.593
II.	63.37	23.06	—	—	3.74	9.45	0.32	0.03	99.97	2.640

\* Including SrO.

L. J. S.

**Minerals from Homestake Mine, Lead, South Dakota.** W. J. SHARWOOD (*Zeitsch. Kryst. Min.*, 1914, 53, 637—639; from *Economic Geology*, 1911, 6, 729—789).—Chlorite: Anal. I and II of dark green, scaly chlorite; III of pale green shells and plates; these analyses give the formula  $\text{Al}_2\text{O}_3 \cdot 2\text{FeO} \cdot \text{MgO} \cdot 2\text{H}_2\text{O} \cdot 2\text{SiO}_2$ . D 3.27. Cummingtonite: IV of pale green, radially-fibrous masses (D 3.387); V of white, asbestiform fibres (D 3.28); VI and VII of greenish-black columnar masses. A black mica decomposed by dilute hydrochloric acid gave VIII, corresponding with:





Garnet from the Homestake mine gave IX, and garnet from the Southern Black Hills, South Dakota, X:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	25·38	25·23	—	32·76*	—	n.d.	trace	—	—	9·60	—
II.	26·21	23·92	1·89	30·63	—	8·05	0·40	—	—	8·80	99·90
III.	24·20	20·90	4·27	32·34	—	9·42	trace	—	—	8·39	99·52
IV.	52·36	1·54	—	33·76	0·45	8·10	0·94	—	0·40	1·68	100·12†
V.	50·36	1·86	—	34·62	0·62	9·86	trace	trace	0·74	0·73	98·78
VI.	45·66	6·87	—	31·40	—	9·20	1·04	0·73	0·50	2·19	—
VII.	46·8	5·02	—	33·0	0·31	9·50	1·16	—	—	2·90	—
VIII.	30·53	16·06	6·81	27·09	0·25	4·04	1·01	6·27	0·37	4·23	—
IX.	38·66	24·03	—	28·10*	3·9	2·71	0·00	n.d.	n.d.	2·35	—
X.	36·4	22·2	—	26·8*	12·9	trace	trace	n.d.	n.d.	1·35	—

\* Including Fe<sub>2</sub>O<sub>3</sub>.

† Including Fe<sub>7</sub>S<sub>8</sub> 0·89.

Six analyses of pyrrhotite show Fe 56·14—59·90, S 36·92—56·14, Cu nil—0·04%; gold, 0·025—0·06 oz. per ton. D 4·40—4·56. Analyses are also given of arsenopyrite. D 5·87. L. J. S.

**Nickeliferous Magnesites from Croatia.** FRAN TUČAN (*Centr. Min.*, 1914, 250—251).—Compact, snow-white magnesite, rendered hard by the impregnation of opal, occurs in intimate association with serpentine and olivine rocks in the Fruška Mountains. Analyses I—III are of material from different localities, and IV is of the serpentine. V is of compact, white magnesite from the Zrinjska Mountains:

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	NiO.	CaO.	MgO.	CO <sub>2</sub> .	Total.
I.	20·21	—	0·63	trace	0·54	0·06	37·49	41·63	100·56
II.	24·01	—	0·62	trace	0·71	0·62	35·23	38·88	100·07
III.	10·37	—	0·18	trace	0·04	trace	42·46	46·75	100·30
IV.	41·48	4·58	3·41	trace	0·80	trace	33·98	—	99·65*
V.	10·40	—	1·21	trace	0·20	1·50	40·70	45·92	99·93

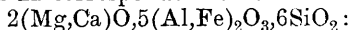
\* Including Cr<sub>2</sub>O<sub>3</sub> 0·75, Al<sub>2</sub>O<sub>3</sub> trace, H<sub>2</sub>O at 107° 0·91, H<sub>2</sub>O over 107° 13·74.

L. J. S.

**Minerals from the Yenisei District.** A. MEISTER (*Zeitsch. Kryst. Min.*, 1914, 53, 596—598; from *Explorations Géologiques dans les régions aurifères de la Sibérie, Région aurifère d'Iénisséi, Livraison IX*, 1910, pp. I—XXXIV + 1—668).—A detailed geographical, geological, and petrographical description of this region. Tatarkaite, didymolite (A., 1912, ii, 950), and angaralite are described as new mineral species from metamorphosed limestone at its contact with nepheline-syenite, in the neighbourhood of the Tatarka river, a tributary of the Angara. *Tatarkaite* forms dark grey to black (in thin sections colourless), elongated plates, which are optically uniaxial and positive with nearly the birefringence of quartz. D 2·744. It is insoluble in acids; analysis I corresponds with the formula R<sub>2</sub>O, 11RO, 13R<sub>2</sub>O<sub>3</sub>, 30SiO<sub>2</sub>, 19H<sub>2</sub>O.

*Angaralite* is a shining, thin-platy mineral, with a black colour due to enclosed carbonaceous material. Under the microscope the plates sometimes show hexagonal outlines, and being optically

uniaxial and positive they perhaps belong to the hexagonal system. D 2·619. Analysis II corresponds with the formula:



	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	42·17	0·50	31·65	1·09	3·46	—	0·17	8·61	0·90	0·86	8·14	97·55
II.	37·96	—	44·68	9·52	—	—	0·46	6·89	—	—	—	99·51
III.	31·75	—	36·20	3·03	22·38	0·24	trace	0·06	0·32	0·98	4·47	99·43
IV.	39·70	—	25·46	0·10	29·10	4·60	0·72	0·79	0·19	—	—	100·66

Analysis III is of ottrelite, and IV of almandine from the same district.

L. J. S.

**Occurrence of Molybdenum in Rocks, with Special Reference to those of Hawaii.** J. B. FERGUSON (*Amer. J. Sci.*, 1914, [iv], **37**, 399—402).—Hillebrand (A., 1899, ii, 112) was able to detect the presence of molybdenum in but few rocks, and then in only the more siliceous; on the other hand, traces of vanadium were frequently found in basic rocks. A black, porous basalt (SiO<sub>2</sub>, 49·74%) from the pit of Halemaumau, Kilauea, was found to contain MoO<sub>3</sub> 0·01%, and a trace was detected in basalt (SiO<sub>2</sub> 50·07%) from the crater of Kilauea. Hillebrand in 1904 found a trace of molybdenum in trachyte-obsidian (SiO<sub>2</sub> 62·19%) from Puu Waa Waa, Hawaii. Detailed analyses are given of these rocks, and also of some others rich in sodium (nephelite-basanite, nephelinite-syenite, etc.), which were specially examined for molybdenum (with negative results) in view of the suggestion that this element might occur in association with sodium.

L. J. S.

**Meteoric Iron from Mount Edith, Western Australia.** W. M. FOOTE (*Amer. J. Sci.*, 1914, [iv], **37**, 391—398).—This large mass of meteoric iron, weighing 161 kilos. and measuring 62 × 55 × 20 cm., was found in 1913 partly embedded in rocky ground near Mount Edith in the Ashburton district, about 160 miles north-east of Roebourne. It is roughly flat-triangular in shape, and is deeply pitted. The structure shown on polished sections is that of a medium octahedrite. A few nodules of troilite enclose rods and nodules of brownish-black olivine. Long blades of schreibersite are present, and kamacite and tænite are also prominent. Analysis by J. E. Whitfield gave:

Fe.	Ni.	Co.	P.	C.	Cu.	Si.	S.	Mn.	Total	Sp. gr.
89·500	9·450	0·625	0·316	0·017	0·013	0·005	0·005	nil	99·931	7·86

L. J. S.

## Analytical Chemistry.

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**Picric Acid as a Standard Substance in Iodometry and Acidimetry and the Iodometric Titration of Acids.** A. SANDER (*Zeitsch. angew. Chem.*, 1914, **27**, 192—194).—The use of pure picric acid is recommended for the standardisation of thio-sulphate solution, since 6 mols. of picric acid liberate 6 atoms of iodine from a mixture of potassium iodide and potassium iodate in aqueous solution. The thiosulphate solution may then be used for standardising iodine solutions. When the potassium iodide-iodate solution has been standardised with picric acid, it may be used for the preparation of standard acid and alkali solutions.

W. P. S.

**N/10-Sodium Thiosulphate Solution.** P. BOHRISCH (*Pharm. Zeit.*, 1914, **59**, 360—362).—Experiments showing that N/10-thio-sulphate keeps unaltered for some twelve months if it is prepared with water previously well boiled and then stored in bottles quite filled; daylight and slight variation in temperature do not exert any influence.

If, however, the bottle is not quite filled, or if a little of the solution is now and then withdrawn, bottles made of brown glass should be used; the solution will then keep about six months. Addition of sodium chloride does not act beneficially.

L. DE K.

**Apparatus for Quantitative, Electrolytic, Micro-estimations, using a Rotating Cathode.** R. HEINZE (*Zeitsch. angew. Chem.*, 1914, **27**, 237—240).—A description of an apparatus by means of which quantities of less than 0.200 mg. of a metal can be estimated by electrolytic methods, using a rotating cathode. Details of results obtained in the estimations of mercury and lead are given. For the weighings it is necessary to use a Nernst microbalance.

T. S. P.

**The Use of Tantalum Electrodes.** O. BRUNCK (*Chem. Zeit.*, 1914, **38**, 565—566. Compare A., 1912, ii, 1128).—A reply to Wegelin (A., 1913, ii, 880), whose unsatisfactory results with tantalum electrodes were due, not to the metal forming the electrode, but to the form of electrodes used. Tantalum foil or sheet electrodes give just as good (or bad) results as electrodes of platinum or sheet; with tantalum gauze electrodes, which can now be obtained, just as good results are obtained as with platinum gauze.

The objections of Oesterheld (A., 1913, ii, 823) are also replied to, and shown not to be of any account in electroanalysis, considering the cost of tantalum as compared with that of platinum.

T. S. P.

**A Cheap Form of Rotating Cathode and Anode for Rapid Electrolytic Analysis.** ERNEST A. LEWIS (*J. Soc. Chem. Ind.*, 1914, **33**, 445).—The rotating cathode used by the author for copper and zinc estimations is made of copper gauze, eight meshes to the cm., supported by stiff copper wire, which projects from the side and helps to cause vigorous circulation of the liquid. It fits over the anode, which consists of a spiral of platinum wire coiled round a glass rod, in order to keep it in position. The total weight of platinum used is about 1 gram. A diagram of the apparatus is given, together with dimensions.

If an ammoniacal or acetic acid solution is used, the cathode must either be made of silver or else be silver-plated. T. S. P.

**A New Nephelometer for Use in Analytical Chemistry.** F. DIENERT (*Compt. rend.*, 1914, **158**, 1117—1118).—A description of an arrangement of a Duboscq colorimeter and a projection lamp by means of which it is possible to measure the amount of crystalline or colloidal matter in a liquid, and also to measure approximately the number of bacteria in suspension in a bouillon culture. W. G.

**Methods for Extractions by means of Immiscible Solvents from the Point of View of the Distribution Coefficients.** J. W. MARDEN (*J. Ind. Eng. Chem.*, 1914, **6**, 315—320).—A practical application of the distribution ratio has been made in the case of a few of the extraction methods now in use, and the fact is emphasised that a larger number of extractions, using a small volume of solvent for each extraction, is better than a smaller number of extractions using a larger amount. The methods investigated were those for the estimation of acetanilide in hydrogen peroxide, acetanilide, vanillin and coumarin in vanilla extracts, and of salicylic acid, benzoic acid, caffeine, etc. Amyl acetate is suggested as a solvent for "saccharin." W. P. S.

**A Simple Substitute for a Lead Crucible or Capsule.** F. L. SHARP (*Chem. News*, 1914, **109**, 232).—A piece of thin lead foil is pressed into a porcelain crucible so as to form a lining to the latter; the lead-lined crucible thus prepared may be used for treating silicates with hydrofluoric acid, etc. W. P. S.

**Estimation of the Acidity or Alkalinity of Waters. A Study in Indicators.** JAS. MOIR (*J. Chem. Met. Min. Soc., S. Africa*, 1914, **14**, 404—407. Compare this vol., ii, 149).—Methyl-orange and Congo-red are practically useless as indicators in estimating the acidity of mine waters containing aluminium salts, as they do not indicate the end-point of the titration. Dimethylaminoazobenzene is much sharper, and gives an end-point corresponding with a small hydrolysis of aluminium sulphate. For the estimation of true neutrality, the water may be titrated against naphtholphthalein and Orange I as indicators, the mean of the two titrations being taken as the correct result. As regards the use of the

phthalein indicators in the titration of alkalis, thymolphthalein gives results, in the case of dilute sodium carbonate solutions, which are about 8% lower than those obtained when phenolphthalein is used; cresolphthalein is more sensitive than phenolphthalein, and carvacrolphthalein is slightly superior to thymolphthalein. The indicator, 2:5-dinitroquinol, proposed by Henderson and Forbes (A., 1910, ii, 541), is trustworthy.

W. P. S.

**Electrolytic Estimation of the Halogens.** W. BÜTTGER [with W. J. KELLY] (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), ii, 361—363).—The following modification of Hildebrand's method for the estimation of the halogens is given. To the solution to be analysed is added a salt of which the cation is more readily deposited than the ions of the alkali metals; the mercury dissolves the deposited metal, and the overvoltage at the surface of the amalgam is so great that hydrions cannot be liberated, and so destroy the neutrality of the solution. Details are given of the estimation of iodine in iodides and bromine in bromides, cadmium sulphate being added to the electrolyte.

Investigation of the deposition potentials indicated that iodides could be separated from chlorides, or from bromides, but not bromides from chlorides, and experiment confirmed this.

T. S. P.

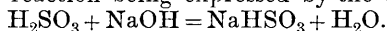
**Estimation of Sulphur Dioxide in the Presence of Thiosulphate and of Sulphuric Acid.** A. SANDER (*Zeitsch. angew. Chem.*, 1914, 27, 194—195).—In a solution containing sulphur dioxide and thiosulphate, the former may be titrated with standard alkali solution, using phenolphthalein as indicator, and in another portion of the solution the two substances may be estimated together iodometrically. Feld has also proposed a method (A., 1913, ii, 617) for this purpose depending on the iodometric estimation of the sulphur dioxide and thiosulphate with the subsequent titration of the sulphuric and hydriodic acids formed; the author modifies this method in so far that he estimates the acidity iodometrically by the addition of potassium iodide and iodate. In the case of a solution containing sulphur dioxide and sulphuric acid, the sulphur dioxide may be titrated with iodine, and the total acidity then estimated iodometrically.

W. P. S.

**Estimation of Minute Quantities of Sulphur Dioxide in Air.** ATHERTON SEIDELL and PHILIP W. MESERVE (*J. Ind. Eng. Chem.*, 1914, 6, 298—301).—Small quantities of sulphur dioxide in air may be estimated by direct titration with *N*/1000-iodine solution; the volume of the sample of air need not exceed 2.5 litres. In carrying out the titration, 5 c.c. of starch solution are added to the bottle containing the sample of air, and the bottle is rotated until the interior has been entirely moistened; *N*/1000-iodine solution is then run in until a blue coloration is obtained. With quantities of sulphur dioxide varying from 4 to 40 parts per million parts of air, the amount of sulphur dioxide recovered is

from 70 to 86% of the quantity present, and the result obtained by the titration is, consequently, multiplied by 1.3. On account of the gradual oxidation of the sulphur dioxide, which is accelerated by the presence of moisture, the titration should be made as soon as possible after the collection of the sample. W. P. S.

**The Volumetric Estimation of Free Sulphurous Acid.** E. KEDESZ (*Chem. Zeit.*, 1914, **38**, 601—602).—Free sulphurous acid can be titrated with sodium hydroxide, using methyl-orange as indicator, the reaction being expressed by the equation



Further neutralisation of the sodium hydrogen sulphite in the presence of phenolphthalein as indicator does not give good results.

The method can be used for estimating the percentage of sulphur dioxide in sulphuric acid. The total acidity is first determined with methyl-orange as indicator; the sodium hydrogen sulphite present in the neutralised solution is then oxidised with hydrogen peroxide, and the solution again titrated until neutral.

T. S. P.

**A Volumetric Method for the Estimation of Ethereal and Inorganic Sulphates in Urine.** OTTO ROSENHEIM and JACK CECIL DRUMMOND (*Biochem. J.*, 1914, **8**, 143—151).—A rapid and accurate method for the estimation of sulphates in urine is described; it consists in precipitation of inorganic sulphates with solution of benzidine, and the subsequent titration of the insoluble benzidine sulphate by means of 0.1*N*-potassium hydroxide. Total sulphates are estimated in the same way after hydrolysis of the ethereal sulphates with hydrochloric acid; the latter are estimated by difference. W. D. H.

**Estimation of Nitrogen in Nitrates and Nitrocelluloses.** A. KOEHLER, M. MARQUEYROL, and H. LORIETTE (*Ann. Chim. anal.*, 1914, **19**, 129—137).—An adverse criticism of Pellet's process (*A.*, 1911, ii, 930).

Pellet's modification, when applied to nitrates, is less convenient and much less accurate than the use of the nitrometer, or of Devarda's process.

In the case of nitrocelluloses, the process is at fault, owing to the evolution of gases other than nitric oxide (carbon dioxide, etc.). The modified Schløesing method for gunpowders and salt-petres, which has been criticised by Pellet, was, however, found to be quite trustworthy. L. DE K.

**Estimation of Nitrogen in Mixtures of Technical Calcium Nitrate and Nitrolim.** A. STUTZER (*Chem. Zeit.*, 1914, **38**, 597).—If the percentages of nitrogen in samples of technical calcium nitrate (air saltpetre) and nitrolim are estimated first separately, and then in a mixture of these two substances, too little nitrogen is found in the mixture when either of the following methods is used: (1) reduction with Devarda metal in the presence of dilute

sulphuric acid, and then the Kjeldahl estimation; (2) treatment with 6% salicylic-sulphuric acid; (3) treatment with 6% phenol-sulphuric acid. The nitron method gave no result at all.

A modification of Schloesing's method gives good results, whereby the nitrate and nitrite nitrogen is estimated as nitric oxide, and the remaining nitrogen according to the Kjeldahl method. The mixture is first decomposed with evolution of the nitric oxide by heating it in a flask, supplied with a Bunsen valve, with a solution of ferrous chloride. The slight excess of pressure produced by the valve facilitates the reaction, the completion of which is told by testing a drop of the liquid with diphenylamine. The contents of the flask are then treated according to the Kjeldahl method.

T. S. P.

**The Detection and Estimation of Hydroxylamine.** HAROLD SCHROEDER (*Chem. News*, 1914, 109, 205).—Angeli's test (A., 1894, ii, 67) for hydroxylamine is best carried out as follows. The test liquid is carefully neutralised, using either hydrochloric acid or sodium hydroxide. To 2 c.c. of the liquid in a test-tube is then added 1 mg. of solid sodium nitroprusside, and the whole made alkaline with 1 c.c. of *N*/10-sodium hydroxide. After shaking, the tube and its contents are rapidly heated to 100° in a water-bath. In the presence of 0.01% of hydroxylamine, a characteristic magenta colour develops, which lends itself to the quantitative estimation of hydroxylamine.

T. S. P.

**The Estimation of Arsenic in Hydrochloric and Sulphuric Acids.** R. F. TARBELL (*J. Ind. Eng. Chem.*, 1914, 6, 400—401).—Arsenic present in hydrochloric and sulphuric acids may be estimated by liberating the arsenic as arsenic hydride in the usual way, passing the gases through a solution of lead acetate to remove any hydrogen sulphide, and then through a known volume of a standard solution of iodine in purified 60° gasoline. The excess of iodine is then estimated by reduction with a known excess of sodium arsenite solution, and titration back with iodine.

T. S. P.

**Quantitative Micro-elementary Analysis of Organic Substances by Fritz Pregl's Methods.** J. V. DUBSKY (*Chem. Zeit.*, 1914, 38, 505—506, 510—511).—Pregl's micro-analytical methods of estimating carbon, hydrogen, nitrogen (Dumas and Kjeldahl), sulphur, and halogens in organic substances, were first published in Abderhalden's "Handbuch der Biochem. Arbeitsmethoden," 1912, 5, ii, 1307, 1344, 1350 (compare also Emich and Donau, A., 1910, ii, 152; Donau, A., 1911, ii, 225; 1912, ii, 199, 384). The present papers describe important simplifications in the estimations of carbon and hydrogen and of nitrogen.

#### I. Nitrogen by the Micro-Dumas Method.

(1) The Kipp's apparatus is charged with pure marble and dilute hydrochloric acid (1:1). Every trace of air must be ex-

pelled from the acid. The addition of a little potassium permanganate suffices to destroy any hydrogen sulphide.

(2) The solution of 50% potassium hydroxide must be absolutely free from foam. For this purpose, 2 c.c. of hot, concentrated barium hydroxide are added to a solution of 200 grams of stick potassium hydroxide in 198 c.c. of water, and the mixture is shaken, kept for fifteen minutes, decanted, and filtered through silk-asbestos. Bubbles of pure carbon dioxide must disappear completely in this solution.

(3) The micro-nitrometer reads to 0.005 c.c. directly and to 0.002 c.c. by estimation. The observed volumes must be diminished by 2% (an empirical correction for the surface-adhesion of 50% potassium hydroxide to glass). One charge suffices for fifteen or more estimations. The micro-nitrometer and all other apparatus for micro-analysis are manufactured by Wagner and Munz, München, Karlstrasse 43.

(4) The micro-balance, manufactured by Wilh. H. F. Kuhlmann, Hamburg-Barmbeck, Steilshoperstrasse 103, is accurate to  $\pm 0.001$  mg. The substance, 2–7 mg., is weighed in a small bottle and transferred to the mixing-tube, a stout, well-corked test-tube 8 cm. in length and 9 mm. in diameter.

(5) The combustion-tube, 34 cm. in length and 10 mm. in

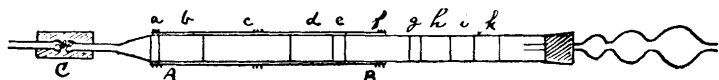


Fig. 1.

external diameter, is made of Jena glass (Fig. 1). The end towards the nitrometer is drawn out into a beak, 5 cm. in length and 5 mm. in external diameter. From this end backwards the tube is filled as follows: (*a*) 1 cm. closely packed asbestos plug; (*b*) 5 cm. copper oxide and asbestos; (*c*) 10 cm. copper oxide (from wire); (*d*) 1–5 cm. roll of oxidised copper gauze; (*e*) 1.5 cm. roll of reduced copper gauze; (*f*) 5 cm. coarse copper oxide; (*g*) 1 cm. fine copper oxide; (*h*) 3 cm. substance + copper oxide and washings; (*i*) 2 cm. coarse copper oxide; (*k*) 1.5 cm. roll of oxidised copper gauze. The portion *AB* of the tube is wrapped in a single layer of asbestos paper, over which a single layer of sheet brass is bound in three places by iron wire. The union of the beak with the micro-nitrometer is effected by a thick-walled capillary tube and stout rubber tubing at *C*; the bore of the tubing is plugged with wadding to facilitate the regulation of the current of gas by the screw clip. The contents of the tube from *a* to *d* remain in situ, and only require oxidising after six estimations. The reduced roll at *e* is only necessary when the contents of the tube from *a* to *d* have been freshly oxidised.

(6) The actual combustion is conducted as follows. The apparatus is connected together, and carbon dioxide is passed through until the bubbles in the alkali are microscopically small.



The tube from *A* to *B* is heated to pale redness. After the bubbles of carbon dioxide again almost disappear, the micro-nitrometer is adjusted to its final position as usual, the first two bubbles of gas are allowed to escape, and the clip is adjusted so that one bubble rises in five seconds. The remainder of the tube is gradually heated in the usual manner, the tap of the Kipp's apparatus being closed; the combustion, if proceeding too rapidly, is moderated by partially opening the tap. When the combustion is finished, the clip is closed completely, the tap of the Kipp's apparatus is opened, and the burners are turned off. When the tube is quite cold, the nitrogen is driven somewhat rapidly into the nitrometer, the pear is raised, the nitrometer is disconnected from the capillary tube, and the pear is raised to drive the alkali into the upper part of the scale; the volume of nitrogen is then read.

## II. Estimation of Carbon and Hydrogen.

(1) The oxygen regulator is shown in Fig. 2, and its principle is obvious. Its use confers the great advantage that the substance

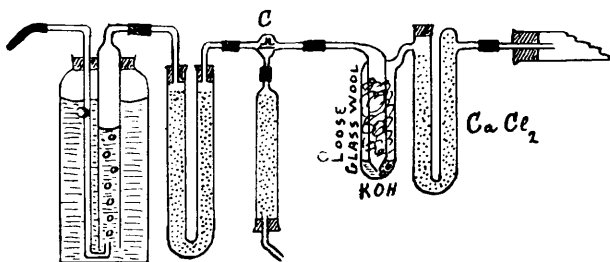


Fig. 2.

undergoing combustion takes up the necessary oxygen almost automatically. The three-way tap at *C* can be used for the admission of air, to diminish the difference of the liquid levels in the oxygen reservoir, and to test whether the apparatus is gas-tight.

(2) The combustion tube, 25 cm. in length and 9—10 mm. in external diameter, is made of Jena glass, and is drawn out at one end into a thick-walled beak, 10 mm. long and 4 mm. in external diameter. From this end backwards the tube is filled with: (a) plug of glass wool, 1 cm.; (b) granular lead peroxide, about 3 cm.; (c) asbestos plug; (d) copper oxide and asbestos (preferably mixed with a little wire oxide), about 4 cm.; (e) long layer of coarse copper oxide; (f) plug of asbestos; (g) platinised asbestos, loosely packed; (h) asbestos; (i) platinum boat; (k) diffusion-stopper. The portion of the tube containing the lead peroxide is enclosed in a copper shell, maintained constantly at 180° by a micro-burner. The shell contains a movable metallic wire, which is bent round and touches the conical part of the combustion tube, and prevents the condensation of water in the beak. The combus-

tion-tube, from the commencement of the platinised asbestos to the copper shell, is surrounded with asbestos paper and sheet brass, as described above.

The diffusion-stopper is an essential part of the apparatus. It is made of Jena glass, 4 cm. long and 5—6 mm. in external diameter. The nearer end, towards the oxygen regulator, is drawn out into a hook. The other end is fused together, and in it are sealed about six pieces (1 cm. long) of fine platinum wire, forming a kind of brush. The cylindrical portion of the stopper is wrapped in a single layer of thin platinum foil, which is affixed to the glass by strong heating. The combustion-tube (and so also the micro-Dumas tube above) is heated by a large, flat burner and by an ordinary Bunsen burner.

(3) The absorption vessels are made of very thin-walled glass tubing, 7 mm. in external diameter, drawn out at each end into capillaries, 3.5 mm. in external diameter. The constrictions shown at *e* and *k* (Fig. 3) render the tubes remarkably independent of the effects of change of temperature, and prevent almost entirely the absorption of atmospheric moisture. The CO<sub>2</sub>-tube (Fig. 3) contains calcium chloride (4 cm.) and six or seven fillets of loose glass wool separated by spaces and moistened with 50% potassium



Fig 3.

hydroxide. The H<sub>2</sub>O-tube (similar to that in Fig. 3) is packed with granular calcium chloride (9 cm.).

(4) A mercury gasometer of capacity 75 c.c. is attached to the end of the CO<sub>2</sub>-tube. It is provided with levelling and exit tubes, and serves, first, to retain the gases in case it is necessary to repass them through the combustion tube, and, secondly, to indicate, by the rise or fall of the mercurial surface, whether or not an excess of oxygen is present.

(5) The actual heating of the tube and the combustion of the substance are effected very nearly in the usual manner. The brush of the diffusion-stopper must touch the platinum boat. The micro-cock of the oxygen regulator is so adjusted that a reduction of pressure (1—2 cm. of mercury) is indicated by the levelling tube of the mercury gasometer.

C. S.

**The Iodine Pentoxide Method for the Estimation of Carbon Monoxide in Air.** **ATHERTON SEIDELL** (*J. Ind. Eng. Chem.*, 1914, **6**, 321—323).—The author describes an apparatus for use in this method, the aim being to diminish the “dead air” space in the apparatus; special forms of absorption bulbs are employed. Both the iodine liberated from the pentoxide and the carbon dioxide produced are collected and estimated volumetrically, the former

being absorbed in potassium iodide solution and the latter in barium hydroxide solution. The iodine titration yields more trustworthy results than the carbon dioxide estimation, the quantity of carbon monoxide calculated from the carbon dioxide result being too low.

W. P. S.

**A New Method for the Estimation of Potassium.** FR. MARSHALL (*Chem. Zeit.*, 1914, 38, 585—587, 615—616).—After dealing with the various objections to the estimation of potassium as platinichloride and as perchlorate, a full account is given of the author's experiments in connexion with a new method, whereby the potassium is precipitated and weighed as the hydrogen tartrate. The principles of this method are as follows. The alkali metals (sodium and potassium) should be present as chlorides. In case of necessity, they are first transformed into sulphates and then into chlorides by means of barium chloride. In soil extracts, any other bases, as well as phosphoric and silicic acids, must be carefully removed. An aliquot portion of the solution of chlorides, containing about 0.05 gram  $K_2O$ , is evaporated to dryness in a beaker on the water-bath. The residue is dissolved in two to three drops of water, and precipitated in the cold with 20 c.c. of a 2% alcoholic solution of tartaric acid which has been kept for several days over solid potassium hydrogen tartrate and then filtered. After the precipitation, 10—20 c.c. of 96% alcohol saturated with potassium hydrogen tartrate are added, and the whole boiled for ten minutes on the water-bath. After remaining covered for twenty-four hours, shaking at times, the precipitate is collected in a Gooch crucible, washed with the alcohol containing potassium hydrogen tartrate, and then with 96% alcohol, after which it is dried at  $80^\circ$  and weighed. Sodium is separated from potassium in this way.

T. S. P.

**Critical Observations on the Estimation of the Hardness of Water According to the Methods of Wartha-Pfeifer and C. Blacher.** JULIUS ZINK and FRIEDRICH HOLLANDT (*Zeitsch. angew. Chem.*, 1914, 27, 235—237).—The authors' experiences are in favour of the correctness of the Wartha-Pfeifer method for the estimation of the hardness of water, in contradistinction to the experiences of Klut (A., 1909, ii, 183).

T. S. P.

**Estimation of Hardness in Water.** ELSE NOCKMANN (*Pharm. Zentr.-h.*, 1914, 55, 435—437).—Blacher's method (A., 1913, ii, 153) was found to be trustworthy, the results obtained not being influenced by the presence of iron and manganese salts and large quantities of magnesium salts.

W. P. S.

**A Method for the Estimation of Magnesium in Calcium Salts.** J. C. HOSTETTER (*J. Ind. Eng. Chem.*, 1914, 6, 392—396).—The usual methods for the estimation of traces of magnesium present in calcium salts are unsatisfactory, owing to the magnesium being carried down when the calcium is precipitated. The method proposed by the author consists in concentrating the

magnesium present in a large sample of the salt into a precipitate containing but a small proportion of the calcium. The ordinary methods of separation may then be used. The concentration is effected by precipitating the magnesium as hydroxide by adding either calcium oxide or a solution of sodium hydroxide in slight excess over that necessary to precipitate the magnesium.

Ten grams of the calcium salt are dissolved in water, and the solution made up to 100 c.c. If acid is necessary to dissolve the salt, the excess is neutralised with sodium hydroxide after the expulsion of carbon dioxide, sulphur dioxide, etc. The calcium oxide made from 0.3—0.5 gram of calcium carbonate by ignition is now added, and the solution heated to boiling. The collected precipitate is not washed, but dissolved in hydrochloric acid, and the calcium removed by two precipitations with ammonium oxalate. The magnesium in the combined filtrates is then estimated by precipitation as magnesium ammonium phosphate.

The various factors affecting the method are discussed fully, and the results given of the analysis of a number of calcium salts from different makers.

T. S. P.

**A Volumetric Method for the Estimation of Lead.** ALFRED ALDER and M. F. COOLBAUGH (*J. Ind. Eng. Chem.*, 1914, **6**, 398—400).—The principles of the method put forward by the authors for the estimation of lead are as follows. The lead is precipitated and collected as sulphate, which is then dissolved in a solution of sodium hydroxide. After slightly acidifying the solution with nitric acid, the lead is precipitated as iodate by means of potassium iodate. The precipitate of lead iodate is dissolved in dilute hydrochloric acid, and the solution titrated with a standard solution of ammonium thiocyanate until the formation of a violet colour, due to liberated iodine, in a supernatant layer of chloroform.

The details of manipulation are lengthy, but the estimation can be carried out in forty-five to sixty minutes. The question of elements which may interfere with the method is discussed.

T. S. P.

**Electrolytic Estimation of Mercury in Mercury Fulminate.** M. S. LOSANITSCH (*Monatsh.*, 1914, **35**, 307—309).—0.4—0.5 Gram of mercury fulminate, dried at 75—80°, is carefully transferred to a moist beaker and then dissolved in 2.5—3.5 c.c. of nitric acid (D 1.40) with gentle warming, the solution being finally heated until all nitrous fumes have disappeared. After dilution to 120 c.c., the mercury is deposited electrolytically on a Fischer stationary gauze electrode, using 0.4 ampere at 1.9 to 2.0 volts at first; after fifteen minutes the current falls to 0.25 ampere at 2.6 volts, and then remains constant, the deposition being complete in six hours. The cathode is washed with water and alcohol, dried over fused potassium hydroxide in a mercury atmosphere, and then weighed.

Using a rotating electrode, and 4.2 amperes at 3.6 to 4 volts, the deposition is complete in twenty-five minutes.

T. S. P.

**Some Errors in the Estimation of the Rare Earths as Hydroxides.** T. O. SMITH and C. JAMES (*Chem. News*, 1914, 109, 219—220).—When the rare earths are precipitated as the hydroxides and ignited to oxides, the results are higher than when they are precipitated as oxalates and ignited. Also, the former method gives results which are not concordant with varying amounts of the precipitant. In order to ascertain the source of error, the following precipitants, using a solution of pure lanthanum chloride, have been compared: oxalic acid, ammonium oxalate, sodium hydroxide, and ammonium hydroxide.

Ammonium oxalate gives figures similar to oxalic acid, with the exception that when an excess is used, the precipitate carries with it some ammonium oxalate, as a complex oxalate. On washing, the complex oxalate is hydrolysed, and the lanthanum oxalate produced is in such a fine state of division that it runs through the filter-paper.

Sodium hydroxide gives high results, owing to the carrying down of sodium in the precipitate, and not because of the formation of a basic salt. Ammonium hydroxide gives results which are not as high as those with sodium hydroxide, a certain amount of basic chloride probably being formed in the precipitation. T. S. P.

**Marshall's Manganese Reaction.** E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1914, 27, 553—562).—Marshall's reaction, which depends on the oxidation of manganese salts to permanganate by ammonium persulphate in the presence of silver salts, yields trustworthy results in the estimation of small quantities of manganese (compare A., 1913, ii, 880), but with amounts of manganese exceeding a few mg. there is a tendency for manganese dioxide to separate during the oxidation. The following modification of the method, however, enables relatively large amounts of manganese to be estimated. The manganese salt (equivalent to not more than 0.2 gram of manganese) is dissolved in water, 30 c.c. of nitric acid (D 1.24) and 8 grams of ammonium persulphate are added, and the mixture is diluted to 100 c.c.; the solution is then added, in small quantities at a time, to a solution consisting of 10 c.c. of *N*/10-silver nitrate solution, 15 c.c. of nitric acid, 10 grams of ammonium persulphate, and 35 c.c. of water, this solution having been heated previously to 50°. The whole is maintained at 50° for ten minutes, then cooled, and the permanganate is titrated with standardised arsenious acid solution. The reaction is a catalytic one, in which silver peroxide acts as the catalyst. W. P. S.

**Estimation and Separation of Iron, Aluminium, Chromium, Zinc, and Manganese.** G. VAN PELT (*Bull. Soc. chim. Belg.*, 1914, 28, 101—127).—The methods of estimating and separating the above metals are dependent either on hydrolysis or on oxidation. An investigation of the first-named class has led the author to the conclusion that they cannot be regarded as exact, since manganese chloride is perceptibly hydrolysed.

The hydrolysis of aqueous solutions of aluminium, ferric, chromium, manganese, and zinc chlorides has been measured at about 25° by the ethyl diazoacetate method. For 10<sup>-3</sup>*N*-solutions, *K* has the values 0·0373 to 0·0388 for aluminium, 0·0334 to 0·0390 for iron, 0·0174 to 0·0197 for chromium, and 0·0050 to 0·0048 for manganese. Solutions of zinc chloride are not perceptibly hydrolysed. The conclusions are confirmed by a series of experiments on the separation of manganese from iron by the barium carbonate, sodium acetate, and sodium succinate methods, a deficit of manganese being invariably found in the filtrates from the iron precipitates.

The separation of chromium from manganese by means of hydrogen peroxide has been described by Jannasch (*Praktische Leitfaden der Gewichtsanalyse*), who recommends the precipitation of the latter and oxidation of the former by hydrogen peroxide either in the presence of sodium hydroxide or of ammonia under pressure. The author emphasises the necessity of using highly concentrated solutions of the pure chemicals, and even thus finds the latter procedure to be inexact, since the precipitated manganous hydroxide retains traces of chromate which cannot be removed by washing, as well as chromium hydroxide which has escaped oxidation.

On attempting to apply the method of Delbuch and Hassel (A., 1903, ii, 243, 454), which depends on the use of ammonium persulphate as oxidising agent, to a solution containing manganese and chromium chlorides, the author finds that precipitation does not occur even after an hour at the temperature of the boiling water-bath, whilst oxidation of chromium readily takes place. He therefore recommends the following procedure, which is based on a combination of the above method with that of Jannasch, and, according to test analyses, yields excellent results. The solution containing the chlorides of chromium and manganese is diluted to 300–400 c.c., and, after addition of 2 grams of solid ammonium persulphate and a few drops of concentrated nitric acid, is heated on the water-bath until pure yellow in colour (about forty minutes). The cooled solution is poured into a mixture of ammonia (75 c.c.) and hydrogen peroxide (75 c.c.), with constant stirring, care being taken that the ammonia is constantly in excess. Under these conditions, manganese is completely precipitated. After heating on the water-bath for thirty minutes, the precipitate is filtered, washed with water containing ammonia, ignited, and weighed. The filtrate is acidified with hydrochloric acid, and concentrated to small volume. The chromate is converted into the chromium salt by means of hydrogen peroxide, and precipitated by ammonia.

For the separation of zinc and manganese, Jannasch recommends the precipitation of manganese hydroxide by the slow addition of a solution of the salts of the metals containing hydrochloric acid to a mixture of water, hydrogen peroxide, and ammonia. According to the author, the method has the disadvantages that the precipitate is not uniform in character (sometimes deep brown in colour and readily washed, at other times pale brown and showing

a marked tendency to pass through the filter), and, in any case, retains zinc. The first disadvantage is shown to be due to decomposition of hydrogen peroxide solution during the slow addition of the manganese and zinc solution, so that its oxidising power is insufficient towards the conclusion of the operation; a uniform precipitate can be obtained by the more rapid addition of the mixture of salts, but zinc is still retained by it.

The following modification of the method, in which the precipitation of zinc is impossible under conditions such that the manganese is precipitated, gives good results. The solution of the salts of zinc and manganese is added, with stirring, to a mixture of ammonia (50 c.c.), ammonium chloride (10% solution, 25 c.c.), and hydrogen peroxide (100 c.c.). To this mixture 50 c.c. of concentrated hydrogen peroxide are added, with constant stirring, and the whole is warmed on the water-bath for thirty minutes and allowed to cool. The precipitated manganese hydroxide is washed with a dilute solution of ammonia, and finally with cold water. The filtrate is boiled with an excess of sodium carbonate to precipitate the zinc.

The application of the above methods to the separation of chromium, manganese, and zinc is also described. The solution of the mixed salts is diluted to 200—300 c.c. Concentrated nitric acid (1 c.c.) and ammonium persulphate (2 grams) are added. The solution is then heated on the water-bath until pure yellow in colour, and poured into a mixture of ammonium chloride (50 c.c.), ammonia (75 c.c.), and hydrogen peroxide (75 c.c.). The precipitated manganese hydroxide is removed as previously described. The filtrate is acidified, treated with hydrogen peroxide, and evaporated to destroy excess of the latter. Chromium is precipitated by ammonium chloride and ammonia in boiling solution, and zinc estimated in the filtrate after ebullition with an excess of sodium carbonate. Test analyses show excellent results.

H. W.

**Estimation of Cobalt in Steel.** G. SLAWIK (*Chem. Zeit.*, 1914, **38**, 514—515).—One to two grams of the sample are dissolved in dilute hydrochloric acid, oxidised with potassium chlorate, and the free acid is expelled by evaporation. After transferring to a 500 c.c. flask, small quantities of zinc oxide emulsion are added until the iron has precipitated. After diluting with water up to the mark and shaking, 250 c.c. of the filtrate are acidified with hydrochloric acid and evaporated to about 100 c.c. After adding 20 c.c. of strong hydrochloric acid, the cobalt is precipitated by adding 30 c.c. of a 2% alcoholic solution of nitroso- $\beta$ -naphthol. After washing first with water containing hydrochloric acid, and then with pure water, the filter and contents are transferred to a weighed porcelain crucible and gradually heated to intense redness, when the cobalt is obtained as  $\text{Co}_3\text{O}_4$ .

If the steel contains much nickel, the cobalt oxide obtained should be redissolved in hydrochloric acid and reprecipitated with

the above reagent. Or the nickel oxide present may be determined by the dimethylglyoxime process, and then allowed for.

L. DE K.

**The Colorimetric Estimation of Cobalt, Nickel, Iron, and Copper.** C. HÜTTNER (*Zeitsch. anorg. Chem.*, 1914, 86, 341—357).—Nickel chloride dissolves in concentrated hydrochloric acid to form a yellow solution without any green shade, but the solution is tinged green by even small quantities of cobalt; 0.1% of cobalt in nickel is easily recognised qualitatively. For quantitative purposes, copper and iron must first be removed. The filtrate is evaporated to dryness, dissolved in hydrochloric acid (D 1.19), and diluted to a fixed volume. In a similar vessel an equal volume of standard nickel chloride solution is placed, and is brought to the same tint by addition of a standard (1:500) cobalt solution. The tint is almost independent of the concentration of the nickel, provided that it is large in comparison with that of the cobalt. From 0.1 to 10% of cobalt in nickel may be estimated in this way, or larger proportions by using several solutions of known composition for comparison. Chlorine or nitric acid must be removed before making the test.

Iron may be detected in concentrated hydrochloric acid solution by a yellow colour even when present only in the ratio 1:100,000. The coloration varies greatly with the concentration of the hydrochloric acid, and is a maximum for 28% acid; but for convenience the 37% acid is used, as in testing for the other metals. The coloration is not affected by manganese, and may be used to detect iron in manganese compounds. From 0.1 to 10% may be estimated in this way.

Copper gives a yellow coloration similar to that given by iron, but of about one half the intensity.

In analysing commercial aluminium, 0.5 gram may be taken, dissolved in hydrochloric acid, and the copper separated as sulphide, ignited to oxide, and dissolved in hydrochloric acid. The filtrate is evaporated to dryness and dissolved in hydrochloric acid, and the iron thus estimated. By similar methods, Kahlbaum's metals have been determined to contain the following impurities (compare Mylius, A., 1912, ii, 450): zinc (electrolytic), 0.025% Cu + Fe; zinc "Kahlbaum," 0.0002% Fe; lead, 0.002% Fe + Cu; cadmium, 0.004% Fe; bismuth, 0.002% Fe; tin, 0.007% Fe + Cu.

C. H. D.

**Detection and Estimation of Petroleum Derivatives in Turpentine Oils.** C. GRIMALDI and L. PRUSSIA (*Ann. Chim. Applicata*, 1914, 1, 324—338).—This method is based on the oxidation of pinene by means of mercuric acetate (compare Balbiano and Paolini, A., 1902, i, 808; 1904, i, 72; Henderson and Agnew, T., 1909, 95, 289). The tar oils are not attacked by this reagent, and the light mineral oils are but slightly affected, owing to the presence of small proportions of ethylenic hydrocarbons. The test is carried out in the following manner.

Into a 500 c.c. measuring flask, graduated on the neck above



the mark at each 0.2 c.c. up to 10 c.c., are introduced 75 grams of mercuric acetate, 200 c.c. of water, 100 c.c. of glacial acetic acid, and 10 c.c. of the oil to be examined. The flask is fitted with a vertical condenser, preferably with a double cooling surface, and is then immersed in a water-bath at 80°, in which it is kept in constant motion for two hours. The cooled liquid is made up to 510 c.c. with dilute nitric acid (2 vols. of D 1.40 to 1 vol. of water), which is added in several portions. A semicircular movement from left to right and vice versa is occasionally given to the flask, and the volume of the oil which collects at the surface read off. This volume represents the adulteration per 10 c.c. of the turpentine oil. The minimum proportions of light petroleum products detectable by this method vary from about 6 to 12%.

The above procedure does not give any satisfactory results when applied to the detection of benzene, toluene, xylene, and other tar oils in turpentine oil, but it answers when about 20% of benzene or 12—15% of solvent naphtha is present.

T. H. P.

#### One Cause of Low Results in the Assay of Peppermint Oil.

HARRY W. REDFIELD (*J. Ind. Eng. Chem.*, 1914, 6, 401—402).—The fact that low results are frequently obtained in the assay of peppermint oils is attributed to inefficient reflux condensation. In a series of parallel estimations with two condensers of an efficient type concordant results were obtained, whereas a third type of condenser gave low results for the menthol present as ester, and especially for the total menthol.

D. F. T.

#### The Vanillin-Hydrochloric Acid Reaction of Essential Oils.

J. CERDEIRAS (*Pharm. Zentr.-h.*, 1914, 55, 339—341).—The vanillin-hydrochloric acid reaction may be utilised to identify, to a certain extent, various essential oils in cases where only very small quantities of the oils can be obtained. The test is carried out by adding one drop of the oil to 5 c.c. of a 0.5% solution of vanillin in hydrochloric acid (D 1.1); after fifteen minutes the coloration is observed, and the mixture is then heated at 100° for five minutes, when the coloration is again observed. The mixture is now cooled, shaken with chloroform, and the colour of the chloroform layer noted. The author records the colorations given by some forty-two essential oils at the three stages of the test; for instance, oil of arnica gives green, red, violet; oil of cardamon, red, blue, blue; oil of eucalyptus, red, violet, violet; oil of cinnamon, red, brown-red, green, etc.

W. P. S.

#### Colour Reaction for the Detection of Methyl Alcohol.

CHRISTO D. MANZOFF (*Zeitsch. Nahr. Genussm.*, 1914, 27, 469—470).—A mixture of nitromethane, ammonia, and vanillin exhibits a red coloration when heated, the colour disappearing when the mixture is cooled; under similar conditions, nitroethane gives a feeble, yellow coloration. This reaction, which is capable of detecting 1 part of nitromethane in 100,000 parts of nitroethane, may be employed for the detection of methyl alcohol in ethyl alcohol.

Two hundred c.c. of the alcohol are mixed with 5 c.c. of concentrated phosphoric acid solution, distilled, and the first 10 c.c. of distillate are mixed with 5 grams of red phosphorus and 20 grams of powdered iodine, then heated for twenty minutes under a reflux apparatus, and distilled. The distillate is treated with 3 grams of silver nitrate and again distilled. The first five drops of distillate are collected in a test-tube, five drops of ammonia and 0.01 gram of vanillin are added, and the mixture is heated; a red coloration denotes the presence of methyl alcohol in the sample. The intensity of the coloration depends to some extent on the quantity of vanillin employed. Vanillin appears to be the only aldehyde which gives the reaction with nitromethane, with the exception of *p*-hydroxybenzaldehyde, which yields an orange-red colour. Ketones do not give the reaction.

W. P. S.

**Characteristic Reaction of Ethyl Alcohol and its Detection in the Presence of Acetaldehyde, Acetone, Methyl Alcohol, &c.** A. TONINELLI (*Ann. Chim. anal.*, 1914, 19, 169—170\*).—Two c.c. of the solution to be tested for the presence of ethyl alcohol are treated in a stoppered tube with 2 c.c. of a 12% solution of iodine in ether; after two minutes, 4 c.c. of 40% potassium hydroxide solution and 2 c.c. of a reagent, prepared by dissolving 1.5 grams of dinitrotoluene in 200 c.c. of a mixture of 1 vol. of carbon disulphide with 2 vols. of ether, are added, and the contents of the tube are shaken. If 3% or more of ethyl alcohol is present, the upper layer of the mixture in the tube exhibits a yellow coloration; this fades, and a bright red coloration develops rapidly. Methyl alcohol and acetone do not yield a coloration with the test, nor does acetaldehyde unless present in large quantity. Higher alcohols, however, must be removed previously by treating the solution to be tested with twice its volume of a 5% alum solution and a quantity of benzene or light petroleum, and submitting the aqueous portion to fractional distillation.

W. P. S.

**Estimation of Methoxy-groups in Substances containing Sulphur.** ALFRED KIRPAL and THEODOR BÜHN (*Ber.*, 1914, 47, 1084—1087).—Zeisel's method is inapplicable to compounds containing sulphur, since hydrogen sulphide is also evolved, and, even if this is carefully removed, the results obtained are invariably too low (Zeisel, A., 1886, 1079; Lindsey and Tollens, A., 1892, 802). The authors propose the following method, which depends on the quantitative absorption of methyl iodide by pyridine, and the titration of pyridine methiodide by silver nitrate, in the presence of sodium chromate as indicator.

The substance is decomposed in the usual manner with hydriodic acid and acetic anhydride, the current of carbon dioxide being, however, replaced by hydrogen. The absorption apparatus consists of two test-tubes, each containing 3—4 c.c. of pyridine, and connected with a small flask containing water to absorb pyridine vapours. At most, traces of iodine can be detected in the water.

\* and *Ann. Chim. applicata*, 1914, 1, 400—404.

Shortly after commencement of the heating, the pyridine in the first tube becomes yellow. Heating is then continued for an hour, and the apparatus allowed to cool. The contents of the two tubes are evaporated to dryness on the water-bath, the residue dissolved in water, and titrated with *N*/10-silver nitrate in the presence of sodium chromate until a permanent red coloration is obtained. The end-point is more sharply marked when a slight excess of silver nitrate is used, followed by sufficient *N*/10-sodium chloride solution to discharge the red colour, the titration being finished by further addition of silver nitrate.

Control analyses, using hemipinic acid in the presence of diphenylthiocarbamide, methyl sulphate, and sodium 2-nitroanisole-4-sulphonate give excellent results.

The authors are led to the conclusion that the low results previously recorded are not due, as usually stated, to loss of methoxy-groups in the form of mercaptan, but to the fact that difficultly decomposable compounds were under investigation.

H. W.

**The Physiological Chemistry of Cholesterol and Cholesteryl Esters. I. The Digitonin Method for the Estimation of these Substances.** TH. E. HESS THAYSEN (*Biochem. Zeitsch.*, 1914, **62**, 89—114).—The author has submitted the digitonin method to a detailed experimental investigation, and obtains the best results under the following conditions. The organs under examination are first dried in a current of air at 32°. They are then successively extracted with ether, alcohol, and ether, and the extracts are combined. Excess of digitonin must be employed for the complete precipitation of the free cholesterol. The cholesteryl esters are obtained from the filtrate by a process fully described, of which the essential feature is the evaporation of the alcoholic liquor to a small bulk, dissolving the concentrated solution with ether, and then adding an amount of water equal in bulk to the concentrated alcoholic solution. The esters will remain in ethereal solution. The cholesteryl esters should be saponified with sodium ethoxide for eight to twelve hours. The ether used for dissolving the cholesterol set free in the saponification process must be fully freed from alkali before precipitation with digitonin is attempted.

S. B. S.

**The Estimation of the Cholesterol Substances in the Presence of One Another.** I. LIFSCHÜTZ (*Biochem. Zeitsch.*, 1914, **62**, 219—244).—The previous publications of the author (A., 1913, ii, 350 and 886) are amplified and illustrated by numerous examples. The combined cholesterol substances are estimated spectrometrically by the acetic anhydride-sulphuric acid (cholesterol) reaction, and the oxysterol by the acetic acid-sulphuric acid reagent. These reactions have been applied to the examination of the digitonin precipitates, which are shown to contain, in the case of the blood-alcohol fraction, oxysterol in addition to cholesterol. It is found, however, that the above-mentioned reactions, with

certain slight modifications, can be applied to the estimation of both these substances in the digitonin precipitate. In this case, the precipitate must be dissolved in glacial acetic acid instead of chloroform, an alteration which entails certain other minor changes in the technique. It is incidentally shown that oxycholesterol is stable in the presence of alkalis, but changes in the presence of even weak acids. The author concludes with a summary of some of the chief technical details of the method. S. B. S.

**Estimation of Nitroglycerin [Glyceryl Trinitrate].** F. W. HEYL and J. F. STALEY (*Amer. J. Pharm.*, 1914, 86, 195—198).—Whilst Scoville's method (*Amer. J. Pharm.*, 1911, 83, 359), in which the nitroglycerin is estimated colorimetrically by means of phenol-disulphonic acid, yields results which agree with those obtained by the Kjeldahl method, the latter method is to be preferred for the estimation of relatively large quantities of nitroglycerin and the former for very small quantities such as are present in medicinal tablets. W. P. S.

**Estimation of Lactose and Glucose by the Copper-Iodide Method.** SYDNEY WILLIAM COLE (*Biochem. J.*, 1914, 8, 134—142. Compare Peters, A., 1912, ii, 492, 871).—A slightly modified form of Peters' method applied to lactose. The copper values for lactose are given, as well as all the details of the method, including standardisation of the thiosulphate, and a method for obtaining the standard heating power.

A slight hydrolysis of the sugar by the alkali seems to take place, so that the reduction is relatively greater when the sugar is present in higher concentrations. Similar indications were obtained when Benedict's method was employed. N. H. J. M.

**Simple Qualitative and Quantitative Test for Lævulose in the Presence of Other Sugars.** E. PINOFF and R. GUDE (*Chem. Zeit.*, 1914, 38, 625—626).—The reaction for lævulose with ammonium molybdate, as described by Pinoff (A., 1905, ii, 865), is uncertain in the presence of other sugars. Satisfactory results can be obtained as follows. Six grams of finely powdered ammonium molybdate are dissolved in 5 c.c. of water by boiling, the solution cooled to 40°, and then added to 5 c.c. of the solution to be tested for lævulose, which should contain not more than 1 gram, and not less than 0.03 gram, of the sugar. On heating the solution at 40° for fifteen minutes, a blue colour is produced if lævulose is present. No free acid should be present, otherwise other sugars give the colour. Dextrose in 20% solution gives only the same depth of colour as the 0.03 gram of lævulose in the above solution, so that the two sugars cannot be confused.

The above method does not give quantitative results, as the depth of colour is not proportional to the concentration of the sugar. The following method gives a quantitative method of estimation: 2.5 c.c. of the solution containing the lævulose, 2.5 c.c. of 96% alcohol, 10 c.c. of a sulphuric acid-alcohol mixture (750 c.c.

of 96% alcohol and 200 c.c. of sulphuric acid, D 1.84), and 0.1 gram of diphenylamine, are heated for fifteen minutes at 70° under reflux, then for a further three minutes after the alcohol boils, and then cooled. The blue solution is poured into a Hahnemann colorimeter vessel, and so much alcohol added that the solution becomes light blue, and the absorption band,  $\mu=500-550$ , can still be seen in the spectroscope. If the dilution, plus 1, is then multiplied by 0.036, the percentage of the levulose in the original solution is obtained. By the dilution is meant the number of times the solution originally heated under reflux is diluted with alcohol. The sugar solution, if possible, should not be stronger than 10%, and in no case should it be stronger than 20%, since a 25% solution of dextrose gives a blue colour which corresponds in intensity with a 0.1% solution of levulose.

The qualitative test by means of the above diphenylamine reaction is very sensitive, the limit of sensitiveness being a 0.036% solution of levulose.

T. S. P.

**Estimation of Sucrose in the Presence of Lactose and in Milk Preparations.** JITENDRA NATH RAKSHIT (*J. Ind. Eng. Chem.*, 1914, 6, 307—308).—In a solution containing both sucrose and lactose, the latter is estimated by titration with Fehling's solution in the usual way. A measured quantity of the sugar solution is then boiled with such a quantity of Fehling's solution that the whole of the copper is precipitated with the simultaneous decomposition of all the lactose; the cuprous oxide is removed by filtration, and the sucrose is estimated in the filtrate after it has been inverted and the solution neutralised. In the case of condensed milks, the proteins, etc., are precipitated by the addition of the minimum requisite quantity of citric acid solution, and separated by filtration before the sugars are estimated, as described.

W. P. S.

**Estimation of Cellulose in Flour with Reference to the Determination of the Degree of Bolting.** L. LINDET (*Bull. Soc. chim.*, 1914, [iv], 15, 384—387; *Ann. Falsif.*, 1914, 7, 169—171).—The following process is proposed. Ten grams of flour are freed from fat by light petroleum or ether. The dried product is treated with 400 c.c. of hydrochloric acid (D 1.025) at the boiling point for half an hour. Fifty c.c. of a solution of hydrated aluminium sulphate (10%) are added, followed by ammonia, and the precipitated aluminium hydroxide which encloses the residue of cellulose is filtered and washed. The precipitate is washed into a conical flask, solid sodium hydroxide (10 grams per 100 c.c. of solution) is added, and the mixture heated for an hour at 100°. The cooled liquid is acidified with hydrochloric acid, then rendered alkaline with ammonia, and the precipitate collected on a tared filter. Aluminium hydroxide is removed by treatment with dilute hydrochloric acid, and the residual cellulose is dried and weighed.

Since the portions of grain nearest the envelope, which are the last to be affected by the grinding machinery, contain a greater

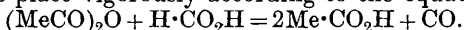
proportion of the fat, nitrogenous matter, cellulose, mineral matter, and phosphoric acid than the central portions, the degree of bolting can be judged by a determination of any of these factors; a series of analyses, however, shows that the greatest difference is exhibited in the cellulose content, and that this, therefore, forms the most accurate basis for evaluation.

H. W.

**Analysis of Cellulose Compounds.** VALENTIN HOTTENROTH (*Chem. Zeit.*, 1914, **38**, 515).—In the estimation of foreign substances in cellulose, the author makes use of the solubility of cellulose compounds in concentrated hydrochloric acid. Hydrolytic fission of the cellulose takes place in the solution, the time necessary depending on the temperature, and the solution can then be diluted without the separation of hydrocellulose occurring. In this way the sulphuric acid content of cellulose acetate can be determined, the acid being precipitated as barium sulphate from the diluted solution.

T. S. P.

**Estimation of Formic Acid.** VALENTIN HOTTENROTH (*Chem. Zeit.*, 1914, **38**, 598).—At ordinary temperatures, acetic anhydride and formic acid have practically no action on each other, but in the presence of a drop of concentrated sulphuric acid, quantitative reaction takes place vigorously according to the equation:



For the quantitative estimation, the formic acid is dissolved in a higher homologous acid or in an indifferent solvent, and the carbon monoxide evolved measured in an appropriate apparatus.

T. S. P.

**Action of Halogens on Oleic Acid and the Estimation of the Iodine Number of Fats.** W. MEIGEN and A. WINOGRADOFF (*Zeitsch. angew. Chem.*, 1914, **27**, 241—244).—Wys' solution is the best, as regards stability, for use in the estimation of the iodine number of fats, the Waller-Hübl, Hanus, and Hübl solutions being less stable. Chlorine acts most energetically on oleic acid, bromine to a less extent, and iodine least. With a mixture of equivalent amounts of chlorine and iodine, more chlorine than iodine combines with the fatty acid, both directly and by substitution. Halogen acids result from this substitution, and the estimation of the quantity produced gives the degree of substitution, the actual iodine number of a fat being the sum of the combined and substituted halogen.

W. P. S.

**Some Reactions of Chrysophanic Acid with Reference to its Detection in Complex Medicinal Preparations.** E. MONROE BAILEY (*J. Ind. Eng. Chem.*, 1914, **6**, 320—321).—If an alcoholic extract containing chrysophanic acid (1:8-dihydroxy-3-methyl-anthraquinone) is diluted, acidified with hydrochloric acid, and shaken with ether, the colouring substance is dissolved by this solvent; on shaking the ethereal solution with dilute ammonia, the latter is coloured red. Similarly treated, picric acid and the colour

principle of *Hydrastis* do not yield a red colour to ammonia, but curcumin, hæmatoxylin, and phenolphthalein yield colours which cannot be distinguished from that given by chrysophanic acid; in the cases of curcumin and hæmatoxylin, however, the coloration disappears after about fifteen hours at 40°. If, after this period of time, the ammoniacal solution is acidified and shaken with ether, curcumin and hæmatoxylin remain in the aqueous portion, whilst chrysophanic acid and phenolphthalein pass into the ether. Phenolphthalein may be eliminated by evaporating the ethereal solution and reducing the residue with zinc and sodium hydroxide; chrysophanic acid is not altered by this treatment, and yields a red coloration when the solution is treated with alkali and a few drops of hydrogen peroxide, whilst phenolphthalein is reduced to phenolphthalin, which does not give a red colour with alkali.

W. P. S.

**Some Physico-chemical Measurements on Milk.** H. B. TAYLOR (*J. Roy. Soc., New South Wales*, 1914, 47, 174—192).—An account of measurements of the viscosity, conductivity, and hydrogen ion concentration of milk is given, and the value of these physical properties in a critical examination of milk is discussed.

It is shown that the viscosity is proportional to the percentage of fat and the "solids not fat," and that the latter quantity can be calculated from the formula, % "solids not fat" = (viscosity - %fat)  $\times$  0.0665/0.177. The viscosity decreases from 20—40°, and is expressed by an equation of the usual type, namely,

$$\eta_t = \eta_0 / (1 + 0.00723t - 0.000156t^2).$$

When milk is heated to any point up to 60°, and then cooled again, it is found to have diminished in viscosity, but, close to 70°, the viscosity is increased as a result of coagulation. The conductivity is increased by the removal of fat to a greater extent than by the removal of the same percentage of water.

The hydrogen ion concentration was estimated by Sørensen's *E.M.F.* method, and by comparing the colours produced by a few drops of milk or of the usual standard solutions in a dilute solution of methyl-red or rosolic acid. The values obtained were fairly constant for a large number of samples, and were  $10^{-6.8}$  for fresh milk and  $10^{-4.65}$  for completely soured milk. The influence of temperature on the speed at which the hydrogen ion concentration increases is considerable.

The loss of total solids due to decomposition is also described, and the influence of atmospheric conditions, especially dust, at the time of milking is shown to be very important.

J. C. W.

**Relation between Specific Gravity and the Percentage of Fat and Dry Matter in Milk.** W. FLEISCHMANN (*J. Landw.*, 1914, 62, 159—172).—Owing to the difficulty of obtaining concordant results in estimating dry matter, it is considered preferable to calculate the amount from the percentage of fat and D. The formula  $t = (4.8 \cdot f + d) / 4 + 0.25$ , which is very similar to  $t = 1.2 \cdot f + 2.665(100 \cdot s - 100) / s$ , may be used in very many cases.

$t$  is the percentage of dry matter,  $f$  the percentage of fat, whilst  $s=D$  and  $d=D/1000$ .  
N. H. J. M.

**Apparatus for the Estimation of Fat by the Röse-Gottlieb Method.** WILLIAM BRINSMAID (*J. Ind. Eng. Chem.*, 1914, 6, 324—325).—Tubes made according to the following specification were found to be useful when the ordinary tubes could not be obtained: (1) internal diameter of tube, 0.625 inch; (2) capacity, 85 c.c.; (3) tapped drainage tube to be placed at the 19.5 c.c. point; (4) the mouth of the tube to be constricted so as to fit a cork. A simple tilting stand for holding a number of the tubes is also described.  
W. P. S.

**The Unsaponifiable Constituents of Natural and Hydrogenised (Hardened) Fats.** J. MARCUSSEN and G. MEYERHEIM (*Zeitsch. angew. Chem.*, 1914, 27, 201—203).—Phytosterol is much more stable than is cholesterol when submitted to the conditions obtaining in the hydrogenisation of oils and fats; whilst 75% of the cholesterol is decomposed at a temperature of 200°, the phytosterol is not attacked. Hydrogenisation at 250° destroys the cholesterol almost completely, but, in the case of a vegetable oil, considerable quantities of phytosterol remain unaltered. Consequently, a hardened fat, prepared at a high temperature from an animal oil, may not yield a precipitate of cholesterol digitonide when treated with digitonin (*A.*, 1913, ii, 885).  
W. P. S.

**A Flame Test for Chloral Hydrate.** W. M. DOHERTY (*J. Roy. Soc., New South Wales*, 1914, 47, 163—164).—A piece of copper wire is fixed in the outer zone of the flame of a spectrum burner as used in the detection of boric acid, and a solution of chloral hydrate is placed in the glass arm attachment. The flame remains colourless, but when the alkali hydroxide is added to the solution so that chloroform is produced, it immediately becomes green. One drop of chloroform in 100 c.c. of water gives a distinct colour.  
J. C. W.

**Vanilla: and a Short and Simple Method for the Determination of Vanillin.** W. M. DOHERTY (*J. Roy. Soc., New South Wales*, 1914, 47, 157—163).—In the author's opinion, the most trustworthy method for the estimation of vanillin in essence of vanilla is as follows. Fifty c.c. are distilled, and the distillate is used to determine the alcohol content and any vanillin which volatilises with the solvent. The residue is extracted with ether, evaporated, shaken with sodium hydrogen sulphite, and the bisulphite compound is filtered after an hour or so and decomposed by sulphuric acid in slight excess. The vanillin is then extracted by three portions of chloroform, and the extract is washed and allowed to evaporate. The residue of fairly pure vanillin is dried in a vacuum and weighed. The purity is controlled by titration with 0.1*N*-alcoholic potassium hydroxide, using phenolphthalein, or by the method described below.



The green coloration produced by adding bromine water and ferrous sulphate to dilute aqueous solutions of vanillin is the basis of the following quick method for the estimation of vanillin. One c.c. of the vanilla essence is extracted with ether, the extract is evaporated over water, and the aqueous solution is filtered and diluted to 50 c.c. in a Nessler glass. Ten drops of freshly prepared bromine water and ten drops of 10% ferrous sulphate are then added, and the colour is matched against a 0.2% solution of pure vanillin. The diluted essence itself may even be tested without extraction.

J. C. W.

**The Presence of Acetone in Commercial Chloroform.** BERNABÉ DORRONSORO and OBDULIO FERNÁNDEZ (*Anal. Fis. Quim.*, 1914, **12**, 191—202).—The authors employ for the estimation of the acetone Walker's method, based on the formation of the oxime from an excess of hydroxylamine hydrochloride and estimation of the unchanged hydrochloride (compare Bennett, *J. Pharm. Chim.*, 1910, [vii], **2**, 261; Fuller, *Amer. J. Pharm.*, 1912, **84**, 4).

G. D. L.

**Estimation of Free Amino-acid Nitrogen in Blood.** G. van Slyke's Method after Precipitation of Proteins with Acid Solutions by Mercuric Chloride. ARTUR H. ROSENBERG (*Biochem. Zeitsch.*, 1914, **62**, 157—160).—The previous precipitation of proteins by Schenk's mercuric chloride solution, followed by the estimation of amino-acid nitrogen in the filtrate by van Slyke's method, gives satisfactory results for the determination of amino-acids in the blood of human subjects.

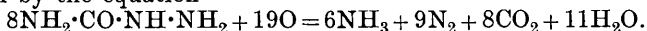
S. B. S.

**Estimation of Monoamino-acids in Blood.** L. LEMATTE (*Compt. rend.*, 1914, **158**, 1379—1381).—To the blood, as soon as drawn, is added an equal volume of 30% phosphotungstic acid solution and 1/25th the volume of pure sulphuric acid. The total volume is made up to 50 c.c., shaken vigorously, and filtered after fifteen minutes. Sodium hydroxide solution is added, drop by drop, until the liquid is just alkaline to phenolphthalein. The excess of phosphotungstic acid is precipitated by calcium chloride, and, before filtering, the excess of calcium precipitated with a solution of potassium oxalate. The volume of the mixture is read, filtered, and in the filtrate, which will contain the amino-acids, these acids estimated by Ronchèse's colorimetric method.

W. G.

**Methods of Estimation of Semicarbazide by its Interaction with Halogens and Halogen Oxy-acids.** RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1914, **36**, 1014—1017).—A study has been made of the action of halogens and halogen oxy-acids on semicarbazide, and it is shown that such reactions can be used for the gasometric estimation of this compound. By the action of potassium chlorate on semicarbazide in presence of hydrochloric acid, two-thirds of the total nitrogen is liberated. The reaction is represented by the

equation  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 + \text{O}_2 = \text{CO}_2 + \text{NH}_3 + \text{N}_2 + \text{H}_2\text{O}$ . Potassium bromate decomposes the base in fairly strong solutions without the addition of acid, and in dilute solutions in presence of acid; in each case nearly three-fourths of the total nitrogen is evolved. Potassium iodate reacts in the absence of acid at all dilutions, with liberation of exactly three-fourths of the total nitrogen. Chlorine and bromine decompose semicarbazide, with evolution of nitrogen. The reaction with bromine can be used as a method of estimation, the nitrogen liberated amounting to three-fourths of the total, as shown by the equation



As these reagents do not decompose carbamide, the estimation of semicarbazide can be carried out in presence of this substance. Sodium hypochlorite and hypobromite, however, react with semicarbazide in the same way as with carbamide, the whole of the nitrogen being liberated.

E. G.

**The Influence of Acetoacetic Acid on the Estimation of Creatinine.** E. P. CATHCART and J. B. ORR (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, 48, xxi—xxii).—Although it is admitted, as Greenwald and, more recently, Graham and Poulton have pointed out, that acetoacetic acid in the urine interferes with the estimation of creatinine, the figures now presented show that the acidosis which occurs in disordered carbohydrate metabolism does not wholly account for the “creatinine” output. Graham and Poulton’s method for the removal of acetoacetic acid is criticised.

W. D. H.

**The Estimation of Creatinine and Creatine in Urine.** OTTO FOLIN [with J. L. MORRIS] (*J. Biol. Chem.*, 1914, 17, 469—473).—Details are given for estimating these substances colorimetrically, the colour obtained with picric acid and sodium hydroxide being compared with standards; the standards are similarly made with known quantities of pure creatinine.

W. D. H.

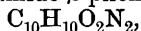
**The Estimation of Creatinine and Creatine in Blood, Milk, and Tissues.** OTTO FOLIN (*J. Biol. Chem.*, 1914, 17, 475—481).—The advantage of using standard creatinine solutions is nowhere more decisive than in the analysis of blood and milk; in the collection of blood, too much oxalate to prevent clotting must be avoided. In muscle and other tissues the laborious separation of creatine from protein is unnecessary; the proteins can be dissolved at the same time that creatine is converted into creatinine, and an estimation can be made in two hours. Full details of analytical procedure are given.

W. D. H.

**Analytical Application of the Carbamido-acid Reaction.** F. LIPPICH (*Zeitsch. physiol. Chem.*, 1914, 90, 124—144. Compare A., 1908, i, 861).—Leucine can be identified by boiling with an aqueous solution of carbamide for from one quarter to one and a-half hours, cooling, and acidifying. The sparingly soluble

carbamido-acid crystallises out sooner or later. The reaction can be carried out with very small quantities of substance. With due precautions, ambiguity is probable only through precipitation of the carbamido-acid of phenylalanine, which can, however, be otherwise detected previously.

The *anhydride* of  $\alpha$ -carbamido- $\beta$ -phenylpropionic acid,



is a crystalline substance, m. p.  $186^\circ$ .

The detection of amino-acids can be effected by taking advantage of the fact that the carbamido-acids and their salts give a flocculent precipitate with mercuric nitrite (*loc. cit.*). Details are given of the procedure to be adopted.

Anthranilic acid readily yields the corresponding carbamido-acid when boiled with carbamide with or without barium hydroxide. It turns very readily into the *anhydride*,  $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$ , m. p.  $340^\circ$ .

Measurements are given of the solubilities, which are small, of a number of carbamido-acids in ether. The anhydrides are much more soluble in ether, and advantage can be taken of this fact for the isolation of the amino-acids.

$\alpha$ -Carbamidoisovaleric *anhydride*,  $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$ , forms colourless, rhombic tablets, m. p.  $132^\circ$ .  $\alpha$ -Carbamidoglutamic *anhydride*,  $\text{C}_6\text{H}_8\text{O}_4\text{N}_2$ , forms prismatic needles, m. p.  $168^\circ$ .

A uniform nomenclature is suggested, the carbamido-acids being denoted by the syllable *ur*, as *leucinuric acid*, and the name of the corresponding anhydride or hydantoin being derived from this, as *leucinuride* or *leucinuroin*.

R. V. S.

**Isolation of Leucine and Other Amino-acids from Animal Liquids.** F. LIPPICH (*Zeitsch. physiol. Chem.*, 1914, 90, 145—157. Compare preceding abstract).—The reactions referred to in the preceding abstract can be applied to the detection and isolation of amino-acids, especially leucine, from liquids of animal origin. Added leucine to the amount of 0.02% can be detected in this way. No amino-acids could be detected in normal or pathological urines, or in serum, except when they had been first added to them. Details are given of the methods pursued.

R. V. S.

**Quantitative Gravimetric Estimation of Carbamide.** R. FOSSE (*Compt. rend.*, 1914, 158, 1076—1079. Compare this vol., ii, 154).—Carbamide can be rapidly estimated gravimetrically by means of xanthhydrol, as follows. To the liquid containing the carbamide three and a-half times its volume of glacial acetic acid is added, and then one half of its volume of a 10% solution of xanthhydrol in methyl alcohol is added in five equal portions at intervals of ten minutes. After one hour, the crystals are collected, washed with alcohol, dried, and weighed, the precipitate containing 6.66% nitrogen. With a 0.5% solution of carbamide the values for this substance are 1% low, whilst for solutions of 0.2% or less they are from 1—2% too high, this being due to the slight impurity of the precipitate at the lower concentrations, and its consequent lower nitrogen content.

W. G.

**Physiology and Pharmacology of Purine Derivatives. III. Estimation of Allantoin in Urine by Titration.** HANS HANDOVSKY (*Zeitsch. physiol. Chem.*, 1914, 90, 211—220).—The process, which is described in detail, is founded on that of Wiechowski (A., 1910, ii, 634). The acetic acid filtrate finally obtained by that method is neutralised with calcium carbonate, and the carbon dioxide removed from the solution with air. The solution is then treated with rather more than the requisite quantity of a reagent containing 0.5% of mercury acetate and 20% of sodium acetate. After half an hour, the liquid is filtered, an aliquot portion treated with iron ammonium alum, decolorised by addition of dilute sulphuric acid, and then titrated with *N*/10-ammonium thiocyanate solution until a yellow coloration appears. From experiments with pure allantoin solutions and with allantoin in urine, the author finds that 1 molecule of allantoin corresponds with 3.62 equivalents of mercury, and from this relation the amount of allantoin present can be calculated. R. V. S.

**Herzig and Meyer's Reaction Applied to Proteins and Amino-acids.** JOSEPH HAROLD BURN (*Biochem. J.*, 1914, 8, 154—156. Compare A., 1894, ii, 219).—Positive results were obtained with gelatin and with Hammarsten's casein. Gelatin gives a black precipitate, owing to the presence of sulphur, which has to be boiled with dilute nitric acid.

It was found that monamino-acids, such as glycine, give silver iodide precipitates, owing, presumably, to the decomposition of the amino-acid, with liberation of carbon dioxide and production of a methyl group. N. H. J. M.

**Estimation of Hæmatin in Blood.** A. AZADIAN (*Bull. Soc. chim. Belg.*, 1914, 28, 91—94).—Five c.c. of the previously defibrinated and filtered blood are added very rapidly, and in small portions, to glacial acetic acid (5 c.c.). Five c.c. of a solution of colourless hydriodic acid (D 1.5, 1.5 c.c.) in alcohol (25 c.c.) are immediately added, and the mixture is briskly shaken, heated, and maintained at the boiling point for about two minutes. Boiling distilled water (15 c.c.) is then added. After centrifuging for ten minutes at about 2000 revolutions per minute, the water is decanted, the crystals washed three times with water, twice with alcohol, and then dried until constant in weight. A table of results obtained with the blood of different species of animals is appended. H. W.

**Modification of Teichmann's Test for Blood.** WILLIAM DUNBAR SUTHERLAND and GOPAL CHANDRA MITRA (*Biochem. J.*, 1914, 8, 128—130).—With reference to Symon's modification of this test (this vol., ii, 228), instead of the hæmin test, the spectroscopic test is recommended as distinctive and more sensitive; the spectrum to be examined is that of cyanhæmoglobin, and the microspectroscope should be used when dealing with small quantities. Even in old stains, moreover, it is usually practicable to obtain microscopic evidence of blood corpuscles, and to distinguish between those of mammals and non-mammals. W. D. H.

**Examination of Blood Stains.** ERCOLE COVELLI (*Boll. Chim. farm.*, 1913, **52**, 823—827, 861—865, 895—903).—An account of a systematic examination of blood stains with the aid of all the most important methods which have been suggested by different authors. R. V. S.

**The Quantitative Extraction of Diastases from Plant Tissues.** R. W. THATCHER and GEO. P. KOCH (*J. Amer. Chem. Soc.*, 1914, **36**, 759—770).—In connexion with an investigation of the enzymes of the wheat kernel, and their distribution to the various products obtained by milling, the authors required a method for the quantitative extraction of active diastases. They find that an apparently quantitative extraction can be made by shaking the powdered sample with water at 0° for one to two hours. The liquid is then filtered whilst still cold, and the diastasic power estimated immediately by measurement of the production of maltose from starch (Sherman, Kendall and Clark, A., 1910, ii, 1012; Sherman and Schlesinger, A., 1913, i, 1400). D. F. T.

**Assay of Digestive Ferments.** HOWARD T. GRABER (*J. Ind. Eng. Chem.*, 1914, **6**, 402—403. Compare A., 1912, ii, 706).—The authors draws attention to the fact that in testing the neutrality of starch intended for the assay of diastatic ferments, litmus is not sufficiently sensitive, and he suggests cochineal solution for this purpose. The starch should be neutral, or at most feebly acid; it should be chosen of average moisture content, and the dilute iodine solution should be used at one temperature. D. F. T.

**Simplified and Inexpensive Oxydase Apparatus.** HERBERT H. BUNZEL (*J. Biol. Chem.*, 1914, **17**, 409—411).—The apparatus consists of three rather wide glass tubes fused together, as in an ordinary three-way glass connexion. The extremities of the two lower tubes are sealed. The third tube, which is vertical when the apparatus is in use, terminates in a ground glass joint, which carries an open mercury gauge. A lateral hole is drilled through both portions of this joint, so that by rotating the gauge the interior of the vessel can be shut off from the air without its volume being altered. In using the apparatus, a measured volume of the plant juice to be examined is run into one of the closed arms, the oxidisable substance into the other, and water is added to make a known total volume (6 c.c.). The apparatus, having been warmed to the desired reaction temperature, is closed by rotating the gauge, and the liquids are mixed by shaking. The amount of oxygen absorbed in the reaction is then deduced from the pressure change, the volume of the apparatus being known. As there is no provision made for the absorption of carbon dioxide produced in the reaction, only comparative results are obtained, but it is simpler and more sensitive than the author's larger apparatus (*U.S. Dept. Agriculture*, 1912, *Bulletin* 238; *Zeitsch. biol. Technik Methodik*, **2**, 307—309). R. V. S.

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## General and Physical Chemistry.

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**The Spark Spectra of Some Elements in the Extreme Ultra-violet.** LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1914, 158, 1416—1418).—By their spectrographic method already described (compare this vol., ii, 317), the authors have prolonged the study of the spectra of a number of elements down to the ray  $\lambda$  1855. The metals examined were arsenic, antimony, tin, bismuth, aluminium, and cadmium, and the lines found, and their relative intensities, are given in tabular form, reference being made to results obtained by previous workers. W. G.

**Arc and Spark Spectrum of Helium.** J. STARK (*Ber. Deut. physikal. Ges.*, 1914, 16, 468—474).—The line  $\lambda$  4686, which is usually ascribed to hydrogen, has been found to be emitted in the jar discharge through a helium tube which showed no trace of the hydrogen spectrum. When this tube was subjected to the discharge furnished by a small induction coil, the spectrum emitted showed the two well-known series of helium lines, but no trace of hydrogen lines or of  $\lambda$  4686. When the tube was placed in circuit with a Leyden jar and a spark-gap, the yellow luminosity was found to be greatly reduced, and, in addition to the relatively feeble series lines of helium, the spectrum showed the line  $\lambda$  4686 in considerable intensity. There was, however, still no trace of the hydrogen lines in the spectrum, and the author considers, therefore, that  $\lambda$  4686 is a helium line.

The general behaviour of the series lines indicate that these are arc lines, whilst  $\lambda$  4686 is a spark line. The carriers of the series lines are helium ions with a single positive charge, whilst the spark spectrum is due to doubly charged helium ions (compare A., 1913, ii, 172, 360). H. M. D.

**The Arc and Spark Spectrum of Copper according to International Normals.** KARL HASBACH (*Zeitsch. Photochem.*, 1914, 13, 399—430).—Accurate wave-length measurements have been made with the aid of a large concave grating, the region covered extending from  $\lambda$  6740 to  $\lambda$  2035. The occurrence of eight pairs of lines with a constant frequency difference, first indicated by Kayser and Runge, is confirmed by the author's more accurate measurements. Three of these pairs of lines belong to the principal series, three to the first subordinate, and two to the second subordinate, series. H. M. D.

**Absorption of Light by Water Changed by the Presence of Strongly Hydrated Salts as Measured by means of the Radiomicrometer.** Bearing of the Results on the Solvate Theory of Solution. E. J. SHAEFFER, M. G. PAULUS, and HARRY C. JONES (*Physikal. Zeitsch.*, 1914, 15, 447—453. Compare A., 1913, ii, 362).—With an improved form of apparatus, further comparative measurements have been made of the absorption of light by pure

water and by the water in solutions of various salts. The results confirm those which were obtained previously, and show that solutions of salts, which have little tendency to combine with water, have practically the same absorption capacity as pure water. Solutions of salts, such as magnesium chloride, magnesium bromide, magnesium sulphate, calcium chloride, zinc sulphate, and zinc nitrate, are, on the other hand, more transparent than a layer of pure water of equivalent thickness. The greatest difference is found for the light rays, which are most readily absorbed by water. The observations are considered to give further support to the solvate theory.

H. M. D.

**The So-called Cyanogen Bands.** W. GROTRIAN and C. RUNGE (*Physikal. Zeitsch.*, 1914, 15, 545—548).—From observations on long continuous current arcs, it has been found that the so-called cyanogen bands  $\lambda$  3360, 3590, 3883, 4216, and 4606 are due to nitrogen.

With 5000 volts it was possible to obtain an arc of 100 cm. in length by means of an arrangement similar to that employed by Schönherr in his apparatus for the fixation of atmospheric nitrogen. The spectrum emitted by the middle portion of such arcs is independent of the nature of the electrodes, and appears to be solely determined by the nature of the gas in the discharge tube. The intensity of the "cyanogen bands" is very marked when discharge takes place in an atmosphere of nitrogen. The intensity is practically the same whether the electrodes used are of carbon, copper, iron, platinum, magnesium, or aluminium. The introduction of small quantities of carbon dioxide into the discharge tube has no appreciable influence on the intensity of the bands. These and other experiments lead to the conclusion that the "cyanogen bands" are really attributable to nitrogen. It is shown that earlier observations on the "cyanogen bands" can be readily explained on this view.

H. M. D.

**Photographic Spectrophotometry of the Absorption Spectra of Dyes.** FRITZ ECKERT and RUDOLF PUMMERER (*Zeitsch. physikal. Chem.*, 1914, 87, 599—618).—A method is described by which the intensity of light of all wave-lengths of an absorption spectrum can be measured. The method consists of the following. The absorption spectrum of a layer of a solution of thickness  $d$  and concentration  $c$  is photographed, and on the same plate the absorption spectrum of the pure solvent is photographed, and also the spectra of the solvent when fractions of the original light pass through. Usually six such weakened spectra are determined. The weakening of the spectrum is brought about by means of a rotating sector, which has an opening that can be varied from  $180^\circ$  to  $0^\circ$ . Thus a number of different blackening effects is obtained on the plate when known amounts of the original light intensity are cut off, and in this way the intensity of the various parts of the dye spectrum can be determined, if  $J$  is the intensity of the absorption spectrum for a given wave-length and  $J_0$  that of the pure solvent. Then  $J = J_0 10^{-kcd}$ , where  $k$  is the Bunsen

constant. The method has been carefully tested, and it is found that an error of about 3% is to be expected. This method has been applied to the absorption spectra of solutions of the quinonoid salts of the thiazine series. Curves of the light intensity transmitted against the wave-length, and of the value  $k$  against the wave-length, are given for the substances: thiazone, 3-hydroxyphenazthionium chloride, hemi-quinonoid 3-hydroxyphenazthionium chloride, 3:6-dimethylphenazthionium chloride, hemi-quinonoid 3:6-dimethylphenazthionium chloride, and 3-acetylaminophenazthionium chloride. It is shown that the intensity curve of the bluish-red thiazone shows a broad band at 500—550  $\mu\mu$ , and not a broad double band at 545—560  $\mu\mu$  and 495—504  $\mu\mu$ , as was stated by Pummerer and Gassner (A., 1913, i, 991). The brown solution of 3-hydroxyphenazthionium chloride gives a spectrum differing from that of thiazone; it has a sharply defined maximum at 445  $\mu\mu$ , and a subsidiary band at 550  $\mu\mu$ . Both these peculiarities are found in the simplest phenazthionium salts, for example, in the 3:6-dimethyl derivative, in which a *p*-quinonoid formula is very unlikely, consequently the *o*-quinonoid formula is to be accepted for the brown hydroxyphenazthionium chloride; thiazone itself, however, has the *p*-quinonoid constitution. The brown solution in hydrochloric acid (D 1.15) on keeping changes in eight hours to a violet-coloured solution; this is due to a half reduction of the quinonoid salt by the hydrochloric acid to a nuclear chlorinated quinhedrone salt; this hemi-quinonoid violet hydroxyphenazthionium chloride shows a fairly sharp maximum at 560  $\mu\mu$ , which occupies practically the same position as the subsidiary band did in the holoquinonoid salt. The development of the subsidiary band in the quinhedrone formation is shown also in the case of 3:6-dimethylphenazthionium chloride and 3-acetylaminophenazthionium chloride. The former of these salts has a sharp maximum at 450  $\mu\mu$  and a subsidiary band at 545  $\mu\mu$ , and the latter band becomes the chief maximum in the hemi-quinonoid salt; 3-acetylaminophenazthionium chloride has a sharp maximum at 455—460  $\mu\mu$ , and a subsidiary band at 550—555  $\mu\mu$ . The curves of the absorption constants ( $k$ ) show a very marked difference as the thiazine derivatives contain one or two auxochrome groups. With one auxochrome group, the bluish-red thiazone and the reddish-violet thiazime hydrochloride have a broad maximum at 550—570  $\mu\mu$ , and the bluish-green phenylthiazime hydrochloride at 585—605  $\mu\mu$ ; these three substances are to be regarded as *p*-quinonoid, and are distinct in the position of their maximum from the brown 3-acetylaminophenazthionium chloride, which has a maximum at 485  $\mu\mu$ , and is *o*-quinonoid.

J. F. S.

**Quantitative Investigation of the Mutual Influence of Two Chromophores in the Absorption of Ultraviolet Rays. Pre-calculation of the Absorption Curves. V.** JAN BIELECKI and VICTOR HENRI (*Ber.*, 1914, 47. 1690—1718. Compare this vol., ii, 318, 319).—In order to ascertain the way in which the absorption of one chromophoric group is influenced by the presence of



another, the authors have carried out a systematic investigation, as follows. Examination of the absorption spectra of acetone, dimethyl diketone, ethyl acetylglyoxalate, and acetonylacetone shows that two carbonyl groups in the  $\alpha$ -position have a hypsochromic action, equivalent to about 160 Ångström units, whereas in the  $\gamma$ -position they exert only a hyperchromic action. The influence of the carboxyl group on the carbonyl group was ascertained from an investigation of acetone, pyruvic acid and its ethyl ester, and ethyl lævulate. The conjugation of the carboxyl group with the carbonyl group has a hypsochromic effect, the absorption band being displaced 600 Ångström units towards the red, and at the same time the height of the band is diminished. When the carboxyl group is in the  $\gamma$ -position with respect to the carbonyl group there is a hyperchromic effect, and the height of the band is increased to about two and a-half times that of acetone.

The absorption curves of pyruvic acid and of ethyl lævulate are quite different from that of an equimolecular mixture of acetone and acetic acid, thus showing the marked mutual effect of two chromophores when present in one and the same molecule. The absorption of the above mixture is not additive.

The absorption curve of oxalic acid is displaced about 500 Ångström units towards the red with respect to that of acetic acid. The displacement of the succinic acid curve is very small, there being probably a hyperchromic effect.

The absorption curves of acetone, allylacetone, methylheptenone, mesityl oxide, and methyl isobutyl ketone show that an ethylene linking, when conjugated with a carbonyl group, has a very marked hypsochromic effect; when further removed, the effect is hyperchromic. From the further investigation of citral and phorone, it is found that the ethylene linking, when conjugated with either a carbonyl group or the grouping  $\cdot\text{C}\cdot\text{CH}:\text{C}<$  causes



the same displacement of the total absorption spectrum towards the red.

From the above results, knowing the alteration in the frequency and the amount of increase in the absorption constants corresponding with the chromophores and their distance apart in the molecule, the authors have been able to calculate the absorption spectrum of phorone from that of mesityl oxide, and find a very good agreement between theory and experiment.

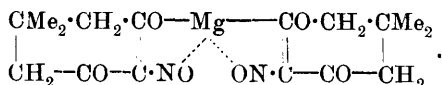
The absorption spectra of benzaldehyde, acetophenone, furfuraldehyde, and cyclohexanone have also been measured, but further experiments are necessary before safe conclusions can be drawn. In contradiction to Waliaschko (A., 1910, ii, 1015), benzaldehyde and acetophenone show three absorption bands, and not two.

The results are further discussed in the light of the theory previously put forward by the authors (this vol., ii, 399).

T. S. P.

**Internal Complex Salts of the Alkali Metals. I.** I. I. LIFSCHITZ (*Zeitsch. physikal. Chem.*, 1914, 87, 562—574).—The present paper

deals with an attempt to prove the existence of alkali salts of the oximino-ketonic and nitrolic acids, in which subsidiary valencies of the metal are active, by measurement of their electrical conductivity. The theory that such salts do exist has been put forward on spectroscopic grounds. The existence is shown of a yellow oximino-ion along with a blue nitrosoenol ion in the sodium and potassium salts of dimethyl- and diphenyl-violuric acids. It is shown that the red colour of the salt is not due to a mixture of the yellow oximino-ketone and the blue nitrosoenol salt, but to an internal complex of the constitution



The dissociation constant of the yellow dimethylvioluric acid is calculated to  $k = 3.95 \times 10^{-6}$ .

The following criteria are given for the existence of internal alkali complex salts: (1) An abnormally small conductivity in comparison with that, for example, of potassium chloride. (2) Of two chromoisomerides, the normal isomeride must possess a much larger electrical conductivity, since here no subsidiary valencies can be active. (3) In solutions of polychromatic salts, a connexion between the colour and the conductivity must exist in the sense that the conductivity is larger the more the colour of the solution approaches the pure blue colour of the nitrosoenol salt. It is shown that in aqueous solution such internal alkali salts cannot be detected, but that the magnesium salt (see above) is easily detected. The conductivity of a series of solutions of the alkali salts of ethylnitrolic acid, diphenylvioluric acid, diphenylthiovioluric acid, dimethylvioluric acid, 4-oximino-3-*p*-bromophenylisooxazolone, 2-oximino-1:3-diketohydrindene, and nitrosoresorcinol monomethyl ether in methyl alcohol and in acetone have been determined at 25°. In the major portion of these salts, the conductivity is very small, and much below that of a normal corresponding alkali salt. The internal complex potassium salt of erythronitrolic acid conducts much less than the colourless, non-complex potassium salt of *isonitrolic* acid, which possesses a conductivity approximating to that of potassium chloride. Of the polychromatic potassium salts, the blue salts conduct the best, and generally have a conductivity approximating to the normal value, then follow in order the green, red, and reddish-violet salts. In all cases, the conductivity increases strongly with dilution. Although, from the small conductivity of the blue oximino-ketone salts, as compared with corresponding inorganic salts, one is unable without further evidence to make a definite statement as to the presence of internal complex salts, still, the very much smaller conductivity of the red and green salts as compared with the blue salts leaves no other conclusion possible in these cases but that such internal complex salts are present. The whole result of the work is to give a general confirmation of the theory put forward on the

basis of spectroscopic work that such internally complex salts do exist.

J. F. S.

**Action of Blood Solutions on Some Coal Tar Dyes.** ROBERTO MAGNANIMI (*Chem. Zentr.*, 1914, i, 900; from *Arch. Pharmacol. experim.*, 1913, 16, 481—483).—If a solution of hæmoglobin is covered with a solution of a dye (methylene-blue), precipitates and colour changes are noticed. The alkaline dyes seem to be reduced and to affect the spectrum in the red and yellowish-green, whereas acid dyes are not reduced, and influence the short-wave end of the spectrum.

J. C. W.

**Radioactive Recoil.** L. WERTENSTEIN (*Ann. Physique*, 1914, [ix], 1, 347—432).—The recoiling atom of an  $\alpha$ -ray change is termed an  $\alpha$ -radiation, that of a  $\beta$ -ray change a  $\beta$ -radiation; for example, the atoms of radium-*B* recoiling in the  $\alpha$ -ray change of radium-*A* would be termed the  $\alpha$ -radiation of radium-*A*. A preliminary study of this  $\alpha$ -radiation gave for the values of the ranges 0.12 mm. in air, 0.72 mm. in hydrogen at atmospheric pressure, and 20  $\mu\mu$  in a silver film. A more exact determination, with many precautions, using strong sources of radium-*A* and canalised rays, gave 0.14 and 0.83 mm. in air and hydrogen respectively. This is about 350 times less than that of the corresponding  $\alpha$ -rays, which possess fifty times greater energy, so that an  $\alpha$ -particle loses more energy in its course than the  $\alpha$ -particle. But the process of absorption presents analogies in the two cases. For the first part of the range, one-half in air and less in hydrogen, the number of  $\alpha$ -particles in the stream remains constant, and then diminishes, slowly at first, and then more rapidly, which is ascribed to the scattering of the  $\alpha$ -particles by the atoms with which they collide. From plane polished surfaces the number of  $\alpha$ -particles projected from radium-*A* has been found to be practically the same as the number of  $\alpha$ -particles. The  $\alpha$ -particles ionise the air, and at the commencement of their course the relative ionisation of the  $\alpha$ -rays is much greater than that of the  $\alpha$ -rays, and in narrow ionisation chambers at reduced pressures may be five times greater. The energy lost by the  $\alpha$ -particle is, however, about seven times greater than that lost by an  $\alpha$ -particle in a path of the same length, so that probably a portion of the energy is communicated as kinetic energy to the molecules encountered. In contradistinction from the behaviour with the  $\alpha$ -particles, the ionising power of an  $\alpha$ -particle diminishes as its speed decreases. They are analogous in this respect to  $\alpha$ -particles at the extreme end of their range. The collisions determining the absorption seem to be intermediate in character between the ordinary collisions between gas molecules and those of the  $\alpha$ -particle at the commencement of its path.

F. S.

**A Radiation Accompanying the Oxidation of Phosphorus.** A. BLANC (*Compt. rend.*, 1914, 158, 1492—1493).—The oxidation of phosphorus in air is accompanied by an ionising radiation, which

resembles the  $\gamma$ -rays of radioactive substances, and possesses but very slight penetrating power. W. G.

**Collisions between Electrons and Molecules of Mercury Vapour and the Ionisation Potential of the Molecules.** J. FRANCK and G. HERTZ (*Ber. Deut. physikal. Ges.*, 1914, 16, 457—467).—From experiments on the ionising power of electrons towards mercury vapour, it has been found that the electrons are reflected by the mercury molecules so long as the speed of the electrons falls below a certain critical value. A method has been devised by which it is possible to determine the critical velocity to 0.1 volt, and in the case of mercury this critical velocity corresponds with a potential of 4.9 volts. The critical velocity obtained for helium by this method is 21 volts, which agrees well with the value 20.5 volts obtained in earlier experiments by a different method.

It is shown that the energy of an electron moving with a velocity of 4.9 volts is exactly equal to the energy quantum characteristic of the resonance line  $\lambda$  2536 which is emitted by mercury vapour. The authors suggest that the collisions between molecules of mercury and electrons moving with the critical velocity may not only be accompanied by ionisation of the molecules, but that some of the collisions may result in the emission of light with the characteristic wave-length  $\lambda$  2536. H. M. D.

**Extraction of Radiothorium.** O. KNÖFLER & Co. (D.R.-P. 269501).—Radiothorium in the form of a good adherent deposit can be obtained by the electrolysis of mesothorium solutions, containing radiothorium, by the use of moderate potential and current strength and electrodes of platinum, silver, etc., for cathode, and platinum, carbon, etc., for anode. By electrolysis strong mesothorium preparations containing little electrolytically deposited impurities, the radiothorium may be obtained on wires, foils, etc., in highly concentrated form, and in a degree of purity unattainable by other methods. F. S.

**Hydrosols of Radioactive Products.** TADEUSZ GODLEWSKI (*Kolloid. Zeitsch.*, 1914, 14, 229—242).—A résumé of recent work on the properties of dilute solutions of radioactive substances. This affords strong evidence in support of the view that the radioactive constituents are present in the colloidal form (compare Paneth, A., 1913, ii, 1075). H. M. D.

**Radio-atoms: their Atomic Weights and Valencies.** F. H. LORING (*Chem. News*, 1914, 109, 241—242).—On the view that the radio-elements are made up of associate atoms differing in atomic weight, and that the atomic weights are exactly whole numbers in a Rydberg series, thorium is regarded as a mixture of atoms of weights 235 and 231 in the proportions 5 to 9, the same as the ratio between the two branches of the thorium disintegration series. The inference is that many of the common elements have two types of atoms, like thorium, but not necessarily more, as in the case of lead. F. S.

**Dielectric Constants of Some Pure Gases at High Pressure, and the Law of Mossotti and Clausius.** A. OCCHIALINI (*Nuovo Cim.*, 1914, [vi], 7, 108—126).—The author has measured the dielectric constants of oxygen, hydrogen (compare this vol., ii, 163) and carbon dioxide at high pressures. That of oxygen at 13.5° varies from 1.01831 at a density of 35 to 1.05843 at a density of 110, whilst that of carbon dioxide varies from 1.00996 at a density of 10 to 1.05082 at a density of 50. The law of Mossotti and Clausius,  $(k-1)/(k+2)d=M$ , is verified, the simpler formula  $(k-1)/d=\text{constant}$  being inapplicable. R. V. S.

**Molecular Condition and Electrical Conductivity of Crystalline Salts.** C. TUBANDT and ERICH LORENZ (*Zeitsch. physikal. Chem.*, 1914, 87, 513—542).—The authors show that the electrical conductivity of solid salts can be used to determine the molecular condition of such substances, and that transition points and melting points can be determined with a great degree of accuracy by this method. Conductivity determinations have been carried out with the chloride, bromide, and iodide of silver and thallium at temperatures below and above the melting point. The measurements were made in a porcelain U-tube fitted with two cylindrical platinum electrodes, which were placed in the widened upper part of the tubes. The tube was heated in an electric furnace, which could be so regulated that the temperature difference between the top and bottom of the U-tube did not exceed 3° at temperatures of 600°, and at lower temperatures was considerably less. In the case of silver iodide, there is a sharp break in the conductivity curve at 552°, namely, the melting point, the conductivity of the solid iodide being greater than that of the molten salt; a second break occurs at 144.6°, the value falling suddenly from 1.31 to 0.00034, this point being the transition point of the regular form into the hexagonal form. In the case of silver bromide and chloride, breaks occur at 422° and 455° respectively; these points are the melting points of the two salts, and the conductivity is smaller below the melting point than above it. In the case of the thallium haloids, the breaks were found to lie at 436°, 457°, and 427° for the iodide, bromide, and chloride respectively, and in these cases also the molten substance conducts better than the solid. No other breaks were observed in any of the curves, and it is shown that the liquid crystalline forms of the silver and thallium haloids supposed to exist were not really such, but plastic mixtures due to the presence of impurities. It is shown that the conductivity of these salts, whether molten or solid, is entirely electrolytic, and in no sense electronic, since they obey Faraday's law to within 0.75%. This was shown by passing a current between a platinum cathode and a silver anode through the salts for a measured time, and weighing the loss of the anode. A scheme for the condition diagram of the halogen derivatives of silver and thallium is given on the assumption that the molten salt contains only two kinds of molecules. It is shown that solid silver iodide is more strongly dissociated than molten silver iodide, and that

the migration velocity of the silver ion in the neighbourhood of the melting point is  $1.13 \times 10^{-3}$  cm. per sec., which is about twice as large as that of the silver ion in aqueous solution at ordinary temperature. This high migration velocity is explained on a theory of R. Lorenz (*Festschrift Nernst*, 1912, 276; A., 1912, ii, 323; 1913, ii, 281), which assumes that there is an interchange between the free ion and the corresponding part of the undissociated medium, so that the apparent migration velocity is made up of the actual velocity of the ion between the molecules of the medium and the velocity with which it reacts with the molecule of the medium with the discharge of the corresponding part of the molecule as ion. The influence of the viscosity of solid and melted salts on the degree of dissociation and migration velocity of the ions is discussed at length. J. F. S.

**Electrical Conductivity as a Method for Determining the Condition Diagrams of Binary Mixtures of Salts.** C. TUBANDT and FRITZ LORENZ (*Zeitsch. physikal. Chem.*, 1914, 87, 543—561. Compare preceding abstract).—The authors have determined the electrical conductivity of a series of binary mixtures of the salts silver bromide—silver iodide and silver chloride—silver iodide. In the case of silver bromide—silver iodide, it is shown that there is a transition of the regular mixed crystals into hexagonal mixed crystals at  $127.1^\circ$  for mixtures containing from 14% to 80% silver bromide. Since the mixed crystals containing up to 80 mol. % silver bromide are of the same composition, and the regular crystals are transformed into hexagonal mixed crystals at the same temperature, it follows that these crystals must have the same composition, and that a complete “unmixing” must take place before the transition. This is marked in the experiments by a sudden change in the conductivity. Mixtures containing more than 80 mol. % of silver bromide do not form mixed crystals on solidification, but a compound,  $4\text{AgBr}, \text{AgI}$ . This is confirmed by thermal and optical examination of the molten mixture. In the case of the mixtures of silver iodide and chloride, the eutectic point is found to lie at  $215^\circ$ , and the transition point of the mixed crystals at  $130.3^\circ$ . In both cases diagrams of condition are drawn from the measurements, and it is shown that the method of electrical conductivity determinations of such diagrams is far more sensitive and trustworthy than the other more usual methods. J. F. S.

**Specific Electrical Conductivity and Density of Palladium-Hydrogen Alloys.** GEORG WOLF (*Zeitsch. physikal. Chem.*, 1914, 87, 575—588).—The conductivity and density of palladium wires containing measured amounts of occluded hydrogen have been measured. In order to calculate the specific conductivity, the change in the length and diameter of the wire was measured after each absorption of hydrogen. The palladium was made active by using it alternately as anode and cathode in the electrolysis of sulphuric acid. The electrical measurements were made by the Matthiessen

and Hockin method. It is shown that the specific conductivity decreases with increasing absorption of hydrogen, and when the maximum amount of hydrogen is absorbed the specific conductivity is about one-half its original value. The curve showing the change in specific conductivity with amount of occlusion can be divided into three parts: (1) up to 40 vols. of hydrogen to 1 vol. of palladium, in which the conductivity decreases proportionately with increasing hydrogen concentration; (2) from 40 vols. to 600 vols. of hydrogen to 1 vol. of palladium, in which the compound  $\text{PdH}_2$  is formed, and in which the conductivity decreases asymptotically; (3) above 600 vols. of hydrogen to 1 vol. of palladium, in which the hydrogen dissolves in the compound  $\text{PdH}_2$ , and in which the conductivity falls proportionately to the further amount of hydrogen absorbed. The density of the alloys decreases with increasing absorption of hydrogen. The curve of the density and concentration can be divided into two parts: (1) a steep, hyperbolic limb, and (2) a slowly falling straight line.

J. F. S.

**Stratification in Pure Gases and the Effect of Impurities.** PAUL NEUBERT (*Physikal. Zeitsch.*, 1914, 15, 430—433).—Experiments have been made to determine the conditions under which the luminous emission exhibits stratification in the passage of the electric discharge through gases. Hydrogen, liberated from palladium and purified by means of metallic potassium, was found to give rise to broad, red-coloured strata. Previous experiments had shown that the admixture of traces of oxygen transformed the colour of the discharge from red to blue, whilst at the same time the stratification became much narrower. The same effect is produced by admixture of traces of iodine. With hydrogen at a pressure of 0.1 mm. Hg, it was found that this transformation is brought about by the presence of 0.006% of iodine.

Pure nitrogen showed no stratification on the passage of the discharge, but the effect was observed when hydrogen or oxygen was mixed with the nitrogen. Pure oxygen was also found to give a negative result, but the addition of 0.4% of hydrogen caused the luminosity to assume a stratified appearance. Some observations with mercury would seem to show that pure mercury vapour does not exhibit stratification, and thus the conclusion drawn by Schuster is confirmed.

H. M. D.

**The Silver Voltameter. I. First Series of Quantitative Experiments.** E. B. ROSA and G. W. VINAL (*Chem. Zentr.*, 1914, i, 730—731; from *Bull. Bureau Standards*, 1912, 9, 151—206).—The somewhat larger amount of silver which is deposited in the filter-paper as compared with the porous-pot form of voltameter has been found to be due to the chemical reactivity of the filter-paper. If two or three layers of filter-paper are used, the excess of deposited silver shows a corresponding increase. The filter-paper effect is not dependent on the presence of the paper during the electrolysis; it is also exhibited if the solution has been in contact with filter-

paper previous to the commencement of the electro-deposition. If successive measurements are made with the same solution in the filter-paper voltameter, it is found that the filter-paper effect increases continuously. This is attributed to the accumulation of impurities in the solutions.

The appearance of the silver deposits affords a valuable criterion in judging of the purity of the deposit. The silver deposited from a solution which has been in contact with filter-paper is non-crystalline and streaky in appearance, whilst the deposit from a pure solution is crystalline, and exhibits no sign of streakiness.

H. M. D.

**The Silver Voltameter. II. Chemistry of the Filter-paper Voltameter and Explanation of the Streakiness.** E. B. ROSA, G. W. VINAL, and A. S. MCDANIEL (*Chem. Zentr.*, 1914, i, 731—732; from *Bull. Bureau Standards*, 1912, 9, 209—282).—If an aqueous solution of silver nitrate is mixed with water which has been in contact with paper, the resulting solution is distinctly turbid. It is supposed that reducing substances are formed by hydrolysis of the cellulose, and that these react with the silver nitrate, giving rise to colloidal silver. Evidence has been obtained that one of these substances is furfuraldehyde, which may be produced from oxycellulose formed in the slow oxidation of cellulose.

If gelatin is added to the silver nitrate solution before electrolysis, a very streaky deposit is obtained which shows little evidence of crystalline structure. In presence of colloidal silver, the deposit is free from streaks, but the crystalline character is quite different from that of the deposit obtained by electrolysis of a similar solution without the addition of colloidal silver. A solution which has been in contact with filter-paper, and furnishes a streaky deposit on electrolysis, may be made to give a smooth deposit if it is filtered through a porous pot.

The previous history of the cathode is also found to have some influence on the nature of the silver deposit. The silver deposited on a platinum wire which has been subjected to the action of electrolytic hydrogen consists of a large number of small crystals, whilst previous treatment of the wire with electrolytic oxygen gives rise to a deposit which consists of a relatively small number of large crystals.

H. M. D.

**The Silver Voltameter. III. Second Series of Quantitative Experiments and the Preparation and Testing of the Silver Nitrate.** E. B. ROSA, G. W. VINAL, and A. S. MCDANIEL (*Chem. Zentr.*, 1914, i, 732; from *Bull. Bureau Standards*, 1913, 9, 493—551).—These experiments show that the small type of porous-pot voltameter yields better results than the large type. This is attributed to the presence of impurities in the solution, which are deposited to a greater or less extent during the electrolysis. The results obtained with the small porous-pot voltameter yield 1.018275 *V* for the *E.M.F.* of the Weston cell at 20°. The temperature-coefficient of the voltameter is zero if the solution used is pure.



New methods are recommended for testing the silver nitrate for impurities. For the estimation of free acid, the authors make use of iodoeosin, and for the detection of reducing substances and colloidal silver a 0.001*N*-solution of potassium permanganate is employed.

H. M. D.

**Comparison of the Silver and the Iodine Coulometers and the Determination of the Value of the Faraday.** STUART J. BATES and GEORGE W. VINAL (*J. Amer. Chem. Soc.*, 1914, 36, 916—937).—Washburn and Bates (*A.*, 1912, ii, 1130) have given an account of an iodine coulometer which was found to have a reproducibility of the same order as that of the silver coulometer.

A careful comparison has now been made of these coulometers using them in series, so that the deposits of silver and iodine should be strictly comparable, and the following results have been obtained. The ratio  $\text{Ag}:\text{I}=0.85017$ , as compared with the value 0.849906 obtained by Baxter (*A.*, 1911, ii, 112) and 0.850013 found by Köthner and Auer (*A.*, 1904, ii, 556), on the basis of  $\text{Cl}=35.457$ . The electrochemical equivalent of iodine was found to be 1.31502, and the value of the faraday 96,515 coulombs ( $\text{I}=126.92$ ), or 96,494 ( $\text{Ag}=107.88$ ); these values were calculated on the basis of the international ampere, using 1.11800 mg. per coulomb as the electrochemical equivalent of silver. As a recent investigation has given 1.11804 mg. per absolute coulomb for the electrochemical equivalent of silver, it seems that the best value to assign to the faraday is 96,500.

E. G.

**Solutions of Metals in Non-metallic Solvents. V. Electromotive Force of Concentration Cells of Solutions of Sodium in Liquid Ammonia and the Relative Speed of the Ions in these Solutions.** CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1914, 36, 864—877. Compare *A.*, 1907, ii, 935; 1908, ii, 486, 834, 835).—It has been shown in an earlier paper (*A.*, 1908, ii, 835) that the process of conduction in solutions of metals in ammonia is ionic. The positive carrier is identical with the positive ion of the salts of the same metal, whilst the negative carrier, which appears to be the same for different metals, can consist only of the negative electron  $e^-$ , either free or associated with ammonia.

In order to determine the ratio of the mean speeds of these two carriers, the *E.M.F.* of concentration cells of solutions of sodium in liquid ammonia has been measured over a wide range of concentrations, and from the results of these experiments the transference numbers have been calculated. It is shown that in dilute solutions the negative carrier carries about seven times as much current as the positive carrier, and the proportion increases with the concentration until, at a mean concentration a little below *N*, the negative carrier carries about 280 times as much current as the positive carrier. Assuming that the speed of the positive ion remains constant, the mean speed of the negative ion increases forty-fold between 0.001*N* and *N*. If the equivalent conductivity of the positive ion is taken as 130 (that of the sodium ion), the

equivalent conductivity of the dilute metal solution is calculated to be 1040.

These results are accounted for on the assumption that the ions  $\text{Na}^+$  and  $e^-$  exist in solution. At high dilutions, the negative electron,  $e^-$ , which serves as negative ion, is surrounded by an envelope of ammonia, which determines its speed. At higher concentrations, some of the negative electrons are free from the ammonia envelope for a fraction of the time. Under these conditions, they move with a speed comparable with that of the negative electrons in metals. This accounts for the rapid increase of the transference number of the negative carrier at higher concentrations, since the number of free electrons increases as the proportion of metal to ammonia increases. E. G.

**Calculation of Electromotive Forces from Thermal Data.** F. POLLITZER (*Zeitsch. Elektrochem.*, 1914, 20, 305—307).—Polemical in reply to Brönsted (A., 1913, ii, 917; see also Pollitzer, A., 1913, ii, 669). J. F. S.

**Thermo-electric Study of Selenium-Antimony Mixtures.** H. PÉLABON (*Compt. rend.*, 1914, 158, 1669—1671).—Bars of antimony or of mixtures of antimony with varying amounts of selenium were prepared by drawing the molten metal or mixture into glass tubes, which were not removed after cooling, and into each end of the bar a platinum wire was fixed. The bottom junction was kept at  $11^\circ$ , and the top junction raised to varying temperatures, and the thermo-electric force measured in each case. The results confirm those previously obtained from a study of the fusibility and a metallographic examination of antimony-selenium mixtures, that there is only one compound, namely,  $\text{Sb}_2\text{Se}_3$  (compare A., 1911, ii, 575, 899). The existence of this compound is shown by the sudden variation of the thermo-electric force, which in the case of the compound is ten times as great at all temperatures as those of mixtures differing even only slightly in selenium content from the compound. Further, antimony selenide, like other metallic selenides, has a very high thermo-electric force in the solid state. With antimony itself, or with the mixtures, the results show that there is no sudden change in the thermo-electric force when one element of the couple melts. W. G.

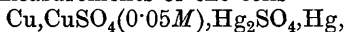
**Improved Hydrogen Electrode.** GEORGE STANLEY WALPOLE (*Biochem. J.*, 1914, 8, 131—133).—A modified form of hydrogen electrode is described (compare A., 1913, ii, 749). The slow rise of the potential difference, due to liberation of alkali from the glass, is avoided by the use of borosilicate Jena glass.

H. M. D.

**Potential of the Copper Electrode and the Activity of Bivalent Ions.** GILBERT N. LEWIS and WILLIAM N. LACEY (*J. Amer. Chem. Soc.*, 1914, 36, 804—810).—Although the determination of the *E.M.F.* of cells involving bivalent or other multivalent ions does

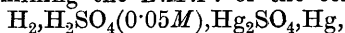
not present any greater difficulty than those involving only uni-valent ions, the interpretation of measurements of cells of the former type is complicated by the lack of means of determining the concentration of intermediate ions, such as  $\text{CuI}$  and  $\text{KSO}_4$ , and by the absence of adequate data for calculating the degree of dissociation or the activity of the ions in salts of higher types than the uni-univalent. For such a calculation, it is necessary to determine the free energy of dilution by measurements of *E.M.F.* or f. p., or of some other property thermodynamically related to these.

The free energy of dilution of copper sulphate has been determined by *E.M.F.* measurements of the cells



and  $\text{Cu}, \text{CuSO}_4(0.005M), \text{Hg}_2\text{SO}_4, \text{Hg}$ . The difference between the values for these *E.M.F.*'s gave 0.0298 volt as the *E.M.F.* corresponding with the free energy of dilution of copper sulphate from 0.05*M* to 0.005*M*. Another method, based on measurements of f.-p. lowering, gave a value corresponding with 0.0344 volt for the free energy of dilution from 0.05*M* to 0.005*M*, and 0.0422 volt for the free energy of dilution from 0.005*M* to 0.0005*M*.

The free energy of dilution of sulphuric acid was obtained similarly by determining the *E.M.F.* of the cells



and  $\text{H}_2, \text{H}_2\text{SO}_4(0.005M), \text{Hg}_2\text{SO}_4, \text{Hg}$ , and also from f.-p. data. The former method gave 0.0615 volt for the free energy of dilution from 0.05*M* to 0.005*M*, whilst the latter gave 0.0613 volt for this dilution and 0.0731 volt from 0.005*M* to 0.0005*M*.

From the results of the *E.M.F.* measurements, the normal electrode potential of copper against cupric ion at 25° was found to be -0.3469 volt, the normal hydrogen potential being taken as zero.

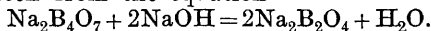
E. G.

**Transference Number, Conductance, and Ionisation of Hydriodic Acid at 25°.** E. K. STRACHAN and YEE GIH CHU (*J. Amer. Chem. Soc.*, 1914, 36, 810—819).—In calculating the degree of dissociation of an electrolyte from the conductivity ratio, it is usually assumed that the transference numbers for the electrolytes are independent of the concentration. In some cases, however, this condition is not fulfilled. For example, the transference number between the concentrations 0.005*N* and 0.1*N* of the strong acids, as obtained by direct measurement, does not accord with the value for the conductivity of the hydrogen ion at infinite dilution. In such cases, the degree of ionisation can be calculated from the values of the individual ion conductivities (Washburn and Strachan, A., 1913, ii, 572). As the data required for this calculation were not available in the case of hydriodic acid solutions, the present work was undertaken.

The transference number of hydriodic acid at 25° was determined by the Hittorf method, using a silver anode and a silver iodide cathode. The value of the transference number of the cation was found to be  $0.826 \pm 0.001$  between concentrations of

0.2*N* and 0.06*N*. In these experiments, it was found that an error was introduced by the adsorption of hydriodic acid by the silver iodide. Determinations of the relative viscosities of hydriodic acid of 0.1963*N* and 0.09839*N* concentration gave the values 0.99542 and 0.99660 respectively. The conductivities of hydriodic acid solutions were measured, and the degree of dissociation was calculated for the concentration range 0.2*N* to 0.002*N*. The results are tabulated. E. G.

**Influence of Impurities in Electrolytes on the Electrolytic Valve Action of Aluminium.** GÜNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1914, 20, 307—310).—The use of aluminium as a current rectifier in technical operations is limited by the fact that it only shows a valve action in comparatively few electrolytes, and that in these the valve action ceases when certain salts, with which it shows no valve action, are present as impurities. The author has made experiments to show to what extent these impurities may be present before they are able seriously to interfere with the valve action of the metal. For this purpose, he has determined the "formation" curves in 0.22*N*-solutions of borax to which various salts have been added. The formation curves were determined by passing a steady current of 25 milliamperes through a solution by means of an aluminium anode and a platinum cathode, and plotting the terminal potential against the time the current had been flowing. It is shown that when the borax solution contains sodium chloride in a concentration of  $2.5 \times 10^{-4}$ *N* the valve action is affected, and with a concentration of  $1 \times 10^{-3}$  it is entirely destroyed, so that for electrolytes which give a chloride precipitate with silver nitrate the aluminium current rectifier cannot be used. In the case of sodium nitrate, a  $4 \times 10^{-3}$ *N*-solution destroys the action. With sodium hydroxide, it is shown that the electrode formation is not affected until the alkali concentration exceeds that of the borax, but when this concentration of alkali is present the formation is delayed. The reason for the peculiarity in the case of sodium hydroxide is seen from the equation



In the case of sodium chloride and nitrate, the aluminium electrode is attacked and powders, whilst in that of sodium hydroxide it remains bright. Similar experiments were carried out with potassium permanganate as impurity. The general result of the work is that sodium chloride is the most serious impurity, and must not be present to a greater extent than 0.5%. Sodium nitrate and potassium permanganate may be present up to 1%, and sodium hydroxide is the least objectionable impurity, but when present in too large quantities the aluminium electrode is slowly dissolved. J. F. S.

**Electrostenolysis.** HARRY N. HOLMES (*J. Amer. Chem. Soc.*, 1914, 36, 784—789. Compare Braun, A., 1891, 393; Coehn, A., 1898, ii, 365).—Braun and Coehn's work on electrostenolysis was done by means of thick glass tubes, closed at one end, which were

heated and plunged into cold water, so that numerous cracks were produced, which served as the capillary spaces. As the effective capillary spaces in such tubes are very limited, the present work was carried out with U-tubes, packed with finely powdered, insoluble substances, such as glass, sulphur, and silica, and filled with aqueous solutions of the salts to be tested.

In addition to the results obtained by Braun, electrostenolytic deposits were obtained with solutions of cuprous bromide, cuprous iodide, cupric sulphate, Fehling's solution, sodium plumbite, sodium stannite, ammonium molybdate, manganese chloride, and nickelous bromide. These were produced by means of a direct current at 110 volts, but a deposit was also secured in a cobaltous bromide solution, using an alternating current. A discharge of bromide ions was observed round an initial deposit of cobalt peroxide formed by electrostenolysis.

E. G.

**Electrical Ignition of Gaseous Mixtures.** W. M. THORNTON (*Proc. Roy. Soc.*, 1914, A, 90, 272—297).—The ignition of mixtures of air and the gases or vapours methane, ethane, propane, butane, pentane, methyl alcohol, ethyl alcohol, benzene, carbon disulphide, hydrogen and carbon monoxide, by means of direct and alternating sparks, has been investigated. The method of investigation consisted in placing a quantity of the gaseous mixture in a strong glass tube, bringing two metal poles into contact, and then producing a spark by rapidly separating them. The metal poles used were of iron, and were 0.254 cm. in diameter. Using direct current, it is shown with the paraffin hydrocarbons that the limits of explosibility lie at 5.60% and 14.80% of combustible gas for methane, 3.10% and 10.70% for ethane, 2.17% and 7.35% for propane, 1.65% and 5.70% for butane, and 1.35% and 4.50% for pentane. Curves are given showing the minimum current required to produce an explosion in each case for a series of air-hydrocarbon mixtures between the above-mentioned limits. It is shown that in each case the curve consists of three distinct portions, consisting of a straight, inclined base line which, if produced, passes through the zero point, a steep branch rising from the lower limit of explosibility, and a less steep branch from the higher end of the base line to the upper limit of explosibility. The fact that the base line passes through the zero point shows that the igniting current is proportional to the absolute number of molecules of combustible gas present, and not merely to the percentage. These curves also show that the same igniting current is required to bring about explosion in the most inflammable mixture in each case, despite the great differences in the calorific values of the combustible gases. It is shown that the ratio  $I/p$ , where  $I$  is the ignition current and  $p$  the percentage of combustible gas, is nearly proportional to the number of hydrogen atoms in the molecule of the combustible gas. It is therefore suggested that if the ignition is preceded by an ionisation of the gas, in these cases an ionisation of the hydrogen atoms is the first step in the disintegration, and the first compounds formed are those of hydrogen and oxygen.

This is in agreement with Dixon's conclusion (T., 1911, 99, 589—599) that it is during the "pre-flame" period of ignition which precedes the true explosion that water vapour influences the propagation. The outstanding result in the foregoing experiment is that each gas of the paraffin series has the same minimum igniting current, and that this occurs with mixtures which are near those for perfect combustion, and although it is clear that combustion is an important factor even in the initial stages, still, there is evidence that the influence of the discharge from the spark acts directly on the atoms in the molecule rather than on the molecules as a whole. The most inflammable mixtures in the paraffin series are at 8.0% for methane, 5.1% for ethane, 3.9% for propane, 3.1% for butane, and 2.5% for pentane. In the case of the alcohols, the limits of explosibility are 5% and 21% for methyl alcohol and 3% and 8.4% for ethyl alcohol, and the most inflammable mixtures are at 9.7% and 5.6% respectively. The slope of the base curve in these cases is slightly decreased by the addition of oxygen, and the alcohol with the greater molecular weight requires more current for ignition. The benzene curve differs from those of the foregoing substances, inasmuch as it lies nearly symmetrically between the limits of explosibility, which are at 1.24% and 6.37%. The most explosive mixture is at 4.8%; this is significant, since the mixture for combustion to carbon dioxide is 2.73%, whilst that for combustion to carbon monoxide is at 4.47%. The evidence, therefore, points to the formation of carbon monoxide as the first product of combustion, and that the formation of carbon dioxide is a much slower process than in the lighter gases. With carbon disulphide, the limits of explosibility are 2% and 45—50%, and the most explosive mixture is 6.5%; the curve in this case shows the same characteristics as the paraffin hydrocarbons. The minimum ignition current is very small, being only 0.32 ampere. In the case of hydrogen, the current is found to be the same in all strengths of mixture, except towards the limits of inflammability. The ignition is therefore an isolated molecular process, independent of concentration, requiring only a certain intensity of molecular movement. The influence of the circuit voltage on the form of the curves is also investigated. Using an alternating current, the following general results are obtained: the igniting current for the paraffins increases as the series is ascended, the product of the minimum current for each gas, and the percentage at which it occurs, being constant. The product of the number of atoms in a molecule of combustible gas, and the percentage at which the minimum current is required, is constant, so that the number of atoms in unit volume in all of the most inflammable mixtures is the same. The igniting current is nearly proportional to the number of atoms in the group, of one molecule of combustible gas and the oxygen required for combustion, forming an explosive unit. The paraffin gases, except methane, are most easily ignited at a percentage giving combustion midway between carbon monoxide and carbon dioxide, and both limits of explosibility are symmetrical from this point. Benzene is most

easily ignited when burning to carbon monoxide, and alcohol when burning to carbon dioxide. Carbon disulphide and hydrogen have the same type of ignition as in the case of continuous current. External ionisation, which does not itself cause ignition, has no measurable influence on the least igniting current. From the great differences in magnitude and type between continuous and alternating current ignition, it is suggested that some kind of ionisation precedes combustion, for the evidence is strong that a relation between electrification and chemical change, not unlike that of ordinary ionisation, occurs at ignition, caused, possibly, by the violent collisions which must occur in the gas in contact with the high-temperature sparks. That a gas has a particular temperature of inflammation may mean that ionisation by collision commences at this temperature. On this view, when the molecular energy set free by combustion of a molecule exceeds that required for initial ionisation of an adjoining molecule, there is true explosion, and since it is probable that all three modes of molecular motion, translation, rotation, and vibration, have part in the process of ionisation by collision, the influence of temperature, which depends only on the translational energy, may be in certain cases of secondary importance. J. F. S.

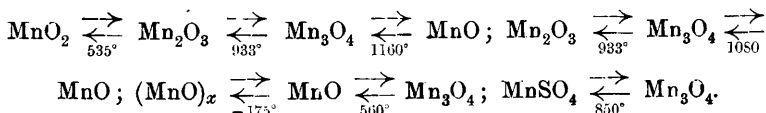
**An Electrical Tungsten-Tube Vacuum-Furnace.** FR. FICHTER and G. OSTERHELD (*Chem. Zentr.*, 1914, i, 934; from *Verh. Naturfor. Ges. Basel*, 1914, 24, 124—135).—The authors have constructed a resistance furnace on the principle of Wartenberg's furnace (*Zeitsch. Elektrochem.*, 1909, 15, 866), which contains a much larger tungsten tube, and allows of its being used for preparative work at temperatures above 2000°. The tungsten tube, which is made by welding tungsten powder, is surrounded by a magnesia tube to prevent loss of heat by radiation; the containing vessels, electrodes, and vacuum vessel are made of copper. The original contains detailed drawings of the furnace. J. F. S.

**Connexion between the Changes of the Magnetic Susceptibility and the Electrical Resistance in Iron, Steel, and Nickel at High Temperatures.** KÔTARÔ HONDA and YOSHINARI OGURA (*Sci. Reports Tôhoku Imp. Univ.*, 1914, 3, 113—125).—The curves showing the variation of the magnetic susceptibility and the electrical resistivity with the temperature show that the change extends in both cases over a considerable interval of temperature, and that there is a close parallelism between the two phenomena. Data are recorded for pure iron and nickel, and also for a number of samples of steel containing varying quantities of carbon.

H. M. D.

**Magnetic Investigation of the Changes of Structure of Manganese Compounds at Higher Temperatures.** KÔTARÔ HONDA and TAKÊ SONÉ (*Sci. Reports Tôhoku Imp. Univ.*, 1914, 3, 139—152).—The authors have investigated the influence of temperature on the magnetic susceptibility of the four oxides

$\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{MnO}$ , and also of manganous sulphate. The curves obtained by plotting the susceptibility against the temperature show irregularities which are attributed to the following changes:



None of the five compounds gives results which are in agreement with the relation  $\chi(T + \Delta) = \text{constant}$ , although this equation affords an approximate representation of the influence of temperature on the magnetic susceptibility.

H. M. D.

**Magnetic Rays in Different Gases and Gas Mixtures.** II AUGUSTO RIGHI (*Physikal. Zeitsch.*, 1914, 15, 558—563).—The apparatus described in a previous paper (*ibid.*, 528) has been employed for the further investigation of the phenomena associated with magnetic rays and the vertical anode by experiments in hydrogen, oxygen, carbon monoxide, carbon dioxide, nitrogen, ethyl ether, and chloroform vapour, and also in mixtures of these gases and vapours. The pressures under which the phenomena can be examined vary considerably according to the nature of the gas. For hydrogen, the experimental range of pressures is very much greater than for carbon dioxide. The phenomena can only be observed with difficulty in the vapours investigated, and the admixture of a small quantity of ethyl ether or chloroform vapour with one or other of the gases reduces the sensitiveness of the gas to a marked extent.

The phenomena are supposed to be due to the combination of positive ions with electrons, whereby neutral doublets are formed.

H. M. D.

**Coefficients of Expansion and Thermal Phenomena.** THADÉE PECZALSKI (*Ann. Physique*, 1914, [ix], 1, 457—477).—A theoretical paper, in which the pressure, volume, temperature relations of gases and liquids are mathematically examined in reference to the coefficients  $\alpha = 1/v \cdot dv/dt$  and  $\beta = 1/p \cdot dp/dt$ . The equations obtained are applied to the compressibility data for hydrogen, water, ethyl alcohol, and ethyl ether.

H. M. D.

**Special Experimental Methods for the Production of High Temperatures in a Vacuum and the Behaviour of some Metals, Oxides, and Carbides.** ERICH TIEDE and ERICH BIRNBRÄUER (*Zeitsch. anorg. Chem.*, 1914, 87, 129—168).—Tantalum is found to be too highly reactive for use as a furnace material for high temperatures. Tungsten wire also, when wound on crucibles of porcelain, pure magnesia, spinel mass, or zirconia, reacts after a short time, so that the wire is destroyed after, for example, eight hours at 1200°.

The furnace of Fischer and Tiede (A., 1911, ii, 694) has been



improved by devices for maintaining a more perfect vacuum. The glass vacuum vessel and ground joints are immersed in water. It has been found necessary to use Acheson graphite heating tubes, on account of the reactivity of tungsten towards every substance yet examined. Magnesia boats are used.

Tiede's cathode-ray furnace (A., 1913, ii, 655) has also been improved. Temperatures are determined by means of a Holborn-Kurlbaum optical pyrometer. The temperatures given below are comparative only.

Copper volatilises readily in a vacuum at  $1360^{\circ}$ , and boils vigorously at  $2000^{\circ}$ . Silver volatilises from  $850^{\circ}$  onwards, and yields a micro-crystalline sublimate, the crystals being spherulitic aggregates. Gold volatilises rapidly at  $1420^{\circ}$ , yielding a brown sublimate, without indication of crystalline structure, and a gold mirror on glass surfaces. Calcium volatilises from a carbon boat at a red heat. The sublimate oxidises rapidly in air, but may be transferred to light petroleum after filling the vessel with dry carbon dioxide. It is then found to consist of spherulitic aggregates.

Purified boron melts in the cathode-ray furnace at  $2200^{\circ}$ , whilst silicon, which cannot be examined in ordinary furnaces, on account of its reactivity, melts at  $1328^{\circ}$ , impurities being removed by distillation. Volatilisation of tin in the carbon furnace is perceptible at  $880^{\circ}$ , and is very rapid at  $1300^{\circ}$ . Tantalum sublimes at or above  $2200^{\circ}$ , and then becomes highly crystalline and brittle. Chromium reacts with carbon, and the carbide then distils. In the cathode-ray furnace, chromium melts at  $1410^{\circ}$ . Tungsten yields a sublimate of rhombic or rhombohedral crystals at  $2450^{\circ}$ . Manganese volatilises rapidly below its melting point, and may be purified by distillation. Zinc, antimony, and tungsten form crystalline sublimates on a hot surface, but condense in the form of mirrors on a cold surface.

Glucinum oxide melts at  $2400^{\circ} \pm 100^{\circ}$ , and does not volatilise much below the melting point, whilst magnesia dissociates readily at  $1900^{\circ}$ , and yields a deposit of magnesium, and lime volatilises from  $1650^{\circ}$  upwards. Baryta and strontia are more volatile than lime. Alumina volatilises at  $1750^{\circ}$ , and melts at  $1890^{\circ}$ . Zirconium dioxide melts at  $2430^{\circ}$ , tantalum pentoxide at  $1469^{\circ}$ , and observations are also recorded of the oxides of boron, lanthanum, cerium, thorium, vanadium, tin, silicon, titanium, chromium, and manganese. Magnesia is not reduced by carbon, but glucina, lime, strontia, alumina, boron trioxide, manganous oxide, and uranic oxide form carbides. Uranium carbide melts at  $2260^{\circ}$ .

C. H. D.

**Gaseous Equilibria and Specific Heat by the Explosion Method.** WILHELM SIEGEL (*Zeitsch. physikal. Chem.*, 1914, 87, 641—668).—The present work is a continuation of that of Piers (A., 1909, ii, 542, 789, 1031), Bjerrum (A., 1912, ii, 540; 1913, ii, 21), and Budde (*Diss.*, Berlin) on the determination of equilibria in gaseous mixtures. The author has investigated the loss of heat

due to radiation between the time of the commencement of the explosion and that at which the maximum temperature is reached. The method employed is identical with that of the previous investigators. It is shown that the loss of heat cannot be calculated quantitatively, but that with large initial pressures of gas (2 atms.) it can be neglected. The specific heat and the degree of dissociation of water vapour between the temperatures 2200° abs. and 2900° abs. are redetermined, and the expression

$$C_p^{(H_2O)} = 5.750 + 0.783 \times 10^{-3}T + 0.626 \times 10^{-6}T^2 + 4.56 \times 10^{-10}T^3 - 2.18 \times 10^{-17}T^5$$

deduced to represent the change of specific heat with temperature. All previous explosion experiments have been made with an excess of hydrogen; the author has shown that such experiments can be carried out with excess of oxygen, and temperatures obtained above 2900° abs. The data obtained in these experiments could not be used for calculations, probably because it is complicated by the presence of an unknown endothermic compound,  $H_2O_4$ , which is formed under the conditions of the experiments. The degree of dissociation of hydrogen and oxygen is discussed, and it is shown that, as a lower limit, the heat of dissociation of hydrogen is probably 150,000 cals., and of oxygen, 160,000 cals. The author has shown that the explosion method can be applied without increased experimental difficulty to initial pressures of more than one atmosphere.

J. F. S.

**The Quantum Effect for Monatomic Gases and Liquids.** A. EUCKEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 682—693).—The formulæ deduced for the heat capacity by application of the theory of quanta vary very considerably, according to whether it is assumed that the energy of the substance at absolute zero is *nil* or is to be represented by a positive quantity. In order to obtain evidence in favour of one or other of these hypotheses, measurements have been made of the specific heats of hydrogen and helium at low temperatures and under different pressures. The observations are distinctly favourable to the theory that the molecules are without energy at absolute zero. This is clearly seen from a diagram, in which the molecular heat  $C_p$  is plotted as a function of the temperature. The two theoretical curves are widely divergent, but the experimental data are represented by points which lie in close proximity to one of the two curves.

H. M. D.

**Determination of the Ratio of the Specific Heats of Chlorine and a Calculation of the Specific Heats by means of Berthelot's Equation of Condition.** JAMES RIDDICK PARTINGTON (*Physikal. Zeitsch.*, 1914, 15, 601—605).—The specific heat ratio was measured by a modification of Kundt's method. Finely divided silica was used to indicate the position of the nodal planes, the definition of which increased in sharpness when the experimental tube was thoroughly dried by heating to a high temperature in a current of dry air. Taking into account the deviation of chlorine from the

requirements of the ideal gas equation, the ratio of the specific heats at  $16^{\circ}$  and one atmosphere is found to be  $1.329 \pm 0.001$ . The molecular heat at constant pressure is  $8.49$ , and at constant volume  $6.39$  cal. These results are compared with the values previously recorded for the specific heat of chlorine. H. M. D.

**Measurement of the Specific Heat of Helium at the Ordinary and at Higher Temperatures.** AUGUST EGGERT (*Ann. Physik*, 1914, [iv], 44, 613—656).—The measurements were made according to Regnault's method, data being obtained for the mean specific heat between the ordinary temperature and  $-15^{\circ}$ ,  $+50$ ,  $100^{\circ}$ , and  $150^{\circ}$ . The results show that the specific heat is practically constant over this range of temperature, the mean value for  $c_p$  being  $1.2662 \pm 0.0011$ . This number gives  $3.01$  for the molecular heat at constant volume, which is in excellent agreement with the theoretical value for a monatomic gas. H. M. D.

**The Thermal Capacity of Metals and [Inter-]metallic Compounds between  $18^{\circ}$  and  $600^{\circ}$ .** PAUL SCHÜBEL (*Zeitsch. anorg. Chem.*, 1914, 87, 81—119).—The specific heats of fifteen metals and eighteen intermetallic compounds have been determined at temperatures up to  $600^{\circ}$ . The specimens are suspended by a platinum wire in a vertical electric furnace, and are allowed to fall into the calorimeter, a device being provided for avoiding loss of heat during the transference. The mean specific heats are thus determined for the intervals from  $18^{\circ}$  to  $100^{\circ}$ ,  $200^{\circ}$ ,  $300^{\circ}$ ,  $400^{\circ}$ ,  $500^{\circ}$ , and  $600^{\circ}$ . The values obtained by former observers are also tabulated. The agreement is, in general, good; the causes of certain divergences are discussed. The differences increase with increasing temperature. Nickel, zinc, and tin exhibit discontinuities corresponding with the known allotropic changes. The true specific heats at intervals of  $100^{\circ}$  have been calculated from the mean specific heats. The metals employed are the same as those examined by Schimpff (A., 1910, ii, 181), gold and silicon being omitted.

The following intermetallic compounds obey the law of Neumann and Kopp within 2%:  $\text{Cu}_2\text{Mg}$ ,  $\text{Cu}_3\text{Al}$ ,  $\text{CuAl}$ ,  $\text{CuAl}_2$ ,  $\text{AgMg}$ ,  $\text{Ag}_3\text{Al}$ ,  $\text{MgZn}_2$ ,  $\text{Co}_2\text{Sn}$ . The specific heat of the compounds  $\text{Ni}_3\text{Sn}$  and  $\text{Ni}_2\text{Mg}$  is too low, and of  $\text{Cu}_3\text{Sb}$  and  $\text{Cu}_5\text{Sb}$  too high. As in Schimpff's results, the specific heat of magnesium compounds is usually lower, and that of antimony compounds higher, than the calculated values. An exception is  $\text{Cu}_2\text{Mg}$ , which at  $500^{\circ}$  has too high a specific heat. The divergences are, for about half the compounds examined, independent of the temperature.

The true atomic heats of both metals and compounds have also been calculated. The curves showing their variation with temperature fall very close together, the curvature being very great between  $-100^{\circ}$  and  $0^{\circ}$ , whilst above  $100^{\circ}$  they are nearly straight, with a few exceptions.

For a number of metals, for which the coefficients of expansion and compressibility are sufficiently well known, the atomic heats

at constant volume have been calculated, certain probable assumptions being made. Aluminium, magnesium, copper, silver, zinc, and antimony give values approaching 5.97, whilst iron, nickel, cobalt, bismuth, tin, and chromium give values considerably exceeding this limit. The requisite data are not available for intermetallic compounds.  
C. H. D.

**Specific Heat of Metallic Alloys Composed of Solid Solutions.** LUIGI ROLLA (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 616—621).—From theoretical considerations, it is deduced that the atomic frequency of a metal in an alloy consisting of a solid solution depends on the concentration of the solution. Corresponding with the melting-point curve there is a curve of atomic frequency for each component. The author has investigated the specific heats of solid solutions consisting of the following alloys: silver-gold, gold-copper, copper-nickel, nickel-manganese, manganese-copper. The specific heats, calculated by means of formulæ based on the principles mentioned above, show agreement between theory and experiment, and, although the agreement is not perfect, it indicates the existence of curves of atomic frequency.

R. V. S.

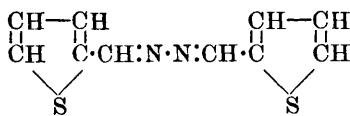
**Atomic Heat and Molecular Homology.** P. LUDWIK (*Zeitsch. Elektrochem.*, 1914, 20, 325—328).—The molecular condition of two substances at absolute temperatures which bear the same relationships to their respective absolute melting points is termed homologous. The molecular homologous condition is considered chiefly in connexion with the atomic heat, and it is shown that the heat required to raise the temperature homologously of unit mass of a substance is very nearly proportional to the quotient of the specific heat and the coefficient of thermal expansion. From this, simple expressions are deduced giving relationships between the melting point, heat of fusion, modulus of elasticity, and atomic concentration. These have the form  $c/\alpha = 50\rho$ ;  $c/\alpha = E_v/\gamma$ ,  $c/\alpha = 1/10RT_s$ , when  $\mu = 1/3$  or  $c/\alpha = 0.3\mu RT_s$ , when  $\mu$  differs from  $1/3$ , in which  $c$  is the specific heat,  $\alpha$  the coefficient of expansion,  $\rho$  the latent heat of fusion,  $E_v$  the volume modulus,  $\gamma$  the specific gravity,  $T_s$  the absolute melting point, and  $\mu$  the Poisson number. Molecular homology is shown to be closely connected with the influence of temperature on the viscosity, the velocity of change of form, and on the processes of recrystallisation of metals which have been distorted cold.  
J. F. S.

**Determination of the Heat of Fusion of  $\text{Li}_2\text{SiO}_3$  and  $\text{Li}_4\text{SiO}_4$ .** ROBERT SCHWARZ and HERMANN STURM (*Ber.*, 1914, 47, 1730—1735).—Using the method described by Plato (A., 1906, ii, 521), and taking sodium chloride as the comparison substance, the authors find the latent heat of fusion of lithium metasilicate to be 80.2 Cal., and that of the orthosilicate 62 Cal. The latent heat of fusion of sodium chloride is taken as 123.5 Cal.

The latent heat could not be determined directly by calorimetric methods.  
T. S. P.

**Relation between the Constitution and the Thermal Properties of Binary Mixtures.** PAUL PASCAL (*Bull. Soc. chim.*, 1914, [iv], 15, 451—464. Compare A., 1913, ii, 292, 304, 1031).—The author has extended this study to mixtures of compounds of the type  $R-\alpha-\beta-\gamma-\delta-R'$ , where  $R$  and  $R'$  are aromatic nuclei, and  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  may be  $\cdot C\cdot$ ,  $\cdot CH\cdot$ ,  $\cdot CH_2\cdot$ ,  $\cdot N\cdot$ , or  $\cdot NH\cdot$ . The compounds studied are those with non-substituted nuclei, and the melting-point curves are given, and the results tabulated for a series of mixtures composed of the following pairs of constituents: (1) diphenylbutadiene and diphenylbutadi-inene; (2) diphenylbutadiene and benzaldazine; (3) diphenylbutadiene and dibenzylhydrazine; (4) dibenzylhydrazine and benzaldazine; (5) benzaldazine and diphenyldiacetylene; (6) benzaldazine and  $\alpha$ -naphthaldazine; (7) benzaldazine and furfuraldazine; (8) furfuraldazine and thiophenaldazine; (9) diphenylbutadiene and cinnamylideneaniline; (10) diphenyldiacetylene and cinnamylideneaniline; (11) benzaldazine and cinnamylideneaniline; (12) diphenylhydrazine and cinnamylideneaniline; (13) diphenylbutadiene and cinnamylidene- $\beta$ -naphthylamine. The following conclusions are drawn. Two symmetrical molecules of the type  $R-\alpha-\beta-\gamma-\delta-R'$  always give a continuous series of mixed crystals unless the aromatic nuclei are not all identical. Asymmetry of structure in the central chain produces isodimorphism. Between these two extreme cases there are a number of examples of isomorphism in the case of compounds the identity and symmetry of nuclear structure of which compensate any slight asymmetry of the central chain. From a study of the curves obtained with mixtures (2), (4), and (5), the author prefers to represent the constitution of benzaldazine by the formula  $CHPh\cdot N\cdot N\cdot CHPh$  rather than by Curtius's formula.

For this work, one new compound has been prepared. *Thiophenaldazine*,



greenish-yellow crystals, m. p.  $156^\circ$ , is prepared by condensing the magnesium derivative of thiophen and orthoformic ester, hydrolysing the acetal formed, and distilling with steam the aldehyde formed into a warm solution of hydrazine sulphate and sodium acetate  
W. G.

**Regularities in the Internal Pressure of Liquids.** W. HERZ (*Zeitsch. Elektrochem.*, 1914, 20, 332—333).—The author has calculated the internal pressure of a number of liquids by means of the formula  $B = L \times 42700 / 2v \times 1033$ , in which  $B$  is the internal pressure in atmospheres,  $L$  the latent heat of vaporisation in calories per gram of the material, and  $v$  the volume in c.c. per gram. Amongst organic liquids, it is shown that for paraffins, benzene homologues, aliphatic saturated alcohols, ketones, aliphatic

esters, and fatty acids the internal pressure decreases with an increasing number of carbon atoms. Acetic and formic acids are exceptional, and this is attributed to the fact that they form double molecules in the vapour phase. Isomeric aromatic liquids have almost the same value, whilst of aliphatic isomerides the normal compound has the higher value. The substitution of hydrogen by chlorine decreases the internal pressure. Analogous compounds of the different halogens have approximately the same value, thus: fluorobenzene, 1540; chlorobenzene, 1500; bromobenzene, 1510; iodobenzene, 1500. Amongst inorganic liquids, relationships are found which are in keeping with the periodic system, thus: chlorine, 2000; bromine, 2780; iodine, 3190; and hydrogen chloride, 2420; hydrogen bromide, 2180; hydrogen iodide, 1950.

J. F. S.

[Chemical Constant of Hydrogen.] VON KOHNER and P. WINTERNITZ (*Physikal. Zeitsch.*, 1914, 15, 645).—A correction of numerical errors in a previous paper (this vol., ii, 429). The several values obtained for the chemical constant of hydrogen by various authors are tabulated.

H. M. D.

**Apparatus for the Measurement of Vapour Pressures by the Dynamic Method and Determinations of the Vapour Pressure of Water at 24·97°.** I. H. DERBY, F. DANIELS, and F. C. GUTSCHE (*J. Amer. Chem. Soc.*, 1914, 36, 793—804).—An apparatus is described for determining vapour pressures by a modification of the air-bubbling method. The saturator consists of two 7·6 cm. bulbs filled with glass pearls of about 4 mm. diameter. These bulbs are connected with each other, and are held in position by a wooden frame, the whole being caused to rotate by means of a small electric motor. A constant temperature is maintained by placing the apparatus in a large electrically heated and regulated water thermostat. An accurate and convenient form of aspirator is employed.

Experiments have shown that by means of this apparatus air can be completely saturated with water-vapour at the rate of at least 50 litres an hour. The value 23·70 mm. was obtained for the vapour pressure of water at 24·97°, and 23·75 mm. at 25·00°. The vapour pressure of alcohol was found to be 58·47 mm. at 25°.

E. G.

**Vapour-pressure Lines of the System Phosphorus.** I. A. SMITS, S. C. BOKHORST, and J. W. TERWEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 1174—1186. Compare A., 1913, ii, 852).—By means of an all-glass manometer of the type described by Jackson (T., 1911, 99, 1066), the authors have measured the vapour pressure of liquid red phosphorus at temperatures between 504° (23·2 atmospheres) and 634° (58·6 atmospheres). The triple point at which solid and liquid red phosphorus co-exist in equilibrium with vapour lies at 589·5°, and at a pressure of 43·1 atmospheres. It has thus been possible to determine the vapour pressure of supercooled

liquid red phosphorus down to  $85^{\circ}$  below the triple point. The experimental data indicate that  $T \log p$  is a linear function of  $T$ , from which it is inferred that the heat of vaporisation is practically independent of the temperature over the range covered by the experiments. The value obtained for the heat of vaporisation from Clausius' formula is 9.96 cal.

The vapour pressure of liquid white phosphorus has also been measured at temperatures ranging from  $169^{\circ}$  (0.039 atm.) to  $366.4^{\circ}$  (9.56 atm.). At temperatures above  $280^{\circ}$ , the glass manometer method was found to be unsatisfactory, on account of the conversion of the white phosphorus into red phosphorus; much better results were obtained at the higher temperatures by the use of a modified form of isotenscope (Smith and Menzies, A., 1910, ii, 1036). The experimental data do not give a straight line when  $T \log p$  is plotted against  $T$ . This indicates that the heat of vaporisation is a function of the temperature. H. M. D.

**Measurement of Small Pressures by means of a Swinging Quartz Filament. Determination of the Vapour Pressure of Mercury and Iodine.** F. HABER and F. KERSCHBAUM (*Zeitsch. Elektrochem.*, 1914, 20, 296—305).—A quartz thread is attached by one end to the top of a vessel in which the measurements are to be made, and the other end left free. The method of determination of the pressure consists in starting the thread swinging by means of a gentle tap, and measuring the time required for the amplitude of its swing to fall to one-half the original value. The amplitude of the swinging thread is observed through a telemicroscope with a graduated scale in the eye-piece. The pressure is then calculated by means of the formula  $b = \{\Sigma(pM^{\frac{1}{2}}) + a\}t$ , in which  $p$  is the pressure of one of the gases present,  $M$  its molecular weight,  $t$  the time required for the amplitude to fall to half value, and  $a$  and  $b$  constants which are dependent on the thickness and elasticity of the filament and on the temperature. The values of  $a$  and  $b$  were determined experimentally in air, oxygen, and hydrogen at known small pressures for threads 9 cm. and 7 cm. long, and 0.037 cm., 0.020 cm., and 0.013 cm. diameter. The vapour pressure of mercury at room temperature was found to be 0.00126 mm. of mercury, and that of iodine to be 0.009 mm. at  $-9.7^{\circ}$ , 0.0025 mm. at  $-20.7^{\circ}$ , 0.00088 mm. at  $-28.9^{\circ}$ , 0.00056 mm. at  $-32.3^{\circ}$ , 0.000084 mm. at  $-46.3^{\circ}$ , and 0.000057 mm. at  $-48.3^{\circ}$ . The theory of the method is worked out, and the necessary working directions are given in the paper.

J. F. S.

**Evaporation of Slightly Superheated Liquids and Solids.** R. MARCELIN (*Compt. rend.*, 1914, 158, 1419—1421. Compare *ibid.*, 1912, 154, 587).—A study of the rate of evaporation of liquids or solids, slightly superheated, or, better, kept in the presence of their vapour, and at a pressure differing from the equilibrium pressure by 5—6 mm. at the most. The substance to be studied is distilled, first, into a very thin glass tube, 0.1—0.3 mm. in

diameter, connected to a large condensing chamber containing some of the liquid under examination, in which has been dissolved a sufficient amount of a second substance to lower its vapour pressure by 5—6 mm. at the most. The whole apparatus is then maintained at a constant temperature, and the rate of evaporation in the glass tube measured by observing the fall in level of the liquid. Measurements were made for nitrobenzene, naphthalene, and iodine at temperatures ranging from 40° to 70°, the vapour pressures in these cases being so low that it was sufficient to maintain a vacuum in the condensing chamber. W. G.

**Exchange of Matter between a Liquid or a Solid and its Saturated Vapour.** R. MARCELIN (*Compt. rend.*, 1914, 158, 1674—1676).—A mathematical discussion of the subject. Taking the velocities of evaporation in a vacuum previously obtained for nitrobenzene, naphthalene, and iodine (compare preceding abstract), the author has calculated for these cases, at different temperatures, the number of gaseous molecules touching the liquid or solid before one is held. The results show that the fixation of matter by the condensed phase from its vapour is less important the lower is the temperature, and that it is possible that, in the cold, all the molecules of vapour rebound from the condensed phase, and that, on the contrary, at higher temperatures they are almost all fixed. Further, that, under comparable conditions, the exchanges of matter between condensed phase and vapour are more intense in the case of a liquid than in the case of a solid. W. G.

**Determination of the Critical Temperature of the Haloids of Aluminium and Antimony.** L. ROTINJANZ and W. SUCHODSKI (*Zeitsch. physikal. Chem.*, 1914, 87, 635—637. Compare this vol., ii, 428).—Using the same method as previously adopted (*loc. cit.*), the authors have determined the critical temperature of the halogen derivatives of antimony and aluminium, and have obtained the following values:  $\text{AlCl}_3$ , 629.5°;  $\text{AlBr}_3$ , 772°;  $\text{AlI}_3$ , 955°;  $\text{SbCl}_3$ , 797°;  $\text{SbBr}_3$ , 904.5°; and  $\text{SbI}_3$ , 1101°. Except in the case of antimony tri-iodide, these values have a possible error of  $\pm 0.5^\circ$ ; in the case of antimony iodide, owing to the difficulty of observing the meniscus on account of the non-transparent nature of the vapour, a possible error of  $\pm 3^\circ$  is attached to the value given. The values of  $T_s/T_k$  are calculated in all cases; the values 0.724, 0.690, 0.652, 0.622, 0.613, and 0.614 are obtained for the salts taken in the order given above. J. F. S.

**Thermodynamical Theory of Ternary Mixtures.** S. A. SHORTER (*Phil. Mag.*, 1914, [vi], 27, 942—963. Compare A., 1912, ii, 24, 437; 1913, ii, 115).—The thermodynamical theory of certain two-phase ternary systems is considered. The thermodynamic relations indicate that the further addition of one component raises the chemical potential of that component, and may either raise or lower the potential of a second component. If the further addi-



tion of a component *A* raises (lowers) the potential of *B*, then the further addition of *B* raises (lowers) the chemical potential of *A*. If these two components mutually increase each other's potentials, any other two components must cause a mutual lowering. These three statements hold good if partial pressure is substituted for chemical potential.

In addition to the equilibrium between liquid and vapour phases, the theory is applied to the solubility influence, to the partition equilibrium in a two-phase liquid system, to the osmotic equilibrium for the case where the membrane is permeable to one compound only, and to the freezing of ternary mixtures.

H. M. D.

**Thermochemistry and the Periodic Law. Heats of Combination are Linear Functions of the Atomic Weights of Related Elements.** W. G. MIXTER (*Amer. J. Sci.*, 1914, [iv], **37**, 519—534).

—For elements which belong to certain of the horizontal series of the periodic table, the quantities of heat which are developed in the combination of 16 grams of oxygen or 71 grams of chlorine are approximately linear functions of the atomic weights.

For elements which belong to the sub-groups, the heat changes vary more regularly than they do in a horizontal series. The thermal data for the three members of the sub-groups which contain elements of the third, fifth, and seventh, or the fourth, sixth, and eighth series, indicate that the heat of formation of the oxide is either a linear function of the atomic weight or that the heat change for the middle member falls below the linear value by an amount which is constant if referred to one atom of oxygen.

H. M. D.

**Measurement of the Heat of Formation of Lead and Silver Haloids and its Application to the Verification of Nernst's Theorem of Heat.** H. BRAUNE and F. KOREF (*Zeitsch. anorg. Chem.*, 1914, **87**, 175—197. Compare Koref and Braune, A., 1912, ii, 1041).—The heat of formation now obtained for lead chloride is 85,700 cal., and for lead bromide 66,350 cal.

Using crystalline silver iodide, with potassium cyanide solution as the solvent, the heat of formation of silver iodide is found to be 15,100 cal., and of silver chloride 30,410 cal.

The heat of formation of lead iodide has been determined by the electromotive-force method to be 41,960 cal., in good agreement with the calorimetric value 41,850 cal.

By utilising the values obtained in this and previous investigations, it is shown that the differences between the observed heat changes and those calculated from Nernst's theorem fall within the limits of experimental error, thus affording a complete confirmation of the theorem.

C. H. D.

**Some Hydrates of Carbonylferrocyanides and their Heats of Formation.** J. A. MULLER (*Bull. Soc. chim.*, 1914, [iv], **15**, 491—494).—Potassium carbonylferrocyanide separates from

aqueous solution with  $3\frac{1}{2}\text{H}_2\text{O}$ , which are lost at  $120^\circ$ . The sodium salt,  $\text{Na}_3\text{FeCO}(\text{CN})_5 \cdot 7\text{H}_2\text{O}$  (instead of  $6\cdot2\text{H}_2\text{O}$  previously given), loses  $5\text{H}_2\text{O}$  when exposed to dry air at  $18^\circ$ , and is completely dehydrated at  $130^\circ$ . The *barium* salt,  $\text{Ba}_3[\text{FeCO}(\text{CN})_5]_2 \cdot 11\text{H}_2\text{O}$ , prepared by neutralising the acid or from the copper salt, loses  $10\text{H}_2\text{O}$  in a vacuum at  $19^\circ$ , and gives the anhydrous salt at  $130^\circ$ . The similarly prepared *strontium* salt forms a hygroscopic, yellow, crystalline powder, which, after being dried in a vacuum at  $15^\circ$ , has the formula  $\text{Sr}_3[\text{FeCO}(\text{CN})_5]_2 \cdot 4\text{H}_2\text{O}$ ; it is only completely dehydrated at about  $200^\circ$ .

The heats of solution of the anhydrous salts and of the hydrates in water at temperatures in the neighbourhood of  $15^\circ$  have been determined, with the following results, expressed in Calories per gram-molecule: sodium salt (anhydrous),  $+4\cdot8$  Cal.,  $(+7\text{H}_2\text{O})$ ,  $-7\cdot5$  Cal.; potassium salt (anhydrous),  $-5\cdot2$  Cal.,  $(+3\cdot5\text{H}_2\text{O})$ ,  $-10\cdot9$  Cal.; strontium salt (anhydrous),  $+39\cdot9$  Cal.,  $(+4\text{H}_2\text{O})$ ,  $+32\cdot4$  Cal.; barium salt (anhydrous),  $+16\cdot9$  Cal.,  $(+11\text{H}_2\text{O})$ ,  $-6\cdot9$  Cal. From these data, the following heats of hydration are calculated:  $\text{Na}_3\text{FeCO}(\text{CN})_5 \cdot 7\text{H}_2\text{O}$ ,  $+12\cdot3$  Cal.,  $t=15\cdot9^\circ$ ;  $\text{K}_3\text{FeCO}(\text{CN})_5 \cdot 3\cdot5\text{H}_2\text{O}$ ,  $+5\cdot7$  Cal.,  $t=18\cdot0^\circ$ ;  $\text{Sr}_3[\text{FeCO}(\text{CN})_5]_2 \cdot 4\text{H}_2\text{O}$ ,  $7\cdot5$  Cal.,  $t=13\cdot3^\circ$ ;  $\text{Ba}_3[\text{FeCO}(\text{CN})_5]_2 \cdot 11\text{H}_2\text{O}$ ,  $23\cdot8$  Cal.,  $t=17\cdot5^\circ$ . Further, the heats of combination of the anhydrous salts with ice at  $0^\circ$  are calculated to be  $1\cdot30$  Cal.,  $0\cdot13$  Cal.,  $1\cdot30$  Cal., and  $6\cdot34$  Cal. respectively for the sodium, potassium, barium, and strontium salts. From these values, the heat of combination of the anhydrous salts with water at  $0^\circ$  is calculated by the addition of  $1\cdot43n$  Cal., where  $n$ =the number of molecules of water in the hydrate.

H. W.

**Heats of Formation of Certain Normal Carbonylferrocyanides from their Elements.** J. A. MULLER (*Bull. Soc. chim.*, 1914, [iv], 15, 494—497).—The heats of formation of certain normal carbonylferrocyanides from their elements have been calculated from the heat of combustion of hydrated carbonylferrocyanic acid (A., 1906, ii, 525), its heat of solution in water and neutralisation by the bases, together with the heats of solution of the anhydrous carbonylferrocyanides (compare preceding abstract) and of formation of the corresponding metallic oxides in solution. The following heats of formation at constant volume are given:  $\text{Na}_3\text{FeCO}(\text{CN})_5$ ,  $123\cdot5$  Cal.;  $\text{K}_3\text{FeCO}(\text{CN})_5$ ,  $140\cdot8$  Cal.;  $\text{Sr}_3[\text{FeCO}(\text{CN})_5]_2$ ,  $254\cdot0$  Cal.;  $\text{Ba}_3[\text{FeCO}(\text{CN})_5]_2$ ,  $254\cdot0$  Cal.

The heat of hydration of carbonylferrocyanic acid cannot be directly determined, since the anhydrous substance has not yet been obtained. If, however, it is admitted that the value approximates to that of the addition of  $1\text{H}_2\text{O}$  to the molecule of a neutral carbonylferrocyanide, the heat of formation of the anhydrous acid from its elements is calculated to be  $-53\cdot7$  Cal. at constant volume.

From the results, it appears that the replacement of the group  $:\text{C}:\text{NH}$  in hydroferrocyanic acid by  $:\text{CO}$  is without marked influence on the energy of the hydrogen atoms remaining in the molecule.

H. W.

**New Thermo-regulator.** M. TALIANI (*Ann. Chim. Applicata*, 1914, 1, 405—408).—Two bimetallic zinc-steel vertical strips are fixed at their lower ends with the more expansive metals facing inwards. The free upper ends are connected by means of a very thin copper wire, on the middle point of which rests the valve regulating the flow of gas to the lamp of the thermostat. The valve is raised by the separation of the strips and lowered by their approach. This apparatus gives a very high degree of constancy of temperature, even when the pressure of the gas-supply varies very considerably.

By means of a slider operated from without, the effective lengths of the strips, and consequently the constant temperature obtained, may be varied. T. H. P.

**Thermo-regulator for Electrically Regulated Constant Temperature Chambers.** H. H. BUNZEL and H. HASSELBRING (*J. Amer. Chem. Soc.*, 1914, 36, 949—951).—An adjustable thermo-regulator is described which has proved very satisfactory, and can be used for any electrically controlled constant-temperature chamber. It consists of a main bulb, the form of which can be varied according to requirements, and a capillary stem provided with a small auxiliary bulb connected with the upper part of the stem by a capillary neck. The main bulb is filled with mercury, and a small quantity of mercury is also placed in the auxiliary bulb. A platinum wire is sealed into the main bulb and another into the stem. When the mercury expands and reaches the latter wire, the current passes and actuates a relay. The regulator can be adjusted by shaking a little mercury from the auxiliary bulb into the stem, or from the stem into the bulb. In order to avoid sparking, the regulator must be used with a current not exceeding 0.01 ampere. The heating current must not be passed through the apparatus. E. G.

**The Critical Density for Associating Substances.** J. D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 1076—1081).—A theoretical paper in which it is shown that the ratio of the critical density to the density calculated from the ideal gas equation has in all probability the same value for associated as for normal non-associated substances. H. M. D.

**Study of the Limit of Some Reactions by means of the Hydrostatic Balance.** JULES ROUX (*Compt. rend.*, 1914, 158, 1506—1508).—The author has used a quartz float, weighted with mercury, to study various physical and chemical changes, by measuring small changes in density of a liquid. The method has been successfully applied to a study of the solubility of sodium sulphate in water, and the neutralisation of a monobasic acid, hydrochloric acid, and a tribasic acid, phosphoric acid, by a base. In the latter case, the three stages corresponding with the formation of the three salts are indicated on the curve. W. G.

**Compressibility of Methyl Chloride.** E. BODAREU (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 491—493).—From his measurements the author finds that the value of the product  $pv$  at  $16.8^\circ$  varies from 1.0000 at 760 mm. to 0.9335 at 2800 mm. R. V. S.

**Theory of Molecular Volumes. III.** GERVAISE LE BAS (*Phil. Mag.*, 1914, [vi], 27, 976—990. Compare this vol., ii, 173, 340).—From a comparison of the molecular volumes of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -substituted straight-chain paraffin hydrocarbons, it is found that if the hydrocarbon has more than one hydrogen atom replaced by a halogen or other unsaturated substituent, the volume of the compound is subject to the additive rule if the substituents are attached to a single carbon atom. If, however, the substituents are distributed amongst several carbon atoms, the volume is less than that required by the additive rule. For one substitution in the  $\beta$ -position, the contraction is a little more than 3.0 units; for two substitutions in the  $\beta$ -position the contraction is nearly twice as great. Substitution in the  $\gamma$ -position involves a greater contraction than the corresponding substitution in the  $\beta$ -position. The substituents Cl, Br, I, OH, and probably  $\text{NH}_2$  and  $\text{CO}_2\text{H}$ , all produce similar effects, but doubly bound oxygen is anomalous in its behaviour.

From a comparison of the volumes of ortho-, meta-, and para-disubstituted benzene compounds, it is found that contraction always occurs in the ortho-compounds; a slight contraction is also found in the meta-compounds, whereas the para-compounds conform to the additive law. The behaviour of ring compounds is therefore quite different from that exhibited by the corresponding open-chain compounds.

An explanation of the constitutive effects is offered which is based on the theory of residual affinity. H. M. D.

**Turbulence Viscosity.** WALTHER SORKAU (*Physikal. Zeitsch.*, 1914, 15, 582—587. Compare A., 1911, ii, 793; 1912, ii, 900; 1913, ii, 301).—New experiments have been made with a capillary tube provided with gradually expanding conical ends. In this way, the author has sought to determine to what extent the previous results are dependent on the special form of the experimental arrangement.

From observations made on ethyl acetate, chloroform, acetone, and ethyl ether at different temperatures, it is found that the turbulence viscosity changes in character when the pressure reaches a certain magnitude. For the lower range of pressure, the connexion between the pressure  $p$  and the time of flow  $t$  of a given volume of liquid through the capillary is given by the equation  $p^{0.63} \cdot t \cdot e^{\theta/273} = k$ , where  $\theta$  is the absolute temperature. For ethyl ether  $k=98.2$ , acetone 112.4, ethyl acetate 129.1, chloroform 164.3. For the connexion between  $p$  and  $t$  at higher rates of flow, the experimental data are in agreement with the equation  $p^{\frac{1}{3}} \cdot t = C$ , where for ethyl ether  $C=37.71$ , acetone 39.05, ethyl acetate 41.0, chloroform 52.65. The constant  $C$  is related to the density  $D$  of

the liquid by the equation  $C=43.57D^{\frac{1}{2}}$ . The equation for frictionless flow of the liquid through the capillary may therefore be written in the form  $t=43.57\sqrt{D/p}$ . H. M. D.

**The Viscosity and Density of Some Molten Metals and Alloys.** RAGNAR ARPI (*Intern. Zeitsch. Metallographie*, 1914, 5, 142—168).—Using a long silica viscometer of special design, maintained at a constant temperature in an electric furnace, the viscosity of molten lead, tin, bismuth, cadmium, and mercury has been determined at various temperatures. The viscosities at a given temperature are of the same order, and the greater the viscosity the more rapidly does it diminish with falling temperature. The temperature-coefficient is less for bismuth than for any of the other metals. The viscosity increases with the melting point. Lead and cadmium have nearly the same melting point, and lead, having the higher atomic weight, has the greater viscosity.

With alloys of lead and tin, the viscosity is very nearly an additive property, but is always slightly less than that calculated from the composition by volume. The deviation is greater in the alloys of lead and bismuth, and the temperature-coefficient is in this case less than that of the pure metals.

The density of some of the molten metals and alloys has been determined in a silica pycnometer. The density of the alloys of lead and tin, and of lead and bismuth, is almost exactly that calculated from the composition by volume. C. H. D.

**Soaps. The "Glue-forming" Capacity of Potassium Laurate, Potassium Oleate, and their Mixtures.** J. KURZMANN (*Koll. Chem. Beihefte*, 1914, 5, 427—484).—Measurements have been made of the viscosity and electrical conductivity of aqueous solutions of the potassium salts of lauric, myristic, and oleic acid, and also of the potassium soap prepared from palm oil. The recorded data show the influence of concentration and temperature on the viscosity and conductivity, and also the change which is brought about by the addition of potassium hydroxide and potassium carbonate to the soap solutions.

The curves obtained by plotting the viscosity against the concentration show a marked difference in the behaviour of solutions of potassium laurate and oleate at the ordinary temperature. This difference is mainly determined by the extremely rapid increase of viscosity with concentration which is shown by the oleate when the concentration reaches 0.4 mol. per litre. Solutions of the oleate of 0.4 to 0.5 molar concentration are characterised by a high viscosity temperature-coefficient as compared with the value found for corresponding solutions of the laurate. The viscosity of solutions of potassium myristate is intermediate in value, and, in general, the behaviour of the solutions approximates to that of corresponding solutions of the laurate.

The addition of small quantities of potassium laurate to solutions of the oleate causes an increase in the viscosity at 90° and a decrease at 20°. The viscosity of the oleate solutions is also

diminished by the addition of small quantities of potassium hydroxide, whereas larger quantities increase the viscosity. The oleate solutions are more sensitive to the influence of the hydroxide than are solutions of the laurate. The curves showing the relation between the molar conductivity and the concentration are similar to those obtained by McBain for the sodium soaps (A., 1910, ii, 177). Addition of potassium hydroxide or carbonate lowers the conductivity of the soap solutions, and the abnormally high value of the temperature-coefficient is thereby reduced very considerably. The conductivity of a mixture of laurate and oleate is greater than the sum of the conductivities of the components, this increase being more marked at the lower temperatures. H. M. D.

**Adsorption in Solutions. VII. Kinetics of Sorption.** G. VON GEORGIEVICS and A. DIETL (*Zeitsch. physikal. Chem.*, 1914, **87**, 669—691; *Monatsh.*, 1914, **35**, 643—675).—The sorption of acids by wool from aqueous solutions has been investigated at 20° for nitric, hydrochloric, hydrobromic, sulphuric, phosphoric, formic, acetic, propionic, butyric, oxalic, succinic, and salicylic acids. The object of the experiments was to determine the relationships existing between: (1) the velocity of sorption and concentration of the acids; (2) the velocity of sorption and the coefficient of diffusion; (3) the velocity of sorption and temperature; and (4) the velocity of the reverse process with dilution. It is shown that sorption by wool takes place more rapidly in concentrated solutions than in dilute solutions, and generally the influence of concentration runs parallel with the  $x$  value of the acid. The influence is greatest with the strong mineral acids, which possess the largest  $x$  value, and smallest with the monobasic fatty acids, which have the smallest  $x$  values. These form a transition to those gases which are adsorbed by charcoal with a velocity which is uninfluenced by pressure, and consequently the process is to be regarded as a pure diffusion. The sorption of acids by wool is therefore, in the main, a diffusion process, and in those cases where the  $x$  value is small, most nearly a diffusion process pure and simple. This confirms kinetically the sorption theory of Georgievics (A., 1912, ii, 140), which states that sorption is a process which consists of adsorption, and solution in the adsorbent, and that the relationship between the two processes is expressed in the  $x$  value of the adsorbed substance. In one and the same group of acids the velocity-coefficient of sorption runs parallel with the diffusion-coefficient, and, as is to be expected, this relationship is most clearly shown in the fatty acid series. The temperature-coefficient for the sorption of acetic acid and hydrochloric acid is 1.5, and consequently in these two cases the process is to be regarded more as a diffusion than as a chemical process. The coefficient is somewhat larger than that for a simple diffusion, since alongside the adsorption there is also the formation of solid solutions. On dilution of a solution which is in equilibrium with wool in the case of acetic, oxalic, hydrochloric, and sulphuric acids, it is shown that the new equilibrium is set up almost

instantaneously. It is shown that the statement generally made in the literature, that sorption occurs very rapidly, is incorrect. The velocity of sorption is very different in different cases, and is strongly influenced by temperature and concentration. Thus, in the case of sorption of dyes by fibres, the equilibrium is sometimes only reached after weeks.

J. F. S.

**Adsorption.** DORA SCHMIDT-WALTER (*Kolloid. Zeitsch.*, 1914, **14**, 242—252).—Experiments have been made on the adsorption of iodine and acetic acid by charcoal from solutions of these substances in various solvents.

Contrary to the observations of Davis (T., 1907, **91**, 1666), it is found that equilibrium is rapidly attained in the case of benzene solutions of iodine. With carbon disulphide solutions, on the other hand, the fall in concentration continues for weeks, and this is attributed to decomposition of the carbon disulphide under the catalytic influence of the charcoal, the sulphur thus liberated combining with the iodine. The slow adsorption observed by Davis with benzene solutions is also supposed to be due to chemical change under the catalytic influence of some impurity in the carbon or of light. No evidence has been obtained which may be interpreted in support of the view that the slow adsorption is due to the formation of a solid solution.

The author's data for the adsorption of iodine from solutions in hexane, carbon disulphide, methyl alcohol, ethyl alcohol, chloroform, and aqueous potassium iodide, and for the adsorption of acetic acid from its solutions in water, benzene, and toluene (concentration < 5%), are found to be in satisfactory agreement with the adsorption formula given by Schmidt (A., 1911, ii, 969). The constants  $A$  and  $S$  in this formula are shown to be independent of the nature of the solvent in which the adsorbed substance is dissolved.

In concentrated benzene and toluene solutions, the adsorption of acetic acid by charcoal appears to be negative, but this is probably due to the simultaneous adsorption of the solvent, the magnitude of which cannot be determined.

H. M. D.

**Influence of Certain Non-electrolytes on the Swelling of Protein.** MARTIN H. FISCHER and ANNE SYKES (*Kolloid. Zeitsch.*, 1914, **14**, 215—223).—Comparative measurements have been made to determine the swelling of gelatin plates in pure water and in aqueous solutions of sucrose, lævulose, dextrose, methyl alcohol, propyl alcohol, propylene glycol, and acetone. The relations are exhibited in the form of curves obtained by plotting the increase in weight of the gelatin as a function of the time.

In all cases, the presence of the non-electrolyte reduces the swelling of the gelatin, and the effect increases with increasing concentration of the non-electrolyte. For the same molar concentration, sucrose has a much greater influence on the swelling than lævulose and dextrose. These two substances are approximately equal in their action, and this activity differs but little from that of the four other substances examined.

Similar experiments on the swelling of fibrin indicate that non-electrolytes exert the same influence as in the case of gelatin. Since animal and vegetable tissues appear to be affected in exactly the same manner as the simple proteins, it is probable that the swelling and contraction phenomena are closely analogous.

H. M. D.

**Action of Solutions of Glauber's Salt on Wool.** M. FORT (*J. Soc. Dyers*, 1914, 30, 228—231).—A reply to the criticism of Herz and Barraclough (this vol., ii, 346) relative to neutral salt reactions and the action of sodium sulphate in the dyeing of wool. Tintometric measurements of the effect of sodium sulphate on wool dyed with sodium picrate and azofuchsine-B show that the sulphate increases the intensity of the colour.

Comparative observations, in which purified wool was subjected to the action of distilled water and of sodium sulphate solutions, give further support to the view that the wool substance reacts with the sodium sulphate.

H. M. D.

**Theory of Gas Dissociation.** OTTO STERN (*Ann. Physik*, 1914, [iv], 44, 497—524).—A theoretical paper in which the equilibrium between ideal gases, represented by the general formula  $AB \rightleftharpoons A + B$ , is submitted to detailed examination. It is shown that the equilibrium constant which is deduced from thermodynamical considerations and the theory of quanta is identical with the constant derived from the application of the molecular theory. The formulæ are applied to the equilibrium in the system  $I_2 \rightleftharpoons I + I$  for which the requisite experimental data are available.

The significance of Nernst's heat theorem in terms of the molecular theory is also discussed.

H. M. D.

**The Diffusion-coefficient of Gases and the Viscosity of Gas Mixtures.** J. P. KUENEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 1162—1166).—A theoretical discussion of the process of diffusion in mixed gases in which the influence of the mutual attraction of the molecules is taken into account. The theory is also applied to the consideration of the viscosity of mixtures of gases, and it is shown that the maximum viscosity observed with mixtures of carbon dioxide and hydrogen, and of argon and helium, can be explained in terms of the intermolecular attraction.

H. M. D.

**Ideal Diffusion-coefficient and a Fundamental Law Concerning the Diffusion of Dissolved Substances in Liquids.** GEORGE MCP. SMITH (*J. Amer. Chem. Soc.*, 1914, 36, 847—864).—If the diffusion-coefficients,  $D$ , determined at a given temperature with dilute solutions of substances which do not ionise or present other complications, are divided by the molecular weights of the respective substances, special diffusion-coefficients,  $D/M$ , are obtained. The ideal diffusion-coefficient,  $D/M=1$ , indicates the



number of mols. of a compound which in unit cross-section would pass in unit time through the unit molal concentration interval with unit velocity, provided that each molecule of the compound, whilst retaining its size, configuration, and free-path velocity, had its momentum reduced to the reciprocal value.

This ideal diffusion-coefficient has been applied to the diffusion of dissolved substances in water with the aid of Öholm's data (A., 1910, ii, 273; 1913, ii, 564). By plotting the logarithms of the values of the ideal diffusion-coefficient as ordinates, and those of the molecular weights as abscissæ, the curve obtained is a straight line. The graph of this straight line is represented by the equation  $\log I + n \log M = \log K$ , in which  $K$  is a constant and  $n$  the slope of the line. From this a new fundamental law of diffusion is obtained, which is represented by the formula  $IM^n = K$ .

The ideal diffusion-coefficient is also considered in relation to the diffusion of gases through water, and to the diffusion of metals in mercury. The analogy between the equation  $IM^n = K$  and the equation  $pv^v = \text{const.}$  for the polytropic expansion of gases is demonstrated.  
E. G.

#### Extension of the Dilution Law to Concentrated Solutions.

JAMES KENDALL (*J. Amer. Chem. Soc.*, 1914, **36**, 1069—1088).—In an earlier paper (T., 1912, **101**, 1275) it was pointed out that Ostwald's dilution law is not obeyed exactly by various acids, even in very dilute solutions, and an equation was suggested which is applicable to the dissociation of all acids, and is intermediate between the dilution law and van't Hoff's formula. In a study (this vol., ii, 93) of more concentrated solutions of acids, it was found that this new equation does not apply to such cases. The results of a further investigation of concentrated solutions are given in the present paper.

A modified form of the dilution law is proposed which has been found to apply in concentrated solutions of weak electrolytes, and is represented by the equation  $c^2_i/c_u \cdot c_s = K$ , where  $c_s$  is the concentration of solvent in the solution. This law is based on the assumption that the dissociation of the molecule  $RX$  into its ions  $R'$  and  $X'$  takes place, not spontaneously, but by impact with the molecules of the solvent. By means of this hypothesis, the dilution law has been derived from thermodynamical considerations, and is found to be simpler than the original form of the law, and applicable to both dilute and concentrated solutions. On comparing and combining the results of the work with those of Walden (*J. Amer. Chem. Soc.*, 1913, **35**, 1649), a simple view of the mechanism of the ionisation equilibrium has been obtained. It is shown that the dissociating power of the solvent molecules is to be ascribed to their unsaturated character, or, in other words, to the presence of free valences.  
E. G.

**Dilatation of Solutions.** B. CABRERA (*Anal. Fis. Quim.*, 1914, **12**, 284—295).—The densities and dilatations of solutions of the chloride, sulphate, and nitrate of nickel are given. The quantity

of salt dissolved in 1 gram of the solution may be expressed by the formulæ:

$$1.0547(D_s - D_{aq})_{15^\circ} - 0.557(D_s - D_{aq})_{15^\circ}^2 \text{ for the chloride ; } 0.9519(D_s - D_{aq}) \\ - 0.559(D_s - D_{aq})_{25^\circ}^2 \text{ for the sulphate, and} \\ 1.1853(D_s - D_{aq}) - 0.765(D_s - D_{aq})_{15^\circ}^2$$

for the nitrate.

G. D. L.

**A Method of Inducing Spontaneous Crystallisation.** G. TAMMANN (*Zeitsch. anorg. Chem.*, 1914, 87, 248—252).—The temperature at which the spontaneous crystallising power of a glass is a maximum is generally unknown, and is found by a tedious method of trial. By establishing a temperature gradient, however, the temperature is readily found, provided that it falls within the limits adopted. A rod of glass, or a column of undercooled liquid, is exposed to a graded temperature, and the point at which the spontaneous crystallising power is a maximum is indicated by the appearance of a turbidity, which gradually extends in both directions, and is followed by the appearance of visible crystals.

A mixture of boron trioxide (66%) and borax (34%) placed in a boat, and so heated that one end is at 750° and the other at atmospheric pressure, shows a spherulite in four hours at a point corresponding with 700°. Potassium metasilicate containing some potassium carbonate has also been induced to crystallise in the same way.

C. H. D.

**Contact Phenomena in Crystallisation.** P. A. ZEMIATTSCHENSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1914, 541—554).—The author has investigated the habit of crystals of potassium iodide deposited in contact with cleavage fragments of mica, gypsum, calcite, quartz, topaz, fluorspar, barytes, orthoclase, and chlorite, and gives reproductions of photographs of the forms obtained.

T. H. P.

**Polymorphism.** FRED. WALLERANT (*Compt. rend.*, 1914, 158, 1473—1474).—Experimental details are given with respect to the polymorphism of a number of substances.

Malonic acid is trimorphic, the stable form at the ordinary temperature being triclinic. On heating at 94°, it passes to a less birefractive monoclinic form. On cooling this form, crystalline superfusion occurs, and a third form, unstable at all temperatures, appears.

Monochlorocamphor crystallises at the ordinary temperature in a monoclinic form, and on heating to 70° these crystals are transformed into the cubic system. The process is reversible, rapid, and unaccompanied by superfusion or superheating.

Benzyl cinnamate in the molten state, on cooling by ethyl chloride, gives monoclinic, lozenge-shaped crystals, quasi-ternary and positive, which are unstable at all temperatures. These are followed by a spherulitic form, biaxial and birefractive, which is stable.

Benzaldoxime, when superfused, on cooling with ethyl chloride yields unstable, biaxial, very birefractive crystals, which melt when

the temperature rises. It is only after solution that the stable, biaxial, positive crystals are obtained.

The stable form of phenyl *p*-tolyl ketone is quasi-uniaxial and negative. The unstable form, obtained by superfusion, is biaxial and positive. The two forms can remain in contact a comparatively long time.

The stable form of trinitro-*m*-cresol is dichroic, biaxial, and negative, whilst the unstable form is biaxial, positive, and less birefractive. The two forms appear at the same time in the super-fused liquid, and can grow in contact with one another at the ordinary temperature.

W. G.

**The Metastable Continuation of the Mixed Crystal Series of Pseudo-components in Connexion with the Phenomenon of Allotropy.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1167—1173).—The equilibria in pseudo-binary systems are further considered, with special reference to the case in which the pseudo-components are isodimorphous.

H. M./D.

**Liquid Crystals and Biology.** O. LEHMANN (*Biochem. Zeitsch.*, 1914, **63**, 74—86).—An historical account of the author's discovery of liquid crystals is given. It is pointed out that there is a difficulty in reconciling the properties of such organisms as amoeba with the idea that they consist of purely amorphous material. Perhaps under the influence of a stimulant a local or transitory anisotropic form may be produced.

It is significant that such substances as protagon, lecithin, cholesterol esters and oleates, which are present in brain, nerves, etc., all form liquid crystals. In all probability, other constituents of living material can exist in this phase, since the double refraction, by means of which the fluid crystals are detected, is always slight, and may be so small as to escape detection.

Attention is drawn to the resemblances between the behaviour of so-called myelin forms and that of living material. A comparison is made between the production of energy in living matter and the development of mechanical energy in a liquid crystalline medium through the action of a molecular directive force.

E. H. R.

**A Thymol-Menthol-Emulsoid in Glycerol.** JOHN DON (*Kolloid. Zeitsch.*, 1914, **14**, 253—255).—If glycerol, thymol, and menthol are mixed together in the ratio 40:2:1 at 80°, a two-phase liquid system is obtained. If this is violently agitated for a short time, an opalescent emulsoid is formed. The dispersive medium consists of glycerol containing about 2% of thymol, whilst the disperse phase consists of minute drops of menthol and the residual thymol. At the end of a week the larger drops have separated and formed a second liquid layer, but the remaining milky liquid appears to be quite stable.

The relations between the viscosities of the emulsoid and of

glycerol, and between the surface tensions of the disperse phase and the dispersive medium, are discussed. H. M. D.

**Diagrammatic Co-ordination of Phenomena Relating to Aggregation of Sols.** GEORGE STANLEY WALPOLE (*Biochem. J.* 1914, 8, 170—192).—A method is given by which the phenomena associated with the coagulation of mixtures of sols and electrolytes can be diagrammatically co-ordinated. This method is applied to the observations made on oil and mastic sols in the presence of gelatin and hydrochloric acid.

In the presence of a small amount of gelatin, mastic and oil sols are coagulated by the addition of a trace of acid, which has no action on the sol in the absence of gelatin. The same quantity of gelatin protects the sol against the coagulating action of hydrochloric acid, which is several thousand times more concentrated. This coagulation effect may be observed equally well with gold sols, and in all cases it is reversible.

The data obtained for mastic-gelatin sols containing hydrochloric acid indicate that there are two critical mixtures which are on the verge of flocculation. These differ very considerably in regard to the hydrion concentration, and the particles in the one mixture are negatively charged, in the other positively. On addition of small quantities of sodium chloride or acetate, the two mixtures approximate much more closely in respect of the gelatin, although the hydrion concentrations remain practically unchanged.

In any series of oil-gelatin or mastic-gelatin mixtures containing minimal traces of electrolyte, and differing only in respect of the hydrion concentration, the mixtures that are flocculated are not those which contain electrically neutral particles. The lack of coincidence of the point of maximum flocculation and the point where the particles are electrically neutral is therefore confirmed.

H. M. D.

**Influence of Electrolytes on the Coagulation of Clay Suspensions.** GEORG WIEGNER (*Landw. Versuchs-Stat.*, 1914, 84, 283—299).—By reference to the results obtained by various observers for the influence of electrolytes on the stability of suspensions of clay in water, it is shown that these may be satisfactorily explained on the basis of Freundlich's theory, according to which the electrical condition of the particles, and therefore the surface tension and the stability, are determined by the adsorption of cations and anions in accordance with coefficients which are characteristic of the various ions.

H. M. D.

**Coagulation of Colloidal Solutions of Mastic by a Mixture of Two Electrolytes.** ROBERT BENDER (*Kolloid. Zeitsch.*, 1914, 14, 255—257).—The coagulating activity of mixtures of electrolytes has been examined by experiments on colloidal solutions of mastic. In most cases hydrochloric acid was used as one of the electrolytes.

The results indicate that, in general, the substitution of an equimolar quantity of a metallic ion for a portion of the hydrogen

ion causes no appreciable change in the coagulating power of the acid. This relationship does not hold, however, in the case of the trivalent metals, and evidence has been obtained in support of the view that the high coagulating activity of salts of trivalent metals is not due to the metal ions, but to the formation of colloidal hydroxides by hydrolysis. Ferrous salts are also more active than the above relation would indicate, and this is also attributed to hydrolysis. The anomalous behaviour of solutions of hydrochloric acid and auric chloride, which indicate that the addition of the gold salt reduces the coagulating power of the acid, is attributed to the formation of complex anions. H. M. D.

**Gel Filtration of Ultra-microscopic and Other Particles. The Action of Asbestos.** MYER COPLAUS (*J. Path. Bact.*, 1914, **18**, 581—590).—A freshly prepared layer of aluminium hydroxide acts as an efficient filtering medium, but after a few hours fissures appear in the layer, due to shrinking, and filtration is then no longer efficient. Fissuring may be prevented by several methods, among which is admixture with inert fibrous substances, such as floss asbestos. This led to the investigation of asbestos, and it was proved that this substance is not inert, and simple adsorption is not regarded as adequate to explain the phenomena observed. It has many actions on fluids in contact with it; for instance, dilute solutions of curare, strychnine, adrenaline, etc., readily lose their active principle. W. D. H.

**Equilibria in Ternary Systems. XIV.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1136—1152. Compare this vol., ii, 350).—A further theoretical discussion of types of equilibrium in ternary systems. H. M. D.

**Equilibria in the Systems, Water, Acetone, and Inorganic Salts.** GEO. B. FRANKFORTER and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1914, **36**, 1103—1134).—Frankforter and Frary (A., 1913, ii, 685) have shown that potassium fluoride is very effective in salting out ethyl and propyl alcohols from aqueous solutions, and it has now been found that this salt has a similar action on aqueous solutions of acetone.

A study has been made of the systems containing: (1) potassium fluoride, water, and acetone; (2) potassium carbonate, water, and acetone; (3) calcium chloride, water, and acetone; and (4) sodium chloride, water, and acetone. The isotherms at 20° for these systems are given and investigated. Temperature effects in the systems are noted; no upper critical solution temperatures were found, but the lower critical solution temperatures of a series of solutions are recorded.

Of the four systems, it has been found that anhydrous potassium fluoride and anhydrous potassium carbonate are equally efficient in dehydrating acetone, but potassium fluoride is the more rapid, and gives sharper separations. Calcium chloride, in large excess, dehydrates the acetone completely, whilst sodium chloride

dehydrates it to 85.8%. A saturated solution of potassium fluoride dehydrates acetone to 98%, saturated potassium carbonate solution to only 96.5%, and saturated calcium chloride solution to 98.4%. Potassium fluoride seems to be the most satisfactory agent for salting out or dehydrating acetone.

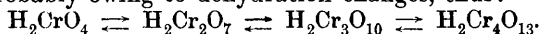
Acetone in aqueous solution can be estimated by means of potassium fluoride by a similar method to that suggested by Frankforter and Frary (*loc. cit.*) for the estimation of ethyl alcohol. This method gives satisfactory results when no third substance is present. It can also be applied to the estimation of acetone in mixtures of this substance with methyl alcohol, provided that the acetone is in excess of the alcohol. E. G.

**The Reciprocal Pairs of Salts**  $\text{KCl} + \text{NaNO}_3 \rightleftharpoons \text{NaCl} + \text{KNO}_3$  **and the Manufacture of Conversion Saltpetre.** W. REINDERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1065—1075. Compare Uyeda, A., 1910, ii, 836).—The composition of the solutions in equilibrium with one, two, and three of the four solid salts has been systematically investigated at 5°, 25°, 50°, and 100°. The data are expressed in accordance with the scheme  $x\text{K}$ ,  $(1-x)\text{Na}$ ,  $y\text{NO}_3$ ,  $(1-y)\text{Cl}$ ,  $m\text{H}_2\text{O}$ , in which  $m$  is the number of mols of water which are associated with 1 mol. of salt. The relations between the various types of systems are readily seen from diagrams which have been constructed on the basis of the solubility data. There are only two systems in which three solid salts co-exist in equilibrium at all the temperatures investigated. These are  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3$ , for which, at 25°,  $x=0.26$ ,  $y=0.36$ , and  $m=3.54$ ; and  $\text{NaCl} + \text{KCl} + \text{KNO}_3$ , for which  $x=0.36$ ,  $y=0.36$ , and  $m=5.01$ . Solutions saturated with respect to both  $\text{KCl}$  and  $\text{NaNO}_3$  are not possible at any temperature between 5° and 100°.

Although the general character of the equilibrium diagram is not altered by this change in temperature, the  $\text{NaCl}$  region expands very considerably as the temperature rises, and this is accompanied by a diminution in the area of the  $\text{KNO}_3$  and  $\text{NaNO}_3$  regions.

The data obtained are utilised in the deduction of the most appropriate process for the conversion of sodium nitrate into potassium nitrate by reaction with potassium chloride and water. Four processes are examined in detail, and it is shown that the best yield is obtained by starting at 100° with a solution which contains sodium nitrate, potassium chloride, and water in the molar ratio 0.80 : 0.62 : 1.81. During the process of evaporation at 100°, this deposits 0.42 mol. of sodium chloride, and on cooling to 5°, the salts which crystallise out are represented by 0.575 mol.  $\text{KNO}_3$  + 0.038 mol.  $\text{NaCl}$  + 0.010 mol.  $\text{NaNO}_3$ . If a suitable quantity of water is added, the separation of solid  $\text{NaCl}$  and  $\text{NaNO}_3$  can be avoided, and 0.563 mol.  $\text{KNO}_3$  obtained in crystalline form. Since this is obtained from 0.62 mol.  $\text{KCl}$ , the yield in terms of potassium amounts to 90.8%. From 100 grams of the original solution, 0.461 mol. of potassium nitrate is obtained by this method of procedure. H. M. D.

**Colorimetric Studies on the Nature of Chromate Solutions.** WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1914, **36**, 829—847).—An account is given of some experiments on the colour of chromate solutions. The results confirm the view of previous observers that the most important equilibrium in aqueous solutions of chromates is expressed by the equation:  $\text{H}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{CrO}_4$ . It has been found that the colours of chromic acid, dichromates, and chromates in solutions more dilute than 0.003% are identical, showing that at such concentrations both chromic acid and dichromates are completely hydrolysed in accordance with the foregoing equation. More concentrated solutions contain molecules and ions of both  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ , whilst at still greater concentrations, or in acid solutions, or when heated, dichromate solutions contain trichromate ( $\text{H}_2\text{Cr}_3\text{O}_{10}$ ), and trichromate solutions contain tetrachromate ( $\text{H}_2\text{Cr}_4\text{O}_{13}$ ). Below the chromate-dichromate transition concentration, hydrated forms of chromate exist, and probably produce colour variations. The colour of chromate solutions does not seem to be affected by ionisation equilibria except in so far as these involve hydrolysis or hydration. When solutions of chromic acid, potassium dichromate, potassium chromate, and potassium chromate containing alkali hydroxide are heated, the colour becomes deeper, probably owing to dehydration changes, thus:



E. G.

**Velocity of Ignition in the Inner Cone of the Bunsen Flame.** L. UBBELOHDE and M. HORSÄSS (*Chem. Zentr.*, 1914, i, 737—738; from *J. Gasbeleucht.*, 1913, **56**, 1225—1232, 1253—1262).—The magnitude of the ignition-velocity in the inner cone of a Bunsen flame depends on the nature of the combustible gas and also on the proportion of the air supply. The dependence of the ignition-velocity on the air supply has been determined for a number of gases. The curves showing the connexion between these factors indicate that the maximum velocity of ignition is reached when the supply of air is less than that required for complete combustion. The maximum velocity decreases in the series hydrogen, acetylene, ethylene, carbon monoxide, methane.

The ignition-velocity of mixtures of two gases cannot be calculated from the velocities of the components by the simple mixture rule. In particular, it has been observed that carbon monoxide has an accelerating influence on the rate of ignition. Inert gases cause a reduction in the velocity of ignition. Preliminary heating of the combustible gases increases the ignition-velocity and reduces the quantity of air which is necessary for the attainment of the maximum velocity.

H. M. D.

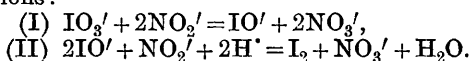
**Velocity of Solution of Metals in Acids. I. The Velocity of Solution of Zinc.** M. CENTNERSZWER and Js. SACHS (*Zeitsch. physikal. Chem.*, 1914, **87**, 692—762).—A critical résumé is given of the various theories which have been advanced to explain the action of acids on pure and impure metals, together with theories

of passivity of metals and the periodic change in the rate of solution of various metals in acids. The authors have carried out a long series of experiments on the rate of solution of pure zinc in hydrochloric and sulphuric acids. The metal was cut into thin, cylindrical or square plates, polished and fastened on a strip of glass. Its edges were coated with varnish so that only the front of it was exposed to the action of the acid. The rate of reaction was determined by measuring the volume of hydrogen liberated. Experiments were carried out with (1) polished zinc, (2) etched zinc, (3) rolled zinc, (4) slowly cooled zinc, (5) rapidly cooled zinc, and zinc which had been kept at  $400^{\circ}$  for eight days. The following main results were obtained. Zinc slowly increases its rate of solubility in a given acid to a maximum, after which its rate of solution slowly falls off in accordance with the law of Boguski (*Kosmos*, 1876, i, 575),  $dx/dt = kF(c-x)$ , in which  $dx/dt$  is the velocity,  $F$  the surface exposed to the acid,  $c$  the concentration of the acid,  $x$  the amount dissolved at time  $t$ , and  $k$  the velocity constant. Thus it is seen that the solution of zinc passes through an induction period. Zinc which has been etched in hydrochloric acid dissolves more rapidly than unetched zinc. Zinc which has reached its maximum velocity of solution in  $2N$ -hydrochloric acid, on removal from the acid and immersion in fresh acid, immediately begins to dissolve with the maximum velocity, and the rate of solution then falls off in accordance with Boguski's law. In acids of equal hydrogen-ion concentration, sulphuric acid dissolves zinc more slowly than hydrochloric acid. Specimens of zinc from the same rod show different solution-velocities, which is to be explained by the different crystal habitus. Plates of rolled zinc, on the other hand, give velocities which are uniform. Zinc which has been rubbed with emery paper dissolves much more quickly than polished zinc, and the finer the emery the more rapid the rate of solution. Zinc plates which have been immersed in iodine solution dissolve more readily than fresh zinc. The velocity of solution of zinc in acids of different concentration increases more rapidly than the concentration of the acid. A mixing of the solution increases the rate of solution. A black deposit is formed on the surface of the zinc during solution; this accelerates the rate of solution, and when it is mechanically removed the velocity decreases. Zinc which has passed through the induction period of solution retains its activity when allowed to remain in water, but loses it if it is kept in the air and allowed to dry. Rapidly-cooled zinc has a longer induction period than slowly cooled zinc, but after the surface has been etched, both dissolve at the same rate. When slowly cooled zinc is heated to  $400^{\circ}$  for prolonged periods its induction period is increased. The results are explained by the assumption that chemically pure zinc is ordinarily in the passive condition, and the increase in the rate of solution during the induction period is regarded as due to the conversion of passive zinc into active zinc. An attempt is made to explain the passivity of zinc and, incidentally, other metals on the basis of an electric double layer according to Helmholtz's theory, and it is shown that this assumption offers



an explanation for the following facts and observations: (1) the influence of foreign metals on the rate of solution, (2) the influence of mechanical and chemical action, on the surface, on the velocity of solution, (3) the induction period, (4) the periodic phenomena observed in solution of metals, (5) the conversion into the passive condition by polarisation and oxidation, (6) the corrosion of iron and other metals, (7) the conversion of passive forms into active forms by hydrogen, (8) the specific influence of certain electrolytes on the condition of metals, and (9) over-voltage. J. F. S.

**Kinetics of the Iodate-Nitrite Reaction.** ALBIN KURTENACKER (*Monatsh.*, 1914, **35**, 407—461).—The reduction of iodic acid by nitrous acid takes place in two stages, which may be represented by the equations:



The velocity of the first reaction has been investigated by following the diminution in the concentration of the iodate. The method of determining the concentration of the iodate consisted in destroying the nitrite and hypiodite by means of carbamide, boiling the solution to remove free iodine, and then estimating the iodate by addition of potassium iodide and titration with sodium thiosulphate. Owing to the lack of analytical methods, the course of the second reaction could not be determined. It was, however, established that its velocity is considerably less than that of the first reaction.

The velocity of reduction of the iodate is found to be directly proportional to the concentration of the iodate, nitrite, and hydrogen ions, and is catalytically accelerated by the hypiodous acid formed in the reaction.

The author was unable to determine whether the accelerating effect of the hypiodous acid is due to the undissociated acid or to the hypiodite ion. Assuming that the catalytic action is due to the hypiodite ion, the velocity of the first reaction can be expressed by the equation:

$$dx/dt = \{K_1 + K_2[\text{IO}']\}[\text{H}'][\text{IO}_3'][\text{NO}_2'].$$

Since the velocity of the reaction is directly proportional to the concentration of the nitrite, the conclusion is drawn that the reduction of the iodate takes place in two stages:

$\text{IO}_3' + \text{NO}_2' = \text{IO}_2' + \text{NO}_3'$ ,  $\text{IO}_2' + \text{NO}_2' = \text{IO}' + \text{NO}_3'$ ,  
the velocity of the second reaction being very much greater than that of the first reaction.

Determinations carried out in the presence of potassium chloride, bromide, and nitrate show that the nitrate ion slightly retards the velocity of reduction of the iodate, whilst the presence of chlorine or bromine ions exerts a marked accelerating effect, the influence of the bromine ion being about twenty times greater than that of the chlorine ion.

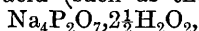
For small concentrations the catalytic action of the halogen ions is directly proportional to their concentration; with large concentrations, however, the accelerating influence falls off, owing to the

conversion of hypiodous acid into iodine monochloride or monobromide, which exert no catalytic action on the reduction of the iodate.

F. B.

**Decomposition of Hydrogen Peroxide and Sodium Perborate in Alkaline Solutions.** RUDOLF SCHENCK, FRANZ VORLÄNDER, and WALTER DUX (*Zeitsch. angew. Chem.*, 1914, 27, 291—296).—The rate of decomposition of hydrogen peroxide in alkaline solution and the corresponding hydroxyl-ion concentrations have been measured. Suitable solutions are prepared by dilution of commercial 3% hydrogen peroxide (containing a trace of preservative which is considered to be without action at the dilutions used), the usual concentration being 0.15%, occasionally 1.5%. The requisite alkalinity is obtained by addition of solutions containing sodium acetate, disodium hydrogen phosphate, borax, or sodium pyrophosphate; sodium dihydrogen phosphate is occasionally used to diminish the alkalinity. The course of reaction is followed by titration of unchanged hydrogen peroxide by means of potassium permanganate. Most of the experiments have been performed at 60°, a few at 80°. In the determination of hydroxyl-ion concentration by the potential method, the hydrogen peroxide solution is replaced by distilled water.

The rate of decomposition of hydrogen peroxide in alkaline solution is dependent on the hydroxyl-ion concentration; but an apparent exception to this rule exists in the case of moderately strongly alkaline sodium pyrophosphate solutions, which exert a preservative action. Such action only occurs within definite limits of alkalinity, and is attributable to the formation of stable salts of a perpyrophosphoric acid (such as the compound,



described by Rudenko, A., 1912, ii, 1169), which are only very slightly dissociated in solution into hydrogen peroxide and pyrophosphate. Solutions of hydrogen peroxide are thus found to be increasingly stable with increasing content of sodium pyrophosphate. Ultimately, however, an optimum point is attained, beyond which the salt becomes less effective, since the tendency towards per-salt formation is more than counterbalanced by the increasing alkalinity of the solution.

The behaviour of perborate solutions is exactly similar to that of hydrogen peroxide, so that such solutions must be considered as equilibrium systems between hydrogen peroxide and borate. In this case, also, sodium pyrophosphate exerts a protective action, which ceases when the hydroxyl-ion concentration exceeds a definite limit.

H. W.

**Esterification of Dibasic Acids by means of Alcoholic Hydrogen Chloride. II. The Esterification of Fumaric and Maleic Acids.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1914, 87, 619—637. Compare this vol., ii, 41).—The velocity of esterification of maleic acid and fumaric acid by hydrogen chloride in absolute alcohol and in aqueous alcohol containing 0.680, 1.376, and 1.439

gram-molecules of water per litre, has been determined at 25°. The method adopted was the same as that previously employed (*loc. cit.*). A similar retarding action of the water is found, as in the previous cases. Whilst in the case of fumaric acid a retarding influence of the replacement of hydroxyl hydrogen by the ethyl group is not detectable, and the course of the esterification of this acid, as in the previously examined cases, can be represented as in the case of the esterification of monobasic acids, such is not found to be so with maleic acid, the replacement of hydroxyl hydrogen by the ethyl group here bringing about a very marked retardation of the esterification on account of the proximity of the carboxyl groups. Since the retardation in the case of maleic acid is greater than in the case of oxalic acid, the conclusion is drawn that the carboxyl groups in maleic acid are closer together than in oxalic acid. In aqueous alcohol a small hydrolysis is found, both in maleic and fumaric esters. A formula is deduced which allows of the calculation of the velocity constant for a unimolecular reaction, as a function of the water and hydrogen chloride concentrations. A comparison with succinic acid shows the retarding effect of the double linking of the  $\alpha$ -carbon atom. This action is smaller with maleic acid than with fumaric acid, and very much less than in the case of cinnamic acid. J. F. S.

**Hydrolysis of Esters of Substituted Aliphatic Acids. VIII. Homologues of Ethyl Cyanoacetate.** W. A. DRUSHEL (*Amer. J. Sci.*, 1914, [iv], 37, 514—518).—The velocities with which the ethyl esters of cyano-substituted fatty acids are hydrolysed under the influence of 0.1*N*-hydrochloric acid have been compared by measurements at 25°, 35°, and 45°. The values obtained for the velocity-coefficient  $K \times 10^5$  are given in the following summary, in which the two sets of numbers refer to the data for 25° and 45° respectively: Ethyl  $\alpha$ -cyanopropionate, 9.14, 45.5;  $\beta$ -cyanopropionate, 13.0, 74.2;  $\alpha$ -cyanobutyrate, 6.15, 35.0;  $\beta$ -cyanobutyrate, —, 47.8;  $\alpha$ -cyanovalerate, 4.67, 31.0;  $\alpha$ -cyanoisovalerate, 2.50, 18.1;  $\alpha$ -cyano- $\alpha$ -ethylbutyrate, 2.58, 14.4. The increase in the velocity for 10° rise in temperature varies from 2.35 for the  $\beta$ -cyanobutyrate to 2.68 for the  $\alpha$ -cyanoisovalerate.

The ratio of the velocities for the cyano-substituted ester and the corresponding non-substituted ester were found to be: cyanoacetate, 0.157;  $\alpha$ -cyanopropionate, 0.128;  $\beta$ -cyanopropionate, 0.180;  $\alpha$ -cyanobutyrate, 0.118;  $\beta$ -cyanobutyrate, 0.169.

The results show that the cyanogen group has a marked retarding effect on the velocity of ester hydrolysis. Unlike that of the halogens, the retarding effect is more pronounced in the  $\alpha$ - as compared with the  $\beta$ -position. H. M. D.

**Catalytic Action.** J. BÖESEKEN (*Rev. trav. chim.*, 1914, 33, 195—203).—A theoretical paper, in which the author enumerates his views on catalysis.

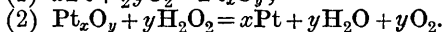
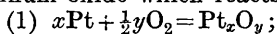
The theories of catalysis may be divided into those which assume the union of the catalyst with one of the molecules, and the attack of the compound formed (hypothesis of intermediate products),

and those in which the catalyst is considered to decompose or disrupt the molecules, thus giving an increase in concentration of the active portions. The first hypothesis can in any case only explain the mechanism, but not the reason, of the catalytic action, whilst if the catalyst forms an additive compound with one of the molecules, it is necessarily paralysed. The fact that a chemical action is accelerated in spite of this paralysis merely shows that the affinity of the atoms of the activated substance is changed by the presence of the catalyst; in other words, that an explanation is to be found solely in the second hypothesis.

The main conclusions are summarised as follows: (1) The maximal catalytic action is exerted by the free catalyst, and the action cannot be explained by the formation of the so-called intermediate additive products (compare Prins, *Thèse, Delft*, 1912; Olivier, this vol., i, 818). (2) The best catalyst is that which forms with the activated substance a dissociable compound, the region of dissociation of which extends over a large region of temperature and pressure. Thus, in the transformation of yellow into red phosphorus by the help of iodine, it is found that the change does not commence at the ordinary temperature, since the iodine combines with phosphorus, and is thus paralysed; at about 75°, a slow formation of red phosphorus is observed, whereas Troost and Hautefeuille (A., 1882, 1264) have shown that the dissociation of  $P_2I_4$  commences at 80°. Similarly, in acetylation by means of acetic anhydride, a variety of catalysts can be employed. Of these, sulphuric acid or zinc chloride, possibly also aluminium chloride or iodine, are most suitable for alcohols or unsaturated substances, since they form unstable additive products; for amides, acidic catalysts such as the chlorides of zinc, aluminium, or iron, are preferable, whilst for a similar reason, tertiary bases are to be recommended for use in the acetylation of feebly acidic substances, such as phenols.

H. W.

**Mechanism of the Catalysis of the Decomposition of Hydrogen Peroxide by Colloidal Platinum.** DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1914, 36, 878—881).—It has been suggested that the catalytic effect of colloidal platinum on the decomposition of hydrogen peroxide is due to the formation of an unstable platinum oxide which reacts with the peroxide:



If the concentration of the unstable oxide remains constant, the reaction would be expected to be of the first order. It is shown, however, from Bredig and Ikeda's determinations (A., 1901, ii, 441) that this is not strictly the case, but that the value of the constant of the first order increases as the reaction proceeds, indicating that the process represented by equation (1) is much more rapid than that represented by (2). As an explanation of this, it is suggested that as the colloidal platinum presents a very large surface to the liquid, the rate of reaction may be influenced by the adsorption of the peroxide on this surface. It is also regarded

as probable that the velocity of this adsorption is more rapid than the rate of decomposition of the hydrogen peroxide. E. G.

**Catalytic Action of Sodium and Related Substances.** H. J. PRINS (*Chem. Weekblad*, 1914, 11, 474–487).—A theoretical paper, discussing catalyses effected by other observers by the aid of sodium, sodium hydroxide, sodium alkyloxide, sodium cyanamide, sodium carbonate, and sodamide, and of rubidium, caesium, and potassium. The other alkali metals are more powerful catalysts than sodium. Numerous examples of catalysis are cited.

A. J. W.

**A Method for the Determination of the Molecular Weight of Very Small Quantities of Gases or Vapours.** MARTIN KNUDSEN (*Ann. Physik*, 1914, [iv], 44, 525–536).—The method depends on the measurement of the resistance offered by the gas at very low pressure to the motion of a sphere rotating about its axis of suspension.

If the number of collisions between the gas molecules is negligibly small in comparison with the number of collisions which take place between the molecules and the rotating system, the molecular weight of the gas or vapour is given by the formula

$$\bar{M} = 522.25 \times 10^6 T k^2,$$

in which  $T$  is the absolute temperature and  $k$  is the force exerted by the gas, at a pressure of 1 dyne/cm.<sup>2</sup>, on unit surface which moves with a tangential velocity of 1 cm./sec.

Data obtained for air and oxygen indicate that the method yields satisfactory results provided that the observations are combined with similar observations for a standard gas. The pressures at which the measurements were made varied from 0.06 to 3.5 dynes per cm.<sup>2</sup>.

H. M. D.

**The First Occurrence of the Name "Chemistry."** EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1914, 38, 685–686).—It is generally supposed that the word chemistry was first used by Firmicus in his astrological work "Mathesis," written in 337, but the author's investigations indicate that the word first appears in Greek works written by Zosimos of Panopolis (Egypt). In these the author speaks of *χημία* or *χημεία* as the art of making gold and silver. Zosimos is regarded by certain historians as a contemporary of Firmicus; by others, however, he is said to have lived in the third century.

H. M. D.

**Filter-desiccator. A New Apparatus for the Isolation of Substances Sensitive to Air.** MAX CLAASZ (*Zeitsch. angew. Chem.*, 1914, 27, 296).—The apparatus consists of two hemispherical, tubulated desiccator covers placed with their broad bases in contact. The lower tubulus carried a funnel provided with a filter plate, which is surrounded by calcium chloride or other desiccating agent. The stem of the funnel communicates by means of a stop-cock with a pressure flask. The upper tubulus has a ground-glass

joint, to which are attached a dropping funnel and two tubes (for admission of an inert gas and for exhaustion respectively), all of which are provided with stopcocks.

In use, the upper cover is removed, and the solution to be filtered is poured into the funnel, the lower stopcock being shut. The cover is replaced and the vessel exhausted, and then filled with an inert gas (hydrogen or carbon dioxide) and the exhaustion and filling repeated. The pressure flask is now exhausted, and filtration allowed to take place without interrupting the current of inert gas. The precipitate is washed by a suitable liquid introduced by means of the dropping funnel. Finally, the stopcocks are closed and the upper part of the apparatus is again exhausted. Generally, the substance is completely dry and stable towards air after the lapse of twenty-four hours.

H. W.

**Lecture Experiments with Ferronitric-oxide Compounds.** W. MANCHOT (*Ber.*, 1914, **47**, 1614—1616).—An arrangement is described by means of which hydrogen and nitric oxide can be passed alternately through an aqueous solution of ferrous ammonium sulphate. The deep brown colour caused by the nitric oxide is rapidly destroyed when this gas is replaced by hydrogen. Using concentrated sulphuric acid as the solvent for ferrous sulphate, a red colour is obtained instead of a brown.

A 0.1% solution of copper chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) in absolute alcohol gives very good colour effects; it is scarcely coloured, but with nitric oxide it becomes deep blue almost immediately, hydrogen then removing the colour in a few seconds.

Other uses of the apparatus are mentioned.

T. S. P.

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## Inorganic Chemistry.

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**Displacement of Acids by Hydrogen Peroxide. IV.** JOACHIM SPERBER (*Chem. Zentr.*, 1914, i, 738—739 ; from *Schweiz. Apoth.-Zeit.*, 52, 2—6. Compare A., 1913, ii, 1047).—It has been found that the halogen acids are all displaced to a measurable extent by hydrogen peroxide. Iodic acid is to a large extent decomposed by hydrogen peroxide with the liberation of iodine. H. M. D.

**Action of Hydrogen Peroxide on Metals and its Application to the Disinfection of Instruments.** WILHELM EICHHOLZ (*Chem. Zentr.*, 1914, i, 908 ; from *Med. Klinik*, 1913, 1—4).—The action of various hydrogen peroxide preparations on iron, silver, nickel, and copper has been studied. Pure solutions of any strength have a preservative action on iron, and the absence of rusting may be taken as a criterion of the purity of a solution of hydrogen peroxide, provided that extraneous impurities are rigidly excluded

during a test. Pure 3% solutions are applicable to the sterilisation of iron, nickel, or copper instruments. J. C. W.

**Action of Weak Acids on Soluble Fluorides.** P. A. ELLIS RICHARDS (*Analyst*, 1914, **39**, 248.—249).—Solutions of potassium or sodium fluorides are decomposed when brought into contact with 1% solutions of acetic, butyric, tartaric, malic, citric, formic, salicylic, and benzoic acids, the hydrofluoric acid liberated having a distinct etching effect on glass. Soluble fluorides are also decomposed by carbon dioxide, but not by boric acid. The acids mentioned do not decompose calcium fluoride. W. P. S.

**Fluorine in Fresh Waters.** ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1914, **158**, 1389—1395).—By their method, already described (compare A., 1912, ii, 681, 805, 806), the authors have determined the amount of fluorine present in samples of water from a number of streams and rivers, one lake and one spring, and the drinking water of Paris. In each case particulars are given as to the time and place of sampling. In no case was a water found containing more than 0.60 mg. of fluorine per litre. The waters of calcareous origin were always less rich in fluorine than those coming from primitive rock beds, and the latter lost in fluorine content the further they passed over calcareous beds. Calcium carbonate, especially if mixed with some calcium phosphate, removes fluorine from very dilute solutions of fluorides. W. G.

**Hydrogen Sulphide Apparatus.** FREDERIC WILLIAM RIXON (*Chem. News*, 1914, **109**, 253).—The apparatus is arranged for a constant or intermittent supply of the gas. The acid reservoir is placed slightly below the ferrous sulphide vessel, and air-pressure is utilised to cause the acid to pass from the reservoir to the lower part of the sulphide vessel. A water-trap on a tube connecting the top of the acid reservoir with the upper part of the sulphide vessel acts as a safety valve. W. P. S.

**Theory of the Lead Chamber Process.** O. WENTZKI (*Zeitsch. angew. Chem.*, 1914, **27**, 312).—The author criticises the conclusions drawn by Hempel from his experiments on the lead chamber reactions (this vol., ii, 455), and maintains that the contraction which accompanies the interaction of  $\text{N}_2\text{O}_4$ ,  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  does not afford a correct measure of the reaction velocity. The experiments cannot therefore be regarded as proving that the action of  $\text{N}_2\text{O}_4$  is much slower than that of  $\text{N}_2\text{O}_3$ , although it is quite possible that such a difference would be shown by comparable experiments. Even if this difference is real, it cannot be used as an argument in favour of the view that intermediate compounds are formed in the process. H. M. D.

**Anodic Oxidation of Ammonia in an Alkaline Medium in the Presence of Silver Salts.** G. SCAGLIARINI (*Gazzetta*, 1914, **44**, i, 543—547. Compare Scagliarini and Casala, A., 1913, ii, 181; Müller and Spitzer, A., 1905, ii, 242, 314).—The formation of



nitrous acid in this process decreases with increasing concentration of ammonia, but is favoured by increase in the amount of free alkali (potassium hydroxide) present. The formation of nitrous acid reaches a maximum at  $52^{\circ}$ . It is favoured, although not very markedly, by increase in the quantity of silver sulphate present up to a concentration of 0.75%, and then remains constant.

R. V. S.

**Electromerides and Stereomerides with Positive and Negative Hydroxyl.** LAUDER WILLIAM JONES (*J. Amer. Chem. Soc.*, 1914, **36**, 1268—1290).—A discussion is given of the constitution and reactions of hydroxylamine and its derivatives, and the conclusion is drawn that hydroxylamine must be regarded as a tautomeric substance. The evidence adduced is considered sufficient to establish a tautomeric relationship in the ordinary structural sense, and to confirm the view that hydroxylamine and its derivatives in many of their reactions also exhibit electronic tautomerism.

E. G.

**Melting Point of Arsenic.** LUIGI ROLLA (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 693—697).—The existence of the curve of atomic frequency (this vol., ii, 531) permits of the calculation of the temperature at which the amplitude of the oscillations of the atoms of arsenic becomes of the same order of magnitude as the interatomic spaces, that is, it permits of the calculation of the melting point of arsenic. From calorimetric measurements with certain alloys of antimony and arsenic the mean value  $1202^{\circ}$  (absolute) is obtained by the author, and this is in fair agreement with the most probable values hitherto arrived at in other ways.

R. V. S.

**Relative Stability of Diamond and Graphite.** H. E. BOEKE (*Centr. Min.*, 1914, 321—325).—A theoretical paper in which, on the basis of the Nernst heat theorem, the relative stability of diamond and graphite is considered. It is shown that at all temperatures at atmospheric pressure diamond is unstable, whereas graphite is stable.

J. F. S.

**Attempt to Determine the Molecular Weight of Silicic Anhydride.** R. SCHWARZ and H. STURM (*Ber.*, 1914, **47**, 1735—1740).—From the depression of the freezing point of lithium metasilicate by the addition of silica, and taking into account the fact that the fusion does not deposit pure lithium metasilicate, but mixed crystals, the molecular weight of silica is calculated, using van Laar's formula, to be 109, that is, the molecular formula is  $(\text{SiO}_2)_2$ .

The melting-point curves obtained by Klooster (A., 1911, ii, 111) for the system  $\text{Li}_2\text{O}-\text{SiO}_2$  show that the metasilicate must dissociate in the fusion, according to the scheme:  $2\text{Li}_2\text{SiO}_3 \rightleftharpoons \text{Li}_4\text{SiO}_4 + \text{SiO}_2$ . The amount of this dissociation is calculated to be 3.42%.

The melting point of lithium metasilicate is found to be  $1209^{\circ}$  (compare Klooster, *loc. cit.*).

T. S. P.

**Gases from Thermal Springs. Rare Gases and Radioactivity. Therapeutic, Geophysical, and Astrophysical Considerations.** CHARLES MOUREU (*J. Pharm. Chim.*, 1914, [vii], 9, 369—374, 446—454, 503—510, 550—559).—An outline of the author's method of analysing gases from thermal springs is given. The gas, free from air, is purified from carbon dioxide, dried, and treated with calcium at a red heat, whereby any oxygen present and nitrogen are absorbed; after combustion of the residue with copper oxide, and absorption of carbon dioxide and water, a mixture of rare gases remains, which is analysed by absorption with charcoal at suitable temperatures.

A series of tables is given showing the composition of the gases evolved from seventy springs situated mainly in France, and also the total volumes of gas evolved. Nitrogen is invariably present, frequently accompanied by a greater or less proportion of carbon dioxide, less frequently by oxygen and combustible gases. The five rare gases are always present, their proportion being roughly parallel to the nitrogen content of the mixture. The proportions of krypton and xenon are always very small and negligible in comparison with those of argon and helium; it is generally the same with neon.

The amount of argon is generally about 1% of the nitrogen. Helium is present in very varying quantities, rising to about 6% and 10% respectively at Mazières and Santenay. The radioactivity of the gases varies within wide limits.

There is no parallelism between the radioactivity of any given source and the proportion of helium. In the majority of cases only a minute fraction of the latter is derived from radioactive substances present in the springs; the great part exists pre-formed (free or occluded) in the strata, and is brought to the surface by the water.

The ratio krypton : argon in nineteen natural and one volcanic gas varies within narrow limits, and is of the same order, although always somewhat greater, than this ratio for air. Possibly, the relative proportions of these gases were, at one time, sensibly constant at all points of the nebula, and, since their inertness precludes the absorption of either, the slight alterations in the proportion are attributable to physical causes, such as occlusion, diffusion, etc. Similarly, the ratio xenon : krypton in air being taken as unity, the ratio in seventeen gases varies from 1.2 to 2.5. There is no proportionality between the amounts of helium and of any other gas, and this is attributed to the continual production of the former from radioactive substances. The ratio argon : nitrogen, in air being taken as unity, that in seventeen cases lies between 0.64 and 0.99; in thirty-nine cases between 1 and 1.29, and in eighteen cases between 1.35 and 1.69; in the gas from Vesuvius it is 1.15, whilst the general mean is about 1.15. A similar series of experiments on the gases from mines shows the analogy in composition of the "crude" nitrogen (nitrogen + rare gases) from this source to that obtained from other natural gaseous mixtures.

The possibility of the production of argon and krypton by disintegration from other atoms is discussed. The author is led to the conclusion that the proportionality between these elements can only with difficulty be reconciled with such an hypothesis, and further that such formation must have occurred, if at all, at an epoch previous to the formation of the earth's crust. H. W.

**Bivalent Silver.** G. SCAGLIARINI and A. GUIDA (*Gazzetta*, 1914, **44**, i, 574—578. Compare Barbieri, A., 1912, ii, 763, 941).—A solution of silver arsenate dissolved in a 65% solution of arsenic acid is subjected to anodic oxidation, the cathodic liquid being a 5% solution of nitric acid. A current of 20 volts and 2.5 amperes is used, and the temperature is kept below 10°. After at least three hours the anodic liquid is immersed in ice, and treated with a concentrated solution of potassium arsenate. A black precipitate is slowly deposited; it has probably one of the following formulæ:  $6\text{AgO} \cdot 4\text{H}_3\text{AsO}_4$  or  $\text{Ag}_3(\text{AsO}_4)_2$ . That the silver in this compound is bivalent is shown by measurements of the ratio silver : active oxygen in the products obtained with various periods of electrolysis. R. V. S.

**Silver Subfluoride.** LOTHAR WÖHLER (*Zeitsch. anal. Chem.*, 1914, **53**, 375—378).—A controversy with Sachs and Vanino (this vol., A., ii, 268), who consider silver subfluoride to be a mixture of silver fluoride and metallic silver coloured green by silver oxide.

The author still regards silver subfluoride as a true compound; the mere fact that it is easily decomposed by the action of water does not prove it to be a mixture. L. DE K.

**Plaster of Paris from the Technical Point of View.** G. GALLO (*Gazzetta*, 1914, **44**, i, 497—537).—This paper records the results of a large number of experiments undertaken with a view to elucidate the nature of plaster of Paris and of the processes involved in its preparation and in the phenomenon of setting.

In the industrial preparation of plaster of Paris at about 180—200°, a rapid loss of water begins above 120°, and the final product is soluble anhydrite, which constitutes the greater part of the substance removed from the oven if the temperature has not exceeded 210°. This product rapidly absorbs water in the air until the compound  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  is formed, and this is the essential constituent of ordinary plaster of Paris. In addition to the water represented in its formula (6.2%), this substance absorbs a variable quantity of water (for it is porous and hygroscopic) up to a maximum of about 8% in all, the amount depending on the atmospheric humidity.

Calorimetric and microscopic observations confirm in the main the theory of the mechanism of the setting of plaster of Paris due to Le Chateliér.

A slow hardening of the set plaster continues for several days, until an excess of water is present. The rapidity of this process depends on the atmospheric humidity and on the degree of porosity

of the plaster, which can be determined by its absorption of petroleum, the air in the pores having been first removed by exhaustion.

The quantity of soluble anhydrite in a plaster can be estimated by keeping a weighed sample for twelve hours over water, then transferring it to a desiccator containing concentrated sulphuric acid (D 1.40) until of constant weight. The increase in weight observed, multiplied by the factor 15.11, gives the quantity of soluble anhydrite.

The quantity of semihydrate in a plaster may be estimated by treating a weighed sample with a large excess of water (so that no paste is formed) and (after one hour) drying at 60–65°, and subsequently over sulphuric acid for twenty-four hours. The observed increase in weight, multiplied by the factor 5.3707, gives the quantity of semihydrate present, any soluble anhydrite being allowed for previously.

Details are given of the ways in which other chemical and mechanical tests may be effected.

R. V. S.

**Atomic Weight of Barium.** W. OESCHNER DE CONINCK (*Chem. Zentr.*, 1914, i, 740; from *Rev. gén. Chim. pure appl.*, 1913, 16, 405. Compare A., 1913, ii, 1055).—Experiments in which barium carbonate was converted into barium sulphate have given 137.38 as the atomic weight of barium.

H. M. D.

**Borates. I. The System  $\text{BaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  at 30°.** U. SBORGI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 530–534).—By the interaction of barium hydroxide and boric acid under various conditions (which are described), borates of the following compositions have been obtained:  $\text{BaO}, \text{B}_2\text{O}_3, 4\text{H}_2\text{O}$ ;  $2\text{BaO}, 3\text{B}_2\text{O}_3, 6\text{H}_2\text{O}$ ;  $\text{BaO}, 3\text{B}_2\text{O}_3, 7\text{H}_2\text{O}$ .

R. V. S.

**The Binary System  $\text{MgO}-\text{SiO}_2$ .** N. L. BOWEN and OLAF ANDERSEN (*Amer. J. Sci.*, 1914, [iv], 37, 487–500\*).—The mixtures of magnesium oxide and silica were heated at constant temperature in a resistance furnace until equilibrium was attained, rapidly cooled by quenching in mercury, and then examined microscopically in order to determine the nature of the solid phases.

The results obtained show that the compounds  $\text{Mg}_2\text{SiO}_4$  and  $\text{MgSiO}_3$  are capable of existence in contact with liquid. The orthosilicate crystallises in the form corresponding with the mineral forsterite, whilst the metasilicate forms crystals which resemble enstatite in most properties, but on account of their monoclinic symmetry are referred to as clino-enstatite.

Clino-enstatite is transformed at 1557° into forsterite + liquid, complete liquefaction requiring a temperature of 1577°. Forsterite melts at 1890° ± 20°. The eutectic point at which  $\text{MgO}$  and  $\text{Mg}_2\text{SiO}_4$  co-exist corresponds with 1850° ± 20° and the approximate composition 14%  $\text{MgO}$ , 86%  $\text{Mg}_2\text{SiO}_4$ . The eutectic point in which

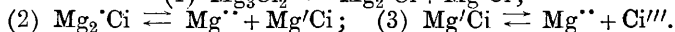
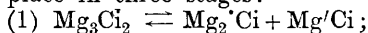
\* and *Zeitsch. anorg. Chem.*, 1914, 87, 283–299.

$\text{MgSiO}_3$  and  $\text{SiO}_2$  are the co-existing solid phases, lies at  $1543^\circ \pm 2^\circ$  and the composition 87.5%  $\text{MgSiO}_3$ , 12.5%  $\text{SiO}_2$ .

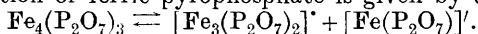
The nature of the relations existing between forsterite and clinoenstatite is discussed in reference to petrological problems.

H. M. D.

**Complex Ionisations.** C. BLOMBERG (*Ch m. Weekblad*, 1914, 11, 458—460).—The author represents the ionisation of magnesium citrate as taking place in three stages:



The ionisation of ferric pyrophosphate is given by the scheme:



A. J. W.

**The Variations in the Atomic Weight obtained with Lead Derived from Different Minerals.** MAURICE CURIE (*Compt. rend.*, 1914, 158, 1676—1679).—Pure lead has been prepared from galena and from minerals containing uranium and thorium, the process of purification being repeated, if necessary. The atomic weight of each sample of lead was then determined by Stas's method from the ratio  $\text{Pb} : \text{Pb}(\text{NO}_3)_2$ . The atomic weight of lead from uranium minerals is distinctly lower (206.36—206.64) than that from galena (207.01), whilst the value for lead from monazite is slightly higher (207.08). These results are in agreement with the theory of classification and transformation of the radioactive elements.

W. G.

**Crystallographic and Thermal Investigation of Systems Formed by Lead Chloride with the Chlorides of Univalent Metals.** KURT TREIS (*Jahrb. Min. Beil.-Bl.*, 1914, 37, 766—818).—The binary systems formed by lead chloride in combination with lithium, sodium, potassium, rubidium, and silver chloride have been investigated by determination of the melting- and freezing-point curves and by examination of the structure of the products of crystallisation. The ternary system lead, sodium, and potassium chlorides was also investigated in detail.

The data for lead chloride in combination with lithium, sodium, and silver chloride indicate that no compounds are formed, and that the chlorides are not miscible in the solid state. The freezing-point diagram shows two curves, which meet in the eutectic point. The eutectic temperature and composition for the three systems are as follows, the composition being expressed in mols. % of lead chloride: lithium chloride  $410^\circ$ , 55%; sodium chloride  $411^\circ$ , 73%; silver chloride  $310^\circ$ , 40.5%.

Lead chloride and potassium chloride give rise to two compounds,  $2\text{PbCl}_2 \cdot \text{KCl}$  and  $\text{PbCl}_2 \cdot 2\text{KCl}$ , the first of which melts at  $440^\circ$ , whilst the second decomposes at  $490^\circ$  with the separation of potassium chloride in the crystalline form. The author's experiments afford no evidence of the formation of the compound  $\text{PbCl}_2 \cdot 4\text{KCl}$ , the existence of which is indicated by observations of Lorenz and Ruckstuhl (A., 1906, ii, 853).

Lead chloride and rubidium chloride yield three double salts of the composition  $2\text{PbCl}_2, \text{RbCl}$ ;  $\text{PbCl}_2, \text{RbCl}$ ; and  $\text{PbCl}_2, 2\text{RbCl}$ . The first and second melt at  $423^\circ$  and  $440^\circ$  respectively, whilst the third decomposes with the separation of solid rubidium chloride at  $448^\circ$ .

All the double salts crystallise in rhombic forms, and those of similar composition appear to be isomorphous.

The system formed by the combination of sodium and potassium chloride has also been further investigated. These chlorides form a complete series of mixed crystals, and the freezing-point curve shows a minimum at  $661^\circ$  and 52 mols. % of sodium chloride. The corresponding melting-point curve was obtained by observations on solidified mixtures, the temperature of which was not allowed to fall below  $500^\circ$ , which is well above the demixing temperature. The demixing curve shows a maximum of  $398^\circ$  at the composition which corresponds with the minimum on the freezing-point curve.

The chlorides of lead, sodium, and potassium afford a ternary system, which is characterised by two eutectic points. The solid phases  $\text{PbCl}_2$ ,  $2\text{PbCl}_2, \text{KCl}$ , and  $\text{NaCl}$  co-exist in the eutectic point at  $383^\circ$ , where the composition of the fused mass is  $71\text{PbCl}_2$ ,  $11\text{KCl}$ , and  $18\text{NaCl}$ . The co-existing solid phases in the second eutectic point are  $2\text{PbCl}_2, \text{KCl}$ ,  $\text{PbCl}_2, 2\text{KCl}$ , and  $\text{NaCl}$ ; the temperature is  $387^\circ$ , and the composition  $48\text{PbCl}_2$ ,  $36\text{KCl}$ , and  $16\text{NaCl}$ . The numbers express the composition as mols. %.

H. M. D.

**Behaviour of Metals, especially Copper, towards Dilute Acids.** J. RICHARD (*Chem. Zentr.*, 1914, i, 859; from *Zeitsch. phys.-chem. Unterr.*, 1914, 27, 31—34).—When copper is left in *N*-nitric acid it becomes brown. This is considered to be evidence in support of the view that the metal is first of all oxidised in the action of nitric acid.

J. C. W.

**Oxidation of Copper. Influence of Temperature and Pressure.** ERNEST BERGER (*Compt. rend.*, 1914, 158, 1502—1505).—The author has shown that oxidation of copper by dry oxygen takes place even at the ordinary temperature, although the process is not visible to the eye. The velocity of oxidation is practically tripled for each  $10^\circ$  rise in temperature, and is apparently directly related to the pressure of the condensed gaseous layer at the surface of the metal.

W. G.

**Hydrolysis of Rare Earth Sulphates.** S. H. KATZ and C. JAMES (*J. Amer. Chem. Soc.*, 1914, 36, 779—784).—Experiments are described in which solutions of the sulphates of lanthanum, cerium, neodymium, samarium, europium, gadolinium, erbium, and ytterbium were treated with potassium iodide and iodate, and distilled by means of a modified form of the apparatus employed by Moody (A., 1905, ii, 765) for estimating aluminium. The comparative degree of hydrolysis of the various sulphates was ascertained by estimating the iodine in the distillates. The sulphates of samarium, europium, and gadolinium gave nearly the same results, but it was observed that throughout the series the tendency to hydrolysis

increased with increasing atomic weight. The experiments indicate that in purifying gadolinium from samarium by fractional precipitation with ammonium hydroxide, the samarium would be concentrated in the last fractions instead of in the early fractions, as found by Boisbaudran (A., 1891, 17) and Benedicks (A., 1900, ii, 209).  
E. G.

**Action of Bromine on the Hydroxides of Lanthanum and the Didymiums.** PHILIP E. BROWNING (*Compt. rend.*, 1914, 158, 1679—1680. Compare A., 1910, ii, 159).—Suspensions of hydroxides of the metals of the cerium group in a dilute solution of potassium hydroxide all dissolve on the addition of bromine water with the exception of cerium hydroxide. Lanthanum hydroxide dissolves far more rapidly than either neodymium or praseodymium hydroxides, and the author suggests treatment with bromine water and filtration, followed by reprecipitation as oxalate, calcining to oxide, and then further treatment with bromine water as a means of separating lanthanum from the didymiums. The method, whilst more rapid, does not give such good results as von Loelsbach's method of crystallisation of the double ammonium nitrates.  
W. G.

[Purification of] Scandium [Compounds]. JOHANN STERBA-BÖHM (*Zeitsch. Elektrochem.*, 1914, 20, 289—295).—The paper deals mainly with the preparation of pure scandium oxide from the residual oxides left after wolframite had been used for the preparation of sodium tungstate. This residue contained oxides of silicon, tin, tungsten, titanium, iron, manganese, lead, bismuth, copper, calcium, molybdenum and rare earth oxides, which were mainly scandium and thorium. About 1 kilo. of the mixed oxide was added slowly to  $1\frac{1}{2}$  kilos. of concentrated hydrochloric acid solution, warmed for four hours on a water-bath, and left until the evolution of chlorine had ceased. A semi-liquid mass was obtained, which was poured into 5 litres of water, well mixed, and filtered through linen. In this way practically the whole of the scandium was obtained in solution. To this solution, a solution of 100 grams of commercial ammonium fluoride in 1 litre of water and enough hydrochloric acid to give it an acid reaction, was added. A precipitate was immediately formed, which redissolved, and on keeping for twenty-four hours a fine, powdery precipitate of scandium fluoride had settled. The supernatant liquid was decanted, and the precipitate washed with *N*-hydrochloric acid until a pure white colour was obtained. In this way 2 kilos. of somewhat impure scandium oxide were rapidly obtained from 700 kilos. of the original oxides. The method can be used for the quantitative estimation of scandium if there is not much thorium present. The oxide thus obtained contained some iron, manganese, calcium, lead, copper, and tin, and traces of molybdenum, tungsten, thorium, ytterbium, and yttrium. For further purification the fluoride was heated with concentrated sulphuric acid in a platinum dish until all the hydrofluoric acid had been expelled, and then

dissolved in a large volume of cold water. The solution so obtained had no absorption spectrum, thus demonstrating the absence of coloured cerium and yttrium earths. This solution was precipitated with ammonia, and the precipitate dissolved in hydrochloric acid and concentrated. Solid potassium carbonate or ammonium carbonate was added until the precipitate of scandium carbonate first formed had redissolved to form a double scandium carbonate; ammonium sulphide was then added, and the iron was precipitated as sulphide. Manganese was removed by adding a solution of iodine in potassium iodide until the solution became permanently brown, when manganic hydroxide settled as a fine powder. Molybdenum was removed by adding ammonia until a precipitate was just formed; a moderate quantity of formic acid was then added, and hydrogen sulphide passed into the solution, when the molybdenum separated as sulphide. Potassium and calcium were removed by precipitating the scandium as hydroxide and washing. The remaining impurities were thorium, yttrium, and ytterbium, the two former of which were separated by the Meyer-Winter method of recrystallising the double sodium scandium carbonate (A., 1910, ii, 854), and the latter by recrystallising the formate. The properties of the formate and oxalate of scandium are described. From the examination of three hundred fractions it is shown that scandium is a uniform substance. In the examination of the precipitate obtained in the second analytical group, a rose-yellow precipitate was obtained, which had previously been described by Ogawa (A., 1908, ii, 952, 953) and Skrabal and Artmann (A., 1909, ii, 243), and stated by them to be due to an hitherto unknown element. The author has obtained large quantities of this sulphide, and has shown that it does not contain a new element, but consists of copper sulphide with small quantities of tin sulphide and tungsten sulphide and much sulphur.

J. F. S.

**Preparation of Aluminium Nitride from its Elements.** JOHANNES WOLF (*Zeitsch. anorg. Chem.*, 1914, **87**, 120—128. Compare A., 1913, ii, 964; Fichter and Spengel, *ibid.*, 711).—Experiments have been made with a carbon resistance vacuum furnace, using nitrogen under various pressures. By heating crude aluminium nitride in nitrogen under atmospheric pressure to 2010—2030° for fifteen minutes a product containing 33·7% of nitrogen (in place of 34·08%) may be obtained, but there is much loss by volatilisation. It is found that the nitride does not volatilise as such, but dissociates. When a large excess of nitrogen is present, the nitride is regenerated as colourless, hexagonal needles on the sides of the tube. Under atmospheric pressure, dissociation takes place at 1850°. The nitride melts at about 2150—2200°.

C. H. D.

**Silicious Iron.** GEORGES CHARPY and ANDRÉ CORNU (*Bull. Soc. chim.*, 1914, [iv], **15**, 497—500).—Polemical against Vigouroux (*ibid.*, 268; and also A., 1913, ii, 512; compare Charpy and Cornu, A., 1913, ii, 512, 852).

H. W.



**Ancient Damascened Steel.** W. GUERTLER (*Intern. Zeitsch. Metallographie*, 1914, 5, 129—141).—The structure of damascened steel is due to the segregation of cementite. Lamellar pearlite is absent, and the bands consist of ferrite containing isolated granules of cementite, which are segregated in certain zones. The structure only occurs in the absence of slag and other impurities. It has not yet been possible to reproduce the structure, but prolonged heating at a temperature below  $700^{\circ}$  must be a necessary condition.

C. H. D.

**The Compounds of Nitric Oxide with Ferrous and Cupric Salts.** W. MANCHOT (*Ber.*, 1914, 47, 1601—1614).—When a solution of ammonium phosphate (1.6 grams in 25 c.c. of water) is added to a solution of 1 gram of ferrous chloride in 20 c.c. of alcohol saturated with nitric oxide at  $0^{\circ}$ , the whole operation being carried out in an atmosphere of nitric oxide, a blackish-brown, viscid oil is precipitated, which crystallises when cooled in a freezing mixture. No nitric oxide is evolved during the precipitation. By appropriate manipulation at low temperatures the substance can be obtained pure, in the form of brown, flaky crystals, m. p.  $16^{\circ}$ , and having a composition corresponding with the formula  $\text{Fe}(\text{NO})\text{HPO}_4$ , which is *ferro-nitric oxide phosphate*. Freshly precipitated ferrous phosphate also absorbs nitric oxide, with the formation of the same compound. It oxidises slowly in the air to white ferric phosphate.

Other similar salts have not yet been characterised, but it is noteworthy that the sparingly soluble ferrous oxalate gives a readily soluble nitric oxide oxalate.

Manchot and Huttner have shown previously (A., 1910, ii, 414) that the quantity of combined nitric oxide in the equilibrium  $\text{FeCl}_2 + \text{NO} \rightleftharpoons \text{FeCl}_2\text{NO}$ , is at first diminished by the addition of increasing quantities of hydrochloric acid, and then increases to a limiting value of 1 mol. of nitric oxide to 1 atom of iron. By similar methods it is now shown that the same holds for the equilibrium  $\text{FeBr}_2 + \text{NO} \rightleftharpoons \text{FeBr}_2\text{NO}$ , as influenced by the presence of hydrobromic acid.

Further experiments with copper salts (fluoride, bromide, nitrate, acetate, tartrate, formate, and glycolate) have shown that only the sulphate, chloride, and bromide combine with nitric oxide according to the reversible action:  $\text{CuR}_2 + \text{NO} \rightleftharpoons \text{CuR}_2\text{NO}$ . The combination takes place in alcoholic solution, the presence of water greatly diminishing the amount of combination.

Migration experiments showed that the brown ferrous nitric oxide compounds contain the complex cation  $(\text{FeNO})^{++}$ , whereas in the green compounds a complex ferrous anion containing nitric oxide exists (compare A., 1910, ii, 414). The red solutions of ferrous sulphate and of copper sulphate in concentrated sulphuric acid containing nitric oxide are quite indifferent to the action of the electric current.

The combination with nitric oxide seems to be characteristic of the normal ferrous (and cupric) compounds, and not of those in

which the metal is present in a stable complex ion; for example, if 2:2'-dipyridyl is added to a solution of ferrous sulphate saturated with nitric oxide, the stable tri-2:2'-dipyridyl ferrous complex is formed, and the nitric oxide is quantitatively evolved. If the complex is less stable, as, for example, in the ferropentacyanamine salts, nitric oxide can enter into combination (compare Manchot, Merry, and Woringer, A., 1912, i, 955). The author is of the opinion that when combination with nitric oxide occurs, the addition is primarily to the whole molecule of the salt, and not to the ion.

The fact that the deep red ferrotridipyridyl salts do not absorb nitric oxide shows that there is no necessary connexion between the colour of iron compounds and their power of absorbing gases (compare Werner, A., 1912, i, 298). T. S. P.

**Transformation Phenomena in Sodium Molybdates and Tungstates.** I. M. AMADORI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 707—711. Compare van Klooster. this vol., ii, 167).—The transformation points of sodium molybdate found by the cooling method are  $616^{\circ}$ ,  $580^{\circ}$ , and  $410^{\circ}$ . When obtained by heating curves, they are found at  $634^{\circ}$ ,  $592^{\circ}$ , and  $444^{\circ}$ . Experiments with sodium tungstate indicate the existence of two transformation points ( $582^{\circ}$  and  $571^{\circ}$ ), and reasons are adduced against Klooster's views, based on observations of the heating curve, that there is only one.

R. V. S.

**The Hydrolysis of Stannic Chloride and Bromide.** PAUL PFEIFFER [with E. MÜLLER and E. PROS] (*Zeitsch. anorg. Chem.*, 1914, 87, 235—247).—The mechanism of hydrolysis of stannic haloids has been studied by means of a comparison with the products of alcoholysis. The hydrates of stannic chloride and bromide and the corresponding basic salts are shown from their conductivities not to be aquo-salts, but non-ionised compounds of the class of the compound of stannic chloride with pyridine. Hydrolysis is preceded by the formation of additive compounds.

*Tin hydroxytrichloride*,  $\text{SnCl}_3\text{OH}\cdot 3\text{H}_2\text{O}$ , is prepared from the compound containing ether (A., 1905, ii, 594). It dissolves in water to a clear solution, and also in organic solvents. The corresponding *bromide*,  $\text{SnBr}_3\text{OH}\cdot 3\text{H}_2\text{O}$ , is also crystalline, but decomposes without melting.

The compounds  $\text{SnCl}_4\cdot 2\text{EtOH}$  and  $\text{SnCl}_4\cdot 2\text{MeOH}$  are crystalline. The glycol compound,  $\text{SnCl}_4\cdot 2\text{C}_2\text{H}_4(\text{OH})_2$ , has m. p.  $124\text{--}130^{\circ}$ , and the *bromide*,  $\text{SnBr}_4\cdot 2\text{C}_2\text{H}_4(\text{OH})_2$ , is also crystalline. The *glycol acetate*,  $\text{SnCl}_4\cdot \text{C}_2\text{H}_4(\text{OAc})_2$ , has m. p.  $60^{\circ}$ . C. H. D.

**The Binary System Stannous Chloride-Lithium Chloride.** G. RACK (*Centr. Min.*, 1914, 326—328. Compare A., 1913, ii, 605).—Stannous chloride (m. p.  $239^{\circ}$ ) and lithium chloride (m. p.  $609^{\circ}$ ) mix completely in fusions, but do not form mixed crystals. There is a eutectic at  $215^{\circ}$  with 15 mol. %  $\text{LiCl}$ . The system  $\text{SnCl}_2\text{--PbCl}_2$  forms a continuous series of mixed crystals, and the systems of lead chloride with alkali chlorides are analogous to those of tin chloride with the corresponding alkali chlorides. L. J. S.

**Investigations at High Temperatures. IV. The Preparation of Articles from Zirconia.** OTTO RUFF and GEORG LAUSCHKE (*Zeitsch. anorg. Chem.*, 1914, **87**, 198—208. Compare A., 1913, ii, 960; this vol., ii, 474).—The zirconia is pressed into shape in a mould and dried at 120—130°, and is then heated very gradually to 1500° in a gas furnace, and maintained for two hours at that temperature. It is found that the greatest resistance to high temperatures (2000—2400°) is given by zirconia obtained by precipitating the hydroxide and igniting at 1400° for ten hours, whilst natural zirconia, containing 83·5%  $\text{ZrO}_2$ , gives the lowest porosity, but crucibles of this material cannot be employed above 1900°, as they soften and lose silica by volatilisation. They require much less rapid heating than crucibles of purified zirconia. The addition of 1% of dry starch when mixing is of advantage, but increases the porosity. C. H. D.

**Preparation of the Elements Thorium, Uranium, Zirconium, and Titanium.** D. LELY, jun. and L. HAMBURGER (*Zeitsch. anorg. Chem.*, 1914, **87**, 209—228).—The method adopted is the reduction of the anhydrous chlorides by means of sodium. For this purpose it is necessary to have the chlorides in a compact, crystalline form, in order to lessen their hygroscopic qualities, and to conduct the operations in a vacuum.

Thorium chloride is best prepared by heating the oxide in a stream of chloride and sulphur chloride at 670°, and subliming the crystalline product in a vacuum. The sodium is also purified by distillation in a vacuum. The solid thorium chloride and sodium are then heated together to 700° in an exhausted steel vessel. Metallic thorium is thus readily obtained, containing 1%  $\text{ThO}_2$ . It is rendered compact by compressing to form a rod, and passing an alternating current through it, contained in a specially designed vacuum furnace. Sintering yields a compact metal, which may be hammered to a thin rod at the ordinary temperature. Thorium is more readily fusible than tungsten, and may be completely volatilised by heating on a tungsten strip. The compact metal is very stable towards reagents.

Uranium tetrachloride is prepared and purified in the same manner. Reduction takes place readily, and the metal may be rendered compact by heating in an alundum tube in an exhausted vessel. It becomes hard and conducting at 1400°, and may then be transferred to the sintering furnace. Metallic uranium is less malleable than thorium. It is readily dissolved by hydrochloric or nitric acid, but is stable towards water and alkalis.

Zirconium chloride is best prepared by the action of chlorine and carbon tetrachloride on the oxide at 800°. It is used without resublimation. The metal is rendered compact by sintering, and is then highly ductile. It is very resistant to acids, except hydrofluoric and hot concentrated sulphuric acids, and aqua regia.

Titanium chloride is best prepared by the action of chlorine on ferro-titanium (62% Ti), the temperature being kept down to

400—500° in order to avoid the sublimation of ferric chloride. Titanium is much more reactive than the other metals examined.

C. H. D.

**Resistance of Platinum Vessels to Hot Nitric Acid.** GREGORY PAUL BAXTER and FRED LESLIE GROVER (*J. Amer. Chem. Soc.*, 1914, **36**, 1089—1091 \*).—In a paper on the atomic weight of selenium, Jannek and Meyer (*A.*, 1913, ii, 948) have stated that when 10 c.c. of halogen-free nitric acid, distilled through a platinum condenser, were evaporated to dryness in a platinum crucible, a non-volatile residue was left, weighing 0.00228 gram.

Experiments have now been carried out which show that concentrated nitric acid, distilled through well-seasoned platinum, does not contain any perceptible quantity of dissolved impurities, and is, in fact, as pure as that distilled through quartz. The large residues obtained by Jannek and Meyer were probably due either to the use of vessels of impure platinum, to their insufficient cleaning, or to the presence of traces of hydrochloric acid in the nitric acid.

E. G.

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### Mineralogical Chemistry.

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**The Solvents of Coal.** LÉO VIGNON (*Compt. rend.*, 1914, 158, 1421—1424.† Compare Bedson, A., 1908, ii, 302).—The author has determined the soluble matter in coal when extracted in the cold and at the boiling point by alcohol, ether, benzene, toluene, aniline, and nitrobenzene respectively. Aniline exerts the greatest solvent action, and it is found to dissolve about 26% of good gas coal, but only 2% of a poor gas coal. The soluble matter was precipitated on the addition of acid. The soluble and insoluble portions of the coal were analysed, and the character of the coke obtained from them was determined. The soluble portion is richer in hydrogen, poorer in ash, and gives an agglomerated, bulky coke, whilst the insoluble portion gives a powdery coke. Pyridine and quinoline were also tried as solvents at their boiling points, and the latter was found to possess a solvent action almost three times as great as that of the former. W. G.

**Composition of Bornite and its Relation to Other Sulpho-minerals.** E. H. KRAUS and J. P. GOLDSBERRY (*Amer. J. Sci.*, 1914, [iv], 37, 539—553).—Crystals of bornite from Bristol, Connecticut, are described, and several new crystal forms are recorded. Analysis of pure, crystallised material, proved to be homogeneous by metallographic methods, gave the results under I, corresponding with the formula  $\text{Cu}_{12}\text{Fe}_2\text{S}_9$ . Since these results differ from those obtained by Harrington (A., 1904, ii, 46) on crystals from the same

\* and *Zeitsch. anorg. Chem.*, 1914, 87, 353—356.

† and *Bull. Soc. chim.*, 1914, [iv], 15, 540—544.

locality, a portion of Harrington's material has been re-analysed, with the results under II, confirming the formula given by him for this sample of material, namely,  $\text{Cu}_{10}\text{Fe}_2\text{S}_8$ :

	Cu.	Fe.	S.	Total.	Sp. gr.
I.	65.665	9.705	24.650	100.020	5.086
II.	63.18	11.38	25.43	99.99	5.072 (Harrington)

The wide variations in composition shown by these and other analyses of bornite may be expressed by the formula  $\text{Cu}_x\text{Fe}_y\text{S}_z$ , where  $y = \frac{x}{2} + 3$ . The individual analyses fall into a more or less continuous series ranging from  $\text{Fe}_2\text{S}_3$  to  $\text{Cu}_2\text{S}$  (chalcocite), in which other intermediate members are chalcopyrite,  $\text{Cu}_2\text{Fe}_2\text{S}_4$ , and barnhardtite ( $\text{Cu}_4\text{Fe}_2\text{S}_5$ ). There is a progressive change in the sp. gr. (from 4.2 for chalcopyrite to 5.51 for chalcocite), and in the topic axes throughout the series.

The numerous thio-salts known as minerals are reduced to the same type,  $\text{M}'_x\text{R}'''\text{S}_y$ , where  $\text{M}'$  is copper, silver, lead, etc., and  $\text{R}'''$  is arsenic, antimony, or bismuth. In the majority  $y = \frac{x}{2} + 3$ , but in some  $y = \frac{x}{2} + 6$ , etc. Morphotropic series similar to the one ( $\text{Fe}_2\text{S}_3$ — $\text{Cu}_2\text{S}$ ) noted above are indicated, for example,  $\text{As}_2\text{S}_3$ — $\text{PbS}$  (including orpiment, sartorite, etc., and galena) and  $\text{Sb}_2\text{S}_3$ — $\text{Ag}_2\text{S}$  (including stibnite, miargyrite, pyrrargyrite, etc., and argentite).

L. J. S.

**"Heliodors" from South-west Africa.** OTTO HAUSER and H. HERZFELD (*Chem. Zeit.*, 1914, 38, 694—695).—The mineral "heliodor" crystallises in yellow, hexagonal prisms,  $D = 2.74$ , showing double refraction of negative type. Its behaviour on cleavage is consistent with the view that it belongs to the group of beryls. Analysis gave:

$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{GlO}$ .	$\text{SiO}_2$ .	Total.
18.60	0.55	13.88	66.89	99.92

It also contains a small amount of uranium, the quantity of which was approximately determined as  $\text{U}_3\text{O}_4$  0.02—0.04%. The colour of the mineral is mainly determined by the iron content.

Under the influence of cathode rays it gives rise to a blue phosphorescence, and when the action is prolonged the colour of the mineral changes from yellow to grey. It is opalescent, and exhibits a weak green fluorescence. Corresponding with the uranium content, it is also found to be slightly radioactive. H. M. D.

**Epidote and Garnet from the Mine of Brosso (Piedmont).** E. GRILL (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 535—538).—The epidote (*pistacite*) has the composition:

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Total.
38.02	19.00	16.20	24.49	6.37	2.31	100.39

Under  $\text{Fe}_2\text{O}_3$  is included 1.06%  $\text{FeO}$ . The garnet is of the grossularia variety.

R. V. S.

**Garnet in Asbestos from the Binnental.** LAURA HEZNER (*Centr. Min.*, 1914, 325).—Small, transparent, emerald-green, rhombic dodecahedra and grains of garnet occur loosely embedded in matted asbestos. The following analysis shows the material to be nearly pure andradite,  $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ :

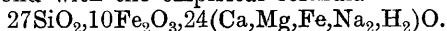
$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Total.
35.40	0.45	31.19	0.08	32.91	0.18	0.27	100.48

L. J. S.

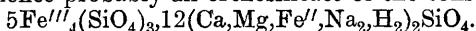
**Speziaite, a New Amphibole from Traversella.** LUIGI COLOMBA (*Atti R. Accad. Sci. Torino*, 1914, 49, 625—634).—The thick, granitiferous pyroxenites of the Riondello deposits at Traversella contain fibres, sometimes isolated and sometimes united in bundles, of a mineral which, although referable to the group of monoclinic amphiboles, the author regards as a distinct variety or perhaps an independent mineral species. This mineral, to which the name *speziaite* is given, may possibly be formed at the expense of pre-existing pyroxene, but is more probably of posterior formation. It forms either geodes or drusy masses of dark green or intense brown, monoclinic fibres;  $\beta = 73\text{--}74^\circ$ ,  $D = 3.362$ . Analysis gives the results:

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
36.21	0.79	34.57	10.53	7.87	3.56	0.67	4.08	0.93	0.50	99.71

which correspond with the empirical formula



Speziaite is hence probably an orthosilicate of the constitution:



T. H. P.

**Fluorine in Mineral Waters.** ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1914, 158, 1631—1640).—By the method already described (compare A., 1912, ii, 805, 806) the authors have estimated the fluorine content of a large number of mineral waters of differing type and origin, including sea-water at different depths and waters of volcanic origin. From their results they draw the following conclusions.

Fluorine exists in all mineral waters, whether cold or thermal, in amounts varying from 0.15 to 6.32 mg. per litre. The waters richest in fluorine are those of volcanic origin. Waters from cold surface springs, particularly those rich in calcium sulphate, may contain upwards of 2 mg. of fluorine per litre, owing to solution of the calcium fluoride, originally deposited with the gypsum. Neither in waters from the same centre nor in those from different centres is there any relationship between fluorine content and temperature. In waters of the same origin, the fluorine content, whilst not proportional to, generally varies in the same direction as, the total salinity, although there are exceptions. Waters containing sulphur dioxide or hydrogen sulphide have the highest fluorine content with respect to total salinity. In sea-water the fluorine

content varies very little either with the locality or the depth, and is generally about 0.30 mg. per litre. Seismic disturbances produce an immediate and notable effect on the fluorine content of thermal waters, producing an increase in one case of nearly 100%, although after a year the water had returned to its initial content. W. G.

**Boron in Mineral Waters.** H. FONZES-DIACON and FABRE (*Compt. rend.*, 1914, 158, 1541—1542).—The authors have estimated the amount of boron in a number of mineral waters from different sources by Bertrand and Agulhon's colorimetric method (compare A., 1910, ii, 241). In the different springs at Vichy the boron content seems to increase with the temperature of the springs.  
W. G.

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## Analytical Chemistry.

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**Copper Cathode in Electroanalysis.** JULIO DE GUZMÁN CARRANCIO (*Anal. Fis. Quim.*, 1914, **12**, 297—305).—A copper electrode may replace one of platinum without loss of accuracy in the estimation of copper, nickel, cobalt, zinc, cadmium, and silver.

G. D. L.

**Estimation of Chlorine Ions in Natural Waters.** L. W. WINKLER (*Zeitsch. anal. Chem.*, 1914, **53**, 359—362).—To 100 c.c. of the sample is added 1 c.c. of 10% potassium chromate and then silver nitrate solution (1 c.c.=1 mg. of chlorine) until the colour turns reddish, which coloration is then again discharged by a drop of dilute sodium chloride solution. This greenish-yellow liquid serves for comparison. To another 100 c.c. of the sample is then also added 1 c.c. of potassium chromate and then silver solution until, when compared with the first test, a just perceptible reddish coloration sets in which lasts for at least five minutes. Artificial light should be employed.

L. DE K.

**Estimation of Iodine, especially in Organic Substances.** R. GRÜTZNER (*Chem. Zeit.*, 1914, **38**, 769—770).—A weighed quantity of the substance is mixed with powdered sodium hydroxide, moistened, dried, sodium peroxide or barium peroxide is added, and the mixture is incinerated. After cooling, a small quantity of charcoal is added and the mixture is again heated. The fused mass is then dissolved in water and the solution is filtered; when barium peroxide has been used, the solution may be treated with carbon dioxide and sodium sulphate before filtration. The alkaline solution is now boiled after the addition of a small quantity of potassium permanganate, then acidified with sulphuric acid, boiled, rendered alkaline, and again boiled after the addition of alcohol. The mixture is filtered while hot, excess of alcohol is expelled by boiling the filtrate, which is then rendered slightly acid with a

mixture of sulphuric acid and phosphoric acid, ammonium sulphate is added, the whole is boiled for three minutes, cooled, and the iodic acid is titrated after the addition of sulphuric acid and potassium iodide. Six atoms of iodine thus liberated and titrated correspond with 1 atom of iodine in the original substance.

W. P. S.

**Estimation of Organically Combined Iodine in Preparations, especially in Iodine-Albumin Preparations.** F. ECKARDT (*Pharm. Zeit.*, 1914, 59, 441. Compare A., 1914, ii, 286).—About 1 gram of the substance is moistened in a flat-bottomed basin with 3 c.c. of 30% sodium hydroxide solution and, after some hours, the mixture is heated cautiously and then incinerated. The carbonised residue is dissolved in water, rendered slightly acid with tartaric acid, and then treated with 3 c.c. of dilute sulphuric acid. The solution is shaken with carbon disulphide after the addition of sodium nitrite, and the solution of the iodine in carbon disulphide is titrated with thiosulphate solution.

W. P. S.

**Greeff's Method for the Volumetric Estimation of Fluorine.** I. BELLUCCI (*Ann. Chim. Applicata*, 1914, 1, 441–446).—The author has made a number of experiments with varying quantities of sodium fluoride in order to ascertain the accuracy and limits of applicability of the method of estimating fluorine devised by Greeff (A., 1913, ii, 975). The conditions given by the latter yield accurate results only when the amount of alkali fluoride does not differ greatly from 0.2 gram; thus 0.05, 0.04, and 0.02 gram taken gave respectively 0.0449, 0.0336, and 0.0078 gram found. With these smaller quantities of fluorides, approximate estimations may be effected if the titrations are carried out in the presence of proportionately small amounts of sodium chloride. T. H. P.

**Estimation of Sulphur in Iron Pyrites.** ERNEST MARTIN (*Mon. Sci.*, 1914, [v], 4, i, 866).—A few further remarks on the process already communicated (this vol., ii, 287). The barium hydroxide solution employed should be titrated and reduced to exactly 21.87 grams of barium oxide per litre. In the assay of pyrites, 60 c.c. and, in the case of burnt pyrites, 25 c.c. of the solution should be used. When passing the current of carbon dioxide, this should be stopped before the pink colour (due to phenolphthalein) has entirely gone. A complete decolorisation soon follows. After titration, it is necessary to ensure that a sufficiency of barium has been used by adding a few drops of barium chloride which should give no turbidity. L. DE K.

**Estimation of Sulphides in Lime Liquors.** JOHN R. BLOCKEY and P. V. MEHD (*Collegium*, 1914, 73–75).—A reply to McCandlish and Wilson (A., 1913, ii, 1068); trustworthy results may be obtained in the titration of sulphides in lime liquors by means of ammoniacal zinc sulphate solution, provided that ammonium

chloride is added to the latter solution. The presence of ammonium chloride prevents the precipitation of zinc hydroxide by the calcium hydroxide present in the liquor. W. P. S.

**Gravimetric Estimation of Tellurium.** A. GUTBIER and J. HUBER (*Zeitsch. anal. Chem.*, 1914, **53**, 430—433).—The process given by Lenher and Homberger and partly based on the fact noticed by Gutbier that hydrazine hydrochloride is an excellent reducing agent for tellurium compounds is strongly recommended by the authors.

The solution of the compound in 10% hydrochloric acid is boiled and mixed first with 15 c.c. of a saturated solution of sulphur dioxide, then with 10 c.c. of 15% aqueous hydrazine hydrochloride, and then again with another 25 c.c. of sulphur dioxide solution. The tellurium is precipitated after five minutes' boiling, and may then be collected, washed with water and finally with alcohol, and dried at 100—105°. L. DE K.

**Properties and Applications of Amalgamated Aluminium.** CLÉMENT BERGER (*Rev. gén. Chim. pure appl.*, 1914, **17**, 1—4).—Aluminium amalgam may be used to reduce concentrated solutions of nitrates or nitrites to ammonia, according to the equation,  $6\text{KNO}_3 + 16\text{Al} + 42\text{KOH} = 6\text{NH}_3 + 16\text{K}_3\text{AlO}_3 + 12\text{H}_2\text{O}$ , and the process may be applied to the estimation of those compounds.

J. C. W.

**Estimation of Ammonia in Illuminating Gas.** J. D. EDWARDS (*J. Ind. Eng. Chem.*, 1914, **6**, 468—469).—Experiments with various forms of apparatus for containing the standard acid employed for the absorption of the ammonia yielded results showing that the Emmerling tower, the Lacey apparatus, the ordinary gas wash-bottle, the official (American) apparatus, and a modified form of the Cumming wash-bottle (in which the gas passes through a small nozzle and circulates the acid continuously), all act as efficient absorption apparatus. Sodium alizarinsulphonate is recommended as a sensitive indicator for use in the titration of solutions containing ammonium salts. W. P. S.

**Proposed Modification of the Kober Method for Quantitative Ammonia Distillation by Aeration.** F. L. DILLINGHAM (*J. Amer. Chem. Soc.*, 1914, **36**, 1310—1312).—In carrying out some experiments by the method described by Kober and Graves (A., 1913, ii, 978), it was found that the ammonia could not be entirely removed. If, however, gentle heat is applied during the aeration process, the whole of the ammonia from ammonium sulphate can be recovered in one and a-half hours. E. G.

**New Modification of the Kjeldahl Method.** L. MARINO and F. GONNELLI (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 523—530).—The use of vanadium pentoxide as a catalyst in the Kjeldahl process has been suggested by Oefele (*Pharm. Zentr.-h.*, 1911, **52**, 1121),

but according to the authors' results recorded in this paper, his method yields figures showing an error of about 1%. Accurate results are obtained, however, by boiling the organic substance (about 1 gram) with 20 c.c. of concentrated sulphuric acid, 7 grams of potassium sulphate and 0.2 gram of vanadium pentoxide until an emerald-green solution is formed. This method may be employed with advantage in cases where Gunning's modification does not suffice to convert all the nitrogen present into ammonia.

R. V. S.

**Indicating Stopper for Some Distillations.** ANNIBALE FERRARO (*Boll. chim. farm.*, 1914, 53, 8—9).—In the distillation in Kjeldahl's process it is convenient to provide the downward portion of the glass tube leading to the condenser with a tubulature at one side. In this is fitted a ground glass stopper, the lower end of which (projecting into the tube) has a small receptacle containing a drop of litmus. The end of the distillation can then be recognised easily.

R. V. S.

**Comparison of Neutral Ammonium Citrate with Sodium Citrate and *N*/10-Citric Acid.** PAUL RUDNICK, W. B. DERBY, and W. L. LATSHAW (*J. Ind. Eng. Chem.*, 1914, 6, 486—487).—The results obtained by the use of sodium citrate solution in the estimation of citrate-soluble phosphoric acid as proposed by Bosworth (this vol., ii, 289) do not agree with those yielded with normal ammonium citrate solution unless a relatively concentrated solution of sodium citrate (500 grams per litre) is employed, and even then the results are not always trustworthy. More favourable figures are obtained when *N*/10-citric acid is used as a substitute for ammonium citrate.

W. P. S.

**Sources of Error in the Analysis of Basic Slag.** M. POPP (*Chem. Zeit.*, 1914, 38, 741—742).—Care should be taken to mix the sample after it has been passed through a sieve, since the sifting operation tends to form layers of material of unequal composition. In the estimation of the phosphoric acid soluble in citric acid, the substance should be shaken for exactly thirty minutes with the acid solution, and the solution then poured on a large filter; fresh portions of the solution should not be added to the latter as it empties, since the solution which remains in contact with the substance meanwhile dissolves further quantities of phosphoric acid. Fifty c.c. of the filtrate are then treated as described previously by the author (*A.*, 1912, ii, 992).

W. P. S.

**Estimation of Phosphates in Soil Extracts.** JAMES ARTHUR PRESCOTT (*J. Agric. Sci.*, 1914, 6, 111—120).—A portion of the extract containing 5—10 mg. of phosphoric oxide is evaporated to dryness, ignited at a dull red heat for fifteen minutes (Neubauer, *A.*, 1906, ii, 52), and digested with 50 c.c. of 10% sulphuric acid for half an hour on a sand-bath. It is then filtered, washed with hot water, and diluted to 110 c.c. The solution is then

treated with 25 c.c. of ammonium nitrate solution (50%), heated to 55°, and precipitated with 25 c.c. of ammonium molybdate solution, previously heated to 55°. After two hours the solution is decanted through a filter and the precipitate washed by decantation several times with 2% sodium nitrate solution, until no longer acid. The filter is transferred to the beaker and the precipitate dissolved in standard alkali and titrated back. The factor for *N*/10-alkali is 1 c.c.=0.0003004 gram of  $P_2O_5$ .

The ammonium molybdate solution is made by dissolving 150 grams of ammonium molybdate in 1000 c.c. of water and adding the solution to 1000 c.c. of nitric acid (D 1.2). N. H. J. M.

**Estimation of Carbon in Steel and Iron by the Barium Carbonate Titration Method.** J. R. CAIN (*J. Ind. Eng. Chem.*, 1914, 6, 465—468).—Details of procedure are given for the titration of barium carbonate resulting from the absorption of carbon dioxide in barium hydroxide solution in the estimation of carbon by combustion. The barium carbonate is collected on an asbestos filter by attaching the Meyer absorption tube directly to the latter, and washed, out of contact with air, with 150 c.c. of water. A slight excess of *N*/10-hydrochloric acid is then added to the carbonate, a portion of the acid being used to rinse out the Meyer tube, and the excess of acid is titrated, using methyl-orange as indicator. W. P. S.

**Estimation of Carbon Dioxide in Air. A Simple and Expeditious Method.** W. M. DOHERTY (*Report. Austral. Ass. Adv. Sci.*, 1913, 14, 100—102).—Several 100 c.c. flasks (say, ten in number) filled with water free from carbon dioxide are emptied at the place where the sample of air is to be taken. The stoppers are then inserted and the samples are tested on the spot or in the laboratory. To the flasks are added arithmetically progressive quantities of standard sodium carbonate solution containing phenolphthalein solution until a limit is reached beyond which it is unnecessary to go. The sodium carbonate solution is of such strength that 1 c.c. is equivalent to 0.01 c.c. of carbon dioxide. W. P. S.

**A Heat-compensated Conductivity Salinometer.** MYER COPLAUS (*J. Path. Bact.*, 1914, 572—576).—The instrument consists of a U-tube, in which the conductivity of a solution is measured between platinum points in insulated copper electrodes. Compensation for temperature is automatically effected by means of "compound bars" (brass and steel strips) connected to the electrodes. When the temperature rises, the bars contract and the electrodes are raised; when it falls, the opposite occurs; a difference in the length of the column between the electrodes thus estimates the effect of temperature. Full details and drawings are given; and a tabular addendum on the saline conductivity of the more important constituents of sea-water is given; these were made by W. Gibbs Lloyd. W. D. H.

**A Simple Method of Estimating the Content of Colloidal Silver Preparations.** F. LEHMANN (*Arch. Pharm.*, 1914, 252, 9—12).—Owing to the presence of silver chloride in "collargol" and other colloidal silver preparations, the method of determining the silver content by removing the organic matter by ignition, and estimating the silver in the residue by solution in nitric acid and titration with thiocyanate, does not give accurate results.

The author, therefore, adopts the following method. The silver preparation (0.2 gram) is treated with water (10 c.c.) and concentrated sulphuric acid (10 c.c.), and potassium permanganate (2 grams) added in small quantities at a time. The mixture is then evaporated until the sulphuric acid begins to volatilise, whereby the organic matter is destroyed and the silver chloride decomposed. After dilution with water and removal of the manganese dioxide by means of ferrous sulphate, the silver is estimated by titration with thiocyanate in the usual manner. F. B.

**Estimation of Silver in Collargol and in Organic Tissue-fluids.** P. W. DANCOWITZ (*Arch. Pharm.*, 1914, 252, 69—76).—For the estimation of silver in collargol and other colloidal silver preparations, the author adopts the following method.

The preparation is ignited to remove organic matter, and the residual silver and silver chloride are brought into solution by successive treatment with nitric acid and ammonia, sufficient ammonia being used to prevent the precipitation of silver chloride on mixing the two solutions.

An excess of standard potassium cyanide solution is then added, and the excess determined by titration with silver nitrate, potassium iodide being used as indicator. For the estimation of silver in lymph a colorimetric method is employed.

The lymph is evaporated to dryness on the water-bath, ignited to remove organic matter, and the residual silver and silver chloride dissolved by successive treatment with nitric acid and ammonia. The combined solutions are made feebly alkaline with ammonia and aqueous hydrogen sulphide is added. The solution is then acidified with nitric acid in order to dissolve the ferrous sulphide, derived from the iron of the blood with which the lymph is always mixed, and the coloration due to the silver sulphide matched with that obtained from a silver nitrate solution of known content.

The author claims that 0.02 mg. of silver can be readily estimated by this method. F. B.

**Estimation of the Hardness of Water.** L. W. WINKLER (*Zeitsch. anal. Chem.*, 1914, 53, 409—415).—The temporary hardness (earthy carbonates) is best determined in 100 c.c. by Lunge's acidimetric process. The total hardness is then estimated in the neutral liquid by Blacher's process (titration with potassium palmitate with phenolphthalein as indicator).

In order to find the hardness caused by calcium only the author

titrates with potassium oleate, as in Clark's process. In order to prevent the co-precipitation of magnesia 5 c.c. of the following reagent are first added.

One hundred grams of pure sodium potassium tartrate and 10 grams of sodium hydroxide are dissolved in 150 c.c. of warm water, and when cold 250 c.c. of 10% ammonia are added, and the whole is diluted to 500 c.c.

Very hard waters should be suitably diluted before titration.

L. DE K.

**Separation of Glucinum and Uranium.** M. WUNDER and P. WENGER (*Zeitsch. anal. Chem.*, 1914, **53**, 371—374).—To 100 c.c. of the solution containing the chlorides or nitrates of these metals (about 0.25 gram of joint oxides) are added 10 c.c. of a 3% solution of hydrogen peroxide and the whole is heated on the water-bath until a rapid evolution of oxygen takes place and the yellow

**Gel Filtration of Ultra-microscopic and Other Particles.**

**The Action of Asbestos.** MYER COPLAUS (*J. Path. Bact.*, 1914, **18**, 581—590).—A freshly prepared layer of aluminium hydroxide acts as an efficient filtering medium, but after a few hours fissures appear in the layer, due to shrinking, and filtration is then no longer efficient. Fissuring may be prevented by several methods, among which is admixture with inert fibrous substances, such as floss asbestos. This led to the investigation of asbestos, and it was proved that this substance is not inert, and simple adsorption is not regarded as adequate to explain the phenomena observed. It has many actions on fluids in contact with it; for instance, dilute solutions of curare, strychnine, adrenaline, etc., readily lose their active principle.

W. D. H.

**Equilibria in Ternary Systems. XIV.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1136—1152. Compare this vol., ii, 350).—A further theoretical discussion of types of equilibrium in ternary systems.

H. M. D.

**Equilibria in the Systems, Water, Acetone, and Inorganic Salts.** GEO. B. FRANKFORTER and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1914, **36**, 1103—1134).—Frankforter and Frary (A., 1913, ii, 685) have shown that potassium fluoride is very effective in salting out ethyl and propyl alcohols from aqueous solutions, and it has now been found that this salt has a similar action on aqueous solutions of acetone.

A study has been made of the systems containing: (1) potassium fluoride, water, and acetone; (2) potassium carbonate, water, and acetone; (3) calcium chloride, water, and acetone; and (4) sodium chloride, water, and acetone. The isotherms at 20° for these systems are given and investigated. Temperature effects in the systems are noted; no upper critical solution temperatures were found, but the lower critical solution temperatures of a series of solutions are recorded.

Of the four systems, it has been found that anhydrous potassium fluoride and anhydrous potassium carbonate are equally efficient in dehydrating acetone, but potassium fluoride is the more rapid, and gives sharper separations. Calcium chloride, in large excess, dehydrates the acetone completely, whilst sodium chloride

is titrated without delay, and with energetic shaking with *N*/100-thiosulphate as usual.

L. DE K.

**Colorimetric Estimation of Lead and Copper in Potable Water.** C. REESE and J. DROST (*Zeitsch. angew. Chem.*, 1914, 27, 307—312).—Two methods are recommended. In the first, the lead is estimated colorimetrically as sulphide in acetic acid solution, the comparisons being made against solutions containing known quantities of lead and prepared with water of the same composition (but originally free from lead) as the water under examination. When copper is present in addition to lead, the two metals are estimated together, colorimetrically, and the lead then separately in the presence of cyanide. In the second method, the two metals are precipitated as their sulphides, collected on an asbestos filter, the lead is separated as sulphate and estimated colorimetrically as sulphide, whilst the copper is estimated in the filtrate from the lead sulphate.

W. P. S.

**The Rapid Electrolytic Separation of Copper from Arsenic.** A. SIEVERTS and W. WIPPELMANN (*Zeitsch. anorg. Chem.*, 1914, 87, 169—174. Compare Richardson, this vol., ii, 148).—Copper may be completely separated from arsenic in nitric acid solution by electrolysis with gauze electrodes and rapid stirring, provided that the arsenic is in the quinquevalent condition, and that the passage of the current is not continued long after the copper is deposited. The conditions as to acidity are given by Richardson.

Ammoniacal solutions may also be used. Using concentric gauze electrodes, 0.1—0.3 gram of copper, in the presence of 0.2 gram of arsenic, may be deposited in a pure condition in fifteen minutes, the volume being 125 c.c., containing 5% of ammonia and 2% of ammonium nitrate at 90°, the current used being 5 amperes. The arsenic acid is not reduced and may be precipitated directly from the solution by magnesia mixture.

C. H. D.

**New Procedure for the Separation of the Copper and Tin Groups.** LOUIS J. CURTMAN and JOSEPH K. MARCUS (*J. Amer. Chem. Soc.*, 1914, 36, 1093—1103).—In view of the disadvantages of the ammonium polysulphide method of separating the metals of the copper and tin groups, a study has been made of other methods which have been suggested for the purpose, namely, the sodium carbonate, sodium hydroxide, and potassium hydroxide methods. These have been tried both alone and in conjunction with hydrogen peroxide, but have not proved altogether satisfactory.

A scheme of analysis has been devised which is free from the objections to the ammonium polysulphide method and provides adequately for the systematic detection of quinquevalent arsenic. The filtrate from group I is treated with hydrogen sulphide to precipitate alkali earth metals together with some of the lead. The filtrate from this precipitate is treated with sulphur dioxide, before passing in hydrogen sulphide, in order to oxidise stannous



tin and to reduce quinquevalent arsenic. The sulphides of the divisions of group II are separated completely by means of potassium hydroxide. The results of several test analyses are quoted, which show that the method is trustworthy. E. G.

**Electrolytic Reduction of Iron for Permanganate Titration.** H. C. ALLEN (*J. Amer. Chem. Soc.*, 1914, **36**, 937—949).—This work was undertaken in order to determine whether in certain analytical operations it is possible to effect the quantitative oxidation or reduction of a substance by means of the electric current before titrating it with a standard solution.

It has been found that ferric iron can be completely reduced by using a large rotating platinum cathode and a small platinum wire anode if the concentration of sulphate is small. By using a soluble anode and platinum cathode, complete reduction is possible with a wide range of acidity, but with low acidity and high current density some of the iron may be deposited on the cathode. When a platinum anode is used, chlorides must be absent, but with a soluble anode, they may be present, unless too high a current density is employed. By using a short-circuited cell with a platinum gauze cathode and zinc anode, complete reduction can be obtained with a wide range of acidity; in this case, chlorides do not interfere with the reduction. In most cases, the best method is to use a short-circuited cell with a copper gauze cathode and amalgamated zinc rod anode; the concentration of the acid must be at least 10 c.c. of concentrated sulphuric acid in 175 c.c. of solution. Under these conditions, 0.12 gram of iron can be reduced at the ordinary temperature in eight minutes with a zinc efficiency of 70%. The rate of reduction is increased in all cases by a rise of temperature. E. G.

**Estimation of Iron in Natural Waters.** OTTO MAYER (*Pharm. Zeit.*, 1914, **59**, 422).—In the case of waters containing large quantities of dissolved organic substances the total iron is estimated after the water has been evaporated and the residue incinerated and oxidised. Another portion of the water is treated with hydrochloric acid and bromine, and the iron is estimated colorimetrically, as described previously by the author (*A.*, 1912, ii, 809); the difference between the results of the two estimations gives the amount of iron in organic combination. The ferrous and ferric iron may also be estimated by modifying the latter method. W. P. S.

**Colorimetric Estimation of Iron in Water.** F. GÖTTE (*Zeitsch. Nahr. Genussm.*, 1914, **27**, 676—683).—The colorimetric method of estimating iron by means of potassium thiocyanate is liable to give low results when the ferrous salts present in a water have been oxidised previously by treatment with hydrochloric acid and potassium chlorate; more trustworthy results are obtained when the oxidation is effected with nitric acid. The error in the first case is due to the influence of the hydrochloric acid on the ferric thiocyanate and to a certain extent on the quantity of

thiocyanate added. The concentration of the acid should be 0.25 gram of hydrogen chloride per 100 c.c. of the solution, and not less than 5 c.c. of 10% potassium thiocyanate solution should be added. The influence of nitric acid is somewhat less than that of hydrochloric acid. Approximately the same concentration of acid and thiocyanate should be present in both the test solution and the comparison solution. The following procedure is recommended: 100 c.c. of the water are acidified with 1 c.c. of hydrochloric acid (D 1.125), a few crystals of potassium chlorate are added, and the mixture is evaporated to dryness. The residue is treated with 1 c.c. of hydrochloric acid (D 1.125), dissolved in water, diluted to 95 c.c., and 5 c.c. of 10% potassium thiocyanate are added. The coloration is compared with that produced by a known quantity of iron under similar conditions.

W. P. S.

**Estimation and Separation of Iron, Aluminium, Chromium, Zinc, and Manganese.** G. VAN PELT (*Bull. Soc. chim. Belg.*, 1914, **28**, 138—143. Compare this vol., ii, 493).—Iron and chromium cannot be completely separated by treatment under pressure with ammoniacal hydrogen peroxide according to the method of Jannasch, since, under these conditions, the chromium is not quantitatively converted into chromate. On the other hand, this change can be completely effected by passing chlorine into a mixture of ferric and chromium chlorides in the presence of an excess of sodium hydroxide. After removal of excess of chlorine, the iron is precipitated by ammonia. Oxidation can also be quantitatively effected by ammonium persulphate in the presence of nitric acid. Iron is directly precipitated in the solution as the hydroxide, whilst chromium is estimated in the filtrate after reduction with alcohol and hydrochloric acid or with hydrogen peroxide in acid solution. The results are excellent.

Chromium cannot be quantitatively separated from aluminium by means of ammoniacal hydrogen peroxide. This can, however, be readily accomplished by treatment with ammonium persulphate in the presence of hydrochloric acid. From the solution so obtained aluminium is precipitated by ammonium chloride and ammonia, and chromium is estimated in the filtrate in the usual manner.

Finally, a method is described for the separation of all the elements of this group. The solution of the chlorides of iron, aluminium, chromium, manganese, and zinc is diluted to 200—300 c.c., and heated on the water-bath with nitric acid and ammonium persulphate until the chromium is completely oxidised. The mixture is cooled and poured into a solution of ammonium chloride, ammonia, and concentrated hydrogen peroxide, which is warmed until separation of the hydroxides of iron, aluminium, and manganese is complete. The precipitate is dried and fused in a platinum crucible with successive portions of a mixture of equal weights of sodium carbonate and potassium nitrate. The cooled fusion is extracted with water, and the residual ferric oxide weighed. The filtrate is treated with hydrogen peroxide in acid solution (to convert the manganate into manganese salt), diluted,

treated with an excess of sodium hydroxide, and the manganese is precipitated by hydrogen peroxide. The filtrate is acidified with hydrochloric acid, and the aluminium precipitated by ammonia in boiling solution.

The original filtrate, containing chromium and zinc, is acidified, concentrated, and reduced with hydrogen peroxide. The residue is dissolved in water and ammonium chloride, and the chromium precipitated by ammonia. Finally, zinc is precipitated from the filtrate by boiling it with sodium carbonate until ammonia is completely expelled. Test analyses give excellent results. H. W.

**Estimation of Nickel with Dimethylglyoxime.** O. BRUNCK (*Zeitsch. angew. Chem.*, 1914, 27, 315—318).—Further experiments showing that the author's dimethylglyoxime method (A., 1907, ii, 989) is quite accurate, even in the presence of cobalt and iron, when the proper precautions are taken. L. DE K.

**Separation and Estimation of Tungstic Acid. A New Application of Nitron.** A. GUTBIER and G. L. WEISE (*Zeitsch. anal. Chem.*, 1914, 53, 426—430).—About 0.15 of the oxide is dissolved in a sufficiency of strong alkali, diluted with hot water to 150 c.c., acidified with acetic acid, and then precipitated at the boiling temperature with a slight excess of Busch's "nitron" acetate reagent. When cold the precipitate is collected, washed with a mixture of 96 c.c. of water and 4 c.c. of the reagent, and finally ignited to trioxide. L. DE K.

**Separation of Titanium from Iron, Aluminium, and Phosphoric Acid with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron").** WILLIAM M. THORNTON, jun. (*Amer. J. Sci.*, 1914, [iv], 37, 407—414).—To 100 c.c. of the solution containing about 0.4 gram of the mixed oxides are added 2 grams of tartaric acid, and after neutralising with ammonia 2 c.c. of dilute sulphuric acid (1:1) are added. Hydrogen sulphide is now passed until the iron is reduced to the ferrous state, and after adding slight excess of ammonia more gas is passed until the iron has precipitated completely as sulphide. After washing with dilute colourless ammonium sulphide, the filtrate is acidified with 40 c.c. of dilute sulphuric acid (1:1) and boiled to expel hydrogen sulphide. When cold, the liquid is made up to 400 c.c., and a 6% solution of "cupferron" is added in excess. The precipitate containing the titanium is collected and washed with dilute hydrochloric acid (1:10). After first drying at 110°, the compound is gradually ignited to oxide. L. DE K.

**New Method for the Estimation of Thorium in Monazite Sand.** R. J. CARNRY and E. D. CAMPBELL (*J. Amer. Chem. Soc.*, 1914, 36, 1134—1143).—Two rapid methods have already been suggested for the estimation of thorium in monazite sand, namely, the iodate method (Meyer and Speter, A., 1910, ii, 459) and the hypophos-

phate method (Rosenheim, A., 1912, ii, 869). The former method gives very accurate results, but it requires considerable care, and the reagent is somewhat expensive. In the case of the latter method, the reagent, sodium hypophosphate, cannot now be purchased.

A new rapid method is now described, which requires only inexpensive and easily procurable reagents, and gives results agreeing closely with those yielded by the iodate method. It is based on the fact that thorium, ceric, and zirconium pyrophosphates are insoluble in dilute acids, whilst the cerous salt and those of the other rare earth metals are readily soluble. The most convenient reagent for precipitating thorium pyrophosphate is the sodium salt,  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

In order to precipitate the thorium completely, the solution must be boiled after adding the sodium pyrophosphate, as otherwise 1—2 mg. of thorium will remain in solution. The acidity should be about 0.3*N* of hydrochloric acid. If the acidity is much too low, some of the thorium may fail to be precipitated owing to the formation of the double salt,  $\text{Na}_4\text{Th}(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ , and, if too high, some of the pyrophosphate may be dissolved by the acid.

The estimation of thorium in monazite sand is carried out in the following manner. The sand is decomposed completely by heating it with sulphuric acid, and the mixture is poured into water and stirred until the sulphates are dissolved. A portion of this solution is treated with hydrochloric acid and diluted, and sodium pyrophosphate solution is slowly added. The mixture is heated to boiling, boiled gently for five minutes, left for five to ten minutes, and then filtered. The precipitate is washed with hot water containing a little hydrochloric acid, and is then heated with sulphuric acid and a little ammonium perchlorate until all the organic matter has been oxidised. Water is added slowly, and the solution of the sulphate is poured into a solution of sodium hydroxide. The precipitated thorium hydroxide is boiled with dilute hydrochloric acid, a small quantity of saturated solution of sulphur dioxide is added, the solution heated to boiling, and the thorium again precipitated as pyrophosphate. This precipitate is again converted into the sulphate and hydroxide in the same way as before, the hydroxide is dissolved in hydrochloric acid, the solution diluted and boiled, and the thorium precipitated by the addition of oxalic acid. The oxalate is filtered, washed with water faintly acidified with hydrochloric acid, and converted into the oxide by ignition.

E. G.

**New Reaction of Vanadium.** VICENTE GARCÍA RODEJA (*Anal. Fis. Quim.*, 1914, 12, 305—309).—The ammonium salt of nitrosophenylhydroxylamine ("cupferron") gives a red precipitate with vanadic acid, and in dilute solutions a red colour, changing to green on oxidation of the reagent. The precipitation is not quantitative, except with a freshly prepared solution of the reagent. The limit of sensitiveness of the colour test is 1 millionth of a gram of vanadium per c.c.

G. D. L.

**Thermoelectric Method for the Determination of the Purity of Platinum Ware.** GEORGE K. BURGESS and P. D. SALE (*J. Ind. Eng. Chem.*, 1914, **6**, 452—454; *J. Washington Acad. Sci.*, 1914, **4**, 282—287).—The thermoelectromotive force of platinum as compared with that of many of its alloys may be used for ascertaining the purity of platinum. In the case of crucibles, etc., two pure platinum wires are connected with opposite sides of the crucible and with a galvanometer; the junction of one wire with the crucible is heated by a small blast flame, whilst the other is cooled by an air blast. A sheet of asbestos is inserted in the crucible to prevent radiation. Temperatures are measured by a platinum-rhodium wire (10% rhodium) joined to the crucible adjacent to the hot platinum wire, and connected through a commutator with the galvanometer. Measurements are made of the temperature at the hot part of the crucible and of the *E.M.F.* developed across the crucible at this temperature. The method provides a sensitive means of ascertaining whether or not the desired limitation of impurity, expressed in terms of iridium-content, is present.

W. P. S.

**Modification of Jäger's Method for Estimating Hydrogen and Methane.** J. P. WIBAUT (*Chem. Weekblad*, 1914, **11**, 498—500).—Addition of cerium dioxide to the cupric oxide employed by Jäger (*A.*, 1899, ii, 526) causes a great acceleration of the velocity of combustion of hydrogen at 270°, but does not induce the oxidation of methane at this temperature.

A. J. W.

**The Magnesium-organo-method for the Estimation of Hydroxyl Groups.** TH. ZEREWITINOV (*Ber.*, 1914, **47**, 1659).—It is the author's wish that the method of estimating hydroxyl groups by the application of magnesium methyl iodide in pyridine solution should not be associated with his name alone, as is the growing custom, but jointly with that of Tschugaev, under whose guidance the process was developed.

J. C. W.

**Critical Temperatures of Solution and Hæmolytic Properties of Alcohols.** A. J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1914, **28**, 149—166\*).—The author has applied Crismer's method of critical temperature of solution (*A.*, 1903, ii, 10; 1907, ii, 134) and the physiological hæmolytic method to the distillates obtained by fractionating commercially pure specimens of *isoamyl* and methyl alcohol; the former method allows differences to be perceived between the various fractions, but the latter is not sufficiently sensitive for the purpose.

The composition of mixtures of *isoamyl* and ethyl alcohol which have the same indices can be determined by means of the critical temperature of solution, whilst, further, a series of solutions having the same properties as Crismer's alcohol but containing less ethyl alcohol can be prepared; moreover, from the author's results, the composition of alcoholic solutions in which the critical temperatures of solution are considerably raised or lowered can be determined.

H. W.

\* and *Biochem. Zeitsch.*, 1914, **63**, 402—408.

**A New Physico-chemical Volumetric Method.** II. RENÉ DUBRISAY (*Bull. Soc. chim.*, 1914, [iv], **15**, 444—451).—A résumé of work already published (compare A., 1913, ii, 388, 712; this vol., ii, 46), and an application of the method to the neutralisation of phenol by *N*/10-sodium hydroxide. A sharp end-point is obtained with a solution of phenol at a dilution of nearly *N*/1000. W. G.

**Detection of Picric Acid.** KÜHL (*Pharm. Zentr. h.*, 1914, **55**, 523—524).—The isopurpuric acid reaction affords a very sensitive test for the detection of picric acid. A deep red coloration is shown when a picric acid solution is heated to 60° with an equal volume of 5% potassium cyanide solution. The test will detect the presence of 0.3 mg. of picric acid in 3 c.c. of solution. In testing sweetmeats, pastry, etc., a dilute alcoholic extract of the acid is employed, and, since small quantities of sugar pass into solution, the coloration obtained is compared with that produced in two control tests, one containing picric acid and the other picric acid plus ten times its weight of sugar. W. P. S.

**Cholesterol and its Estimation in Fats.** M. KLOSIERMANN and H. OPITZ (*Zeitsch. Nahr. Genussm.*, 1914, **27**, 713—723).—Cholesterol is shown to be an important constituent of fatty foods, since it prevents the hæmolytic action of certain poisonous substances. As a rule, solid edible fats are practically free from cholesteryl esters, the cholesterol contained in these fats being present in the free state; consequently, previous saponification of the fat is unnecessary when it is desired to separate the cholesterol by precipitation with digitonin. In cod liver oil, however, about one-half of the total cholesterol is present in the form of esters. In the case of vegetable oils, the greater part of the phytosterol occurs as esters, and in the detection of vegetable oils in animal fats, by precipitating the phytosterol and cholesterol with digitonin, and identifying the former by the m. p. of its acetate, it is essential to saponify the fat in order to obtain the phytosterol in the digitonin precipitate. W. P. S.

**Modification of Clerget's Method for the Estimation of Sugar in Molasses.** VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1914, **38**, 429—440).—In the process described the molasses is decolorised and clarified by the addition of bromine, and the polarisation is determined in the presence of definite quantities of citric acid and potassium chloride. It is shown that excess of bromine is without effect on sucrose and invert-sugar. Two citrate solutions are employed, and are prepared as follows: 380 grams of potassium hydroxide are mixed with 250 c.c. of water, and, when about three-fourths of the hydroxide has dissolved, the solution is decanted and 400 grams of citric acid mixed with 200 c.c. of water are added to it. The remaining hydroxide is then dissolved in water and added to the citrate solution until the latter is feebly alkaline to phenolphthalein; the solution is now cooled and diluted to 1 litre (neutral citrate solution). Five hundred c.c. of this solution

are then mixed with 250 c.c. of hydrochloric acid (D 1·188), and diluted to 1 litre (acid citrate solution). A double-normal quantity of the molasses is dissolved in water and diluted to 200 c.c. Fifty c.c. of this solution are transferred to a 100 c.c. flask, 20 c.c. of the acid citrate solution are added, and the mixture is diluted to 100 c.c. with saturated bromine water; after filtration, the solution is polarised in a 200 mm. tube. A second quantity of 50 c.c. of the molasses solution is now treated with 10 c.c. of hydrochloric acid (1:1), inverted, cooled to 20°, 10 c.c. of neutral citrate solution are added, and the solution is diluted to 100 c.c. with bromine water. The reading is taken after the lapse of twenty minutes. An inversion-constant of 132·6 is employed in calculating the quantities of sucrose and invert-sugar from the readings obtained at 20°.

W. P. S.

**Detection of Carbohydrates in Normal Urine.** R. BERNIER (*J. Pharm. Chim.*, 1914, [vii], 9, 493—503).—In a previous paper (A., 1910, ii, 163) Grimbert and Bernier have shown that the osazones of glycuronic acid and dextrose can be obtained from normal urine after hydrolysis. The present paper deals with the origin of the latter. The following are the main conclusions: Normal urine does not contain free dextrose, and its feeble reducing power appears to be due to a small quantity of glycuronic acid. The usually feeble lævo-rotation is attributable to compounds of this acid. Glucosazone, obtained after the hydrolysis of normal urine by acids, appears to be derived from invert-sugar. The increase in reducing power, the return of rotation to the lævo-direction, and the formation of glucosazone from normal urine which has been subjected to the action of invertase, points to the presence of free or combined sucrose, which appears to be a frequent, if not a constant, ingredient.

The following method of estimation is proposed: 100 c.c. of urine are treated with a few crystals of thymol or with a drop of essence of mustard, and divided into two portions, each of 50 c.c., to one of which invertase (0·25 gram) is added. After being maintained at 33° for forty-eight hours, an excess of Patein and Dufau's reagent is added, which is immediately neutralised to avoid hydrolysis; the solutions are allowed to remain for an hour to complete the precipitation of creatinine, after which they are made up to 100 c.c. and filtered. Mercury is eliminated by means of zinc, and the filtered solutions are titrated with Fehling's solution.

H. W.

**Detection and Estimation of Some Carbohydrates in Fæces.** H. DEJUST and A. CONSTANT (*Chem. Zentr.*, 1914, i, 822; from *Bull. Sci. Pharmacol.*, 1913, 20, 707—710).—Details are given of a process for the extraction and estimation of sugars in fæces.

J. C. W.

**Detection and Estimation of Some Carbohydrates in Fæces.** H. DEJUST and A. CONSTANT (*Chem. Zentr.*, 1914, i, 1020; from *Bull. Sci. Pharmacol.*, 1914, 21, 28—36).—Microscopical and chemical

methods for the detection of starch in fæces are discussed. The fermentation method of Strasburger and Schmidt, using Goiffon's apparatus, is recommended for the estimation of starch.

W. P. S.

**Methods of Estimating Carbohydrates. II. Estimation of Starch in Plant Material. The Use of Taka-diastase.** WILLIAM A. DAVIS and ARTHUR JOHN DAISH (*J. Agric. Sci.*, 1914, 6, 152—168).—The fresh material is immediately placed in much boiling 95% alcohol, containing 1% by volume of ammonia. The enzymes being in this manner destroyed, the substance is extracted, with boiling alcohol, in a Soxhlet apparatus, for eighteen to twenty-four hours. It is then freed from alcohol in a hydraulic press, broken up, and dried for eighteen hours in a steam-oven, after which it is ground. About 10 grams are dried until the weight is constant in a vacuum over phosphoric oxide at 100° or 110°.

To estimate starch, the substance (previously extracted with water to remove gums, etc., if necessary) is heated for thirty minutes with 200 c.c. of water, cooled to 38°, after which 0.1 gram of Taka-diastase and 2 c.c. of toluene are added, and the mixture left for twenty-four hours. It is then washed by decantation, through a filter, until the filtrate amounts to about 475 c.c., precipitated with lead acetate (avoiding a large excess), diluted to 500 c.c. at 15°, and filtered; 100 c.c. of the filtrate, in a 110 c.c. measuring flask, is precipitated with sodium carbonate, made up to 110 c.c. at 15°, and polarised in a 400 mm. tube; 50 c.c., filtered from lead carbonate, are used for the reduction.

The whole of the dried, ground material must be thoroughly mixed before taking a sample, as there is a tendency for the more starchy particles to gravitate towards the bottom of the bottle; and it is necessary to extract any water-soluble non-sugars which are optically active.

The Sachsse method is not trustworthy in the case of plant materials owing to the presence of pentosans, and to the destruction of dextrose in the prolonged treatment with acid. O'Sullivan's method gives low results owing to the loss of dextrin during the purification of the solution after the conversion by diastase.

Results of estimations of starch in leaves of turnips and nasturtiums are given. Mangold leaves, sampled at various periods, night and day, during the period in which sucrose is actively stored by the roots, were invariably found to be free from starch.

N. H. J. M

**Estimation of the Acidity of Urine.** ALCIDES GODOY (*Chem. Zentr.*, 1914, i, 1119; from *Memor. Inst. Oswaldo Cruz*, 5, 256—261).—A definite volume of urine is titrated with *N*/1-hydrochloric acid, using methyl-orange as indicator; an equal volume of the urine is then titrated with *N*/10-alkali solution until alkaline to phenolphthalein. The sum of the two titrations gives the quantity which must be added to change the dissociation number of the urine from  $pH^*=4$  to  $pH^*=8$ .

W. P. S.



**"Vacuum Distillation" Method for the Detection of Formic Acid.** THEODOR MERL (*Zeitsch. Nahr. Genussm.*, 1914, 27, 733—743).—Small quantities of formic acid can be separated from solutions also containing sugars, organic acids, etc., by distillation under low pressure, and there is no tendency for the continuous formation of traces of formic acid from the distillation materials. Distillation under reduced pressure in the presence of steam yields less trustworthy results.  
W. P. S.

**Estimation of the Acetyl Number of Fats, Oils, Etc.** EDWARD B. HOLLAND (*J. Ind. Eng. Chem.*, 1914, 6, 482—486).—Five grams of the fat are heated for one hour under a reflux apparatus with 10 c.c. of acetic anhydride; a quantity of ceresin is then added sufficient to form, with the fat, a solid disk when cold. The mixture is heated a short time on a water-bath, diluted with 150 c.c. of hot water, and cooled; the aqueous portion is then drawn off, and the cake is washed in a similar way with about five more successive quantities of water. The saponification number of the fatty mixture is now estimated, and the result expressed in terms of the original fat. The difference between the saponification number of the fat before and after acetylation gives the acetyl number. A correction is made when the fat contains free soluble fatty acids.  
W. P. S.

**Estimation of Fatty Acids in Soaps.** A. A. BESSON (*Chem. Zeit.*, 1914, 38, 645—647, 686—687).—Ether is found to be a better solvent than light petroleum for the fatty acids separated from soap, and the author prefers a piece of apparatus termed a sapometer in place of a separating funnel in the estimation. A quantity of from 10 to 25 grams of the soap is dissolved in about 100 c.c. of water, and the solution is transferred to the sapometer, which already contains 25 c.c. of 2*N*-sulphuric acid and a quantity of methyl-orange; 100 c.c. of ether are then added, the mixture is shaken, and when separation has taken place, the volume of the ethereal layer is noted. An aliquot portion of the ethereal solution is withdrawn, evaporated in a weighed flask, and the residue is weighed; this residue is then dissolved in alcohol and titrated with *N*/2-alkali solution. Another aliquot portion of the ethereal solution is now titrated directly with alcoholic potassium hydroxide solution. Should the second titration require more alkali than the first, the presence of volatile fatty acids is denoted, and their quantity may be calculated approximately.  
W. P. S.

**Applied Plant Microchemistry. IX. The Microchemistry of Fungus Laricis.** O. TUNMANN (*Chem. Zentr.*, 1914, i, 1016; from *Apoth. Zeit.*, 1914, 29, 120—122).—When a trace of agaricic acid is heated on a slide with a drop of 10% sodium carbonate solution, the acid dissolves with evolution of carbon dioxide, and needle-like crystals are deposited; after a time the crystals collect into nodules. The drug itself gives a similar reaction. The green coloration obtained when the drug is treated with copper acetate is not due

to the presence of the agaricic acid. The crystalline sublimate obtained on heating *Fungus laricis* or agaricic acid contains the anhydride of methylhexadecylmaleic acid, and probably also small quantities of stearic acid.

W. P. S.

#### Method of Estimating Benzoyl in Benzoyl Derivatives.

A. W. VAN DER HAAR (*Chem. Weekblad*, 1914, **11**, 460—463 \*).—The benzoyl compound is saponified with alcoholic potassium hydroxide, the benzoate formed is decomposed by phosphoric acid, and the benzoic acid is extracted by ether and sublimed from a weighed vessel. The loss in weight corresponds with the benzoic acid formed.

A. J. W.

**Analysis of Milk.** G. MELLIERE (*J. Pharm. Chim.*, 1914, [vii], **9**, 489—493, 559—563).—A résumé is given of the methods of determining the physical constant of milk (density, cryoscopic point, electrical conductivity, surface tension, and index of refraction). The author is led to the conclusion that only the first and second of these have an analytical value, and that the determinations should preferably be made on samples deprived of fat by centrifuging.

A modification of Adam's process for estimating fat in milk is described. The sample of milk (25 c.c.) is shaken with 50 c.c. of a solution of alcohol (65%, 1000 c.c.) and ether (1100 c.c.) in the presence of ten drops of ammonia. Separation of the layers generally occurs readily, but if the milk has been boiled or strongly pasteurised, or if formaldehyde or sublimate has been added, it is advisable to warm the lower layer at 40—45°. The latter is subsequently run off, and the residue shaken with 10 c.c. of light petroleum (D 0.650) and 3 drops of tincture of cochineal, which readily causes the separation of water and alcohol retained in the ethereal layer. The ethereal solution is subsequently evaporated, preferably in a nickel capsule, and the residual fat weighed.

H. W.

#### Method for the Estimation of Fat in Milk (Nephelometric

Method). W. R. BLOOR (*J. Amer. Chem. Soc.*, 1914, **36**, 1300—1304).

—The following method for the estimation of fat in milk is accurate and rapid, and requires only a very small quantity of milk. One c.c. of the milk is added slowly to about 80 c.c. of a mixture of alcohol and ether (3:1) in a 100 c.c. flask. The liquid is heated until it boils, and is then cooled and diluted to 100 c.c. Five c.c. of this solution are stirred into 100 c.c. of water with production of a slightly opalescent, colloidal solution. A similar solution is made with 5 c.c. of a standard solution of triolein in a mixture of alcohol and ether (equivalent to about 2 mg. of triolein). To the standard and test solutions are added simultaneously 10 c.c. of 10% hydrochloric acid, and after being stirred and left for five minutes, the solutions are transferred to the nephelometer. The two tubes of the nephelometer are filled to the same height with the two solutions, the movable jacket on the standard

\* and *Arch. Pharm.*, 1914, **252**, 205—209.

side is set at a convenient point, and comparisons are made by adjusting the jacket on the test solution until the images of the two tubes show equal illumination. The mode of calibrating the nephelometer is described. Results obtained by this method were found to agree closely with those afforded by the Babcock and the Adams (Soxhlet) methods.

E. G.

**Comparison of Methods for the Estimation of Fat in Cream with Special Reference to Sichler's "Alcohol Sin-acid" Method.** E. BLANCK (*Milch. Zentr.*, 1914, **43**, 316—325).—Sichler's method was found to yield results which agreed with those yielded by Gerber's and Vieth's methods. The Röse-Gottlieb method gave results slightly lower than those obtained by the above-mentioned methods.

W. P. S.

**A Rapid Method of Estimating Fat in Cheese, Cream, and Butter.** KUNO KROPAT (*Arch. Pharm.*, 1914, **252**, 76—82).—Rupp and Müller (*Zeitsch. Nahr. Genussm.*, 1912, **23**, 338) have shown that in the estimation of fat in milk the extraction of the fat may be facilitated by gelatinising the aqueous layer by means of gum tragacanth. The method has been extended by the author to the estimation of fat in cream, cheese, and butter.

In the case of cheese the following procedure is adopted: The cheese (2—3 mg.) is heated with 5 c.c. of 25% hydrochloric acid until dissolved, and the solution then treated with alcohol (3—5 c.c.). After cooling, the solution is shaken with ether (25 c.c.), and when the separation is complete, 25 c.c. of light petroleum are added. The aqueous layer is gelatinised by the addition of 1—1.5 grams of gum tragacanth, the ethereal layer separated, and the residue washed with light petroleum, the fat being determined in the extract by evaporation in the usual manner.

A similar method is adopted in the case of cream and butter.

F. B.

**Modification of Halphen's Reagent.** Utz (*Chem. Zentr.*, 1914, **i**, 1022—1023; from *Chem. Rev. Fett-Harz-Ind.*, 1913, **20**, 291—295).—A 1% solution of sulphur in pentachloroethane is recommended for use in Halphen's test in place of the usual solution of sulphur in carbon disulphide. The oil to be tested is simply heated with the reagent over a flame, and amyl alcohol may be omitted.

W. P. S.

**Some Vegetable Oils.** M. RAFFO and G. ADANTI (*Boll. chim. farm.*, 1914, **53**, 33—36).—The method of recognising different oils by measurements of viscosity has disadvantages which are obviated if the viscosity measurements are effected, not with the oils themselves, but with the liquid fatty acids (at 15°) obtained from them by saponification with alcoholic potassium hydroxide, conversion of the soaps formed into lead salts, extraction of these with ether, and final decomposition of the lead salts. The viscosities of the mixtures of fatty acids obtained in this way differ according to the

oil used much more than do the viscosities of the original oils, and the method can even be used to recognise mixtures of oils. Tables showing the viscosities of the liquid acids derived from various oils, and mixtures of oils, are given.

R. V. S.

**Analysis of Drying Oils.** G. MALATESTA and E. DI NOLA (*Boll. chim. farm.*, 1914, **53**, 6—7).—A review of methods suitable for the detection of cobalt in drying oils.

R. V. S.

**Quantitative Separation of Acetaldehyde and Acetone.** ERIK HÄGGLUND (*Zeitsch. anal. Chem.*, 1914, **53**, 433—439).—The process is based on the fact that acetaldehyde is quantitatively oxidised by an alkaline silver solution, whilst acetone is scarcely affected. The decrease in the strength of the silver solution thus represents the acetaldehyde.

The silver solution is prepared by mixing 15 c.c. of water, 50 c.c. of *N*/2-silver nitrate, 9 c.c. of *N*-sodium hydroxide, and 25 c.c. of ammonia (D 0.92); 10 c.c. of the mixture of acetaldehyde and acetone (about 0.3 gram of acetaldehyde) are added, and the whole is heated in a pressure flask for ten hours in the boiling-water bath. When cold, the liquid is transferred to a 300 c.c. flask, and made up to the mark; when clear, 50 c.c. are withdrawn, acidified with nitric acid, and titrated with *N*/10-ammonium thiocyanate using iron-alum as indicator.

L. DE K.

**Reactions of Vanillin.** E. P. HÄUSSLER (*Zeitsch. anal. Chem.*, 1914, **53**, 363—371).—A few crystals or drops of the reagent are dissolved in 1—2 c.c. of dilute alcohol, a few crystals of vanillin added, and the whole is evaporated on the water-bath almost to dryness. Sometimes a coloration is already noticed, but it will form plainly on the addition of 2 or 3 drops of 20% hydrochloric acid and warming (25% sulphuric acid may also be used, but it has a different action); 1—2 c.c. of water are added, then a slight excess of ammonia, and then again a slight excess of hydrochloric acid.

In this manner characteristic, yellow colorations are obtained with amines, acid amides and imines, and a red and violet coloration with phenols. A large number of other organic substances have also been experimented with. In each case a blank experiment should be made.

L. DE K.

**Estimation of Acetone in Urine.** L. SOBEL (*Chem. Zentr.*, 1914, i, 1025; from *Schweiz. Apoth. Zeit.*, 1914, **52**, 62—63).—Two hundred c.c. of the urine are treated with a few drops of hydrochloric acid and distilled, 50 c.c. of distillate being collected. To the distillate are added potassium hydroxide and iodine solution, the precipitated iodoform is collected on a filter, washed, and the filter and precipitate are heated under a reflux apparatus with a mixture of fuming nitric acid and silver nitrate. After dilution, the silver iodide is collected, washed, dissolved in ammonia, reprecipitated by the addition of nitric acid, again collected, ignited, and weighed. The amount of acetone is found by multiplying the weight of silver iodide by 0.1171.

W. P. S.

**Estimation of Camphor in Tablets and Pills.** EDWIN DOWZARD (*J. Ind. Eng. Chem.*, 1914, 6, 489—490).—A number of the pills or tablets, corresponding with about 3 grams of camphor, are submitted to steam distillation, the distillate (collected in a receiver which can be closed with a rubber stopper) is shaken with 25 c.c. of benzene, the benzene solution of the camphor is separated, filtered through cotton-wool, and its rotation determined at 25° in a 100 mm. tube; 0.009806 gram of camphor in 25 c.c. of solution shows a rotation of 0°1'.  
W. P. S.

**The Combustion Method for the Direct Estimation of Caoutchouc.** L. G. WESSON (*J. Ind. Eng. Chem.*, 1914, 6, 459—462).—Further work on a method described previously, and based on the combustion of the caoutchouc nitrite (A., 1913, ii, 631), shows that the method is fairly trustworthy, both in the case of raw rubber and in vulcanised materials.  
W. P. S.

**Estimation of Caoutchouc by Bromination.** GERHARD HÜBENER (*Chem. Zentr.*, 1914, i, 1028; from *Gummi-Zeit.*, 1913, 28, 320—322).—The author corrects erroneous assumptions by Vaubel (this vol., ii, 301) regarding the bromination methods of Budde and Axelrod and of the author.  
W. P. S.

**Gravimetric Estimation of Urea in Urine.** R. FOSSE (*Compt. rend.*, 1914, 158, 1588—1590. Compare this vol., i, 859).—Under the conditions given, urea is the only constituent of urine giving a xanthhydrol compound which is practically insoluble. The estimation is carried out as follows. The urine is diluted to ten times its volume with water; 10 c.c. of this liquid are placed in a conical flask, and 35 c.c. of glacial acetic acid added. Five separate portions of 1 c.c. of a 10% solution of xanthhydrol are added at intervals of ten minutes, and the mixture allowed to remain one hour. The crystalline precipitate is collected, washed with alcohol, detached from the paper, and weighed. The author uses a modified form of a Büchner funnel, made of silver, the plate being slightly concave, by means of which the whole precipitate, which forms a white, rigid mat, can be readily removed by means of a pair of forceps. The apparatus is sketched in the original.  
W. G.

**Volumetric Estimation of Cyanamide.** G. GRUBE and J. KRÜGER (*Zeitsch. angew. Chem.*, 1914, 27, 326—327).—Cyanamide may be estimated volumetrically by a method which depends on the insolubility of silver cyanamide in dilute ammonia. It is essential, however, to add an excess of standard silver nitrate solution to a slightly acid solution of the cyanamide, and then render the mixture just alkaline with ammonia; the excess of silver nitrate is titrated in the usual way. Considerable quantities of silver cyanamide are dissolved by solutions containing large amounts of free ammonia or ammonium salts (compare A., 1911, i, 118).  
W. P. S.

**Detection of Cyanides in the Presence of Ferro- and Ferri-cyanides and Thiocyanates.** O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1914, **36**, 1092—1093).—When a bubble or two of hydrogen sulphide is passed into a dilute ammoniacal solution of copper sulphate, a precipitate of copper sulphide is formed or a deep blue to brownish-black coloration is produced, depending on the amount of hydrogen sulphide dissolved, the temperature, and the dilution of the solution. On the addition of an alkali cyanide, the solution becomes clear and colourless. The test is capable of detecting about 1 part of hydrogen cyanide in 100,000 parts of solution. In the presence of 50 c.c. of 4% solution of potassium thiocyanate, 0.5 mg. of hydrogen cyanide can be detected; in the presence of 50 c.c. of 4% solution of potassium ferro- or ferri-cyanide, 1 mg. and 0.5 mg. respectively can be detected. In presence of smaller quantities of these cyanogen compounds, the test becomes much more delicate. If the test is applied to a solution containing much ferricyanide, a blank experiment should be made, using the same quantities of ferricyanide and copper sulphate as are present in the actual test, and the difference in the tints should be noted. E. G.

**Volumetric Estimation of Hydroferricyanic Acid in the Presence of Ferric and Cyanogen Ions.** ERICH MÜLLER and FRIEDRICH SEIDEL (*Zeitsch. anal. Chim.*, 1914, **53**, 416—420).—The process is based on the fact that in the presence of potassium fluoride ferric salts do not act on potassium iodide.

After adding excess of the fluoride, any cyanide present is removed by adding a few drops of sulphuric acid and expelling the hydrogen cyanide by means of a current of carbon dioxide. Potassium iodide and zinc sulphate are then added, and the iodine liberated (due to ferricyanogen) is titrated with thiosulphate.

L. DE K.

**Oxidimetric Estimation of Ferrocyanides by Alkali Bromates.** L. L. DE KONINCK and N. JOASSART (*Bull. Soc. chim. Belg.*, 1914, **28**, 144—148).—On the supposition that action occurs in accordance with the equation:

$3K_8Fe_2Cy_{12} + KBrO_3 + 6HCl = 3K_6F_2Cy_{12} + KBr + 6KCl + 3H_2O$ ,  
the authors have attempted to estimate ferrocyanides by titration with potassium bromate in hydrochloric acid solution, approximately *N*/10-ferric alum solution being used as outside indicator. The results vary greatly with the acidity of the solution, and are only exact when the concentration of the acid is approximately normal at the commencement of the titration, the permissible variation being 10—15%. Probably action occurs in three stages:

(1)  $2KBrO_3 + 12HCl = 2KCl + Br_2 + 5Cl_2 + 6H_2O$ ,

(2)  $K_8Fe_2Cy_{12} + Br_2 = 2KBr + K_6Fe_2Cy_{12}$ ,

and (3)  $5K_8Fe_2Cy_{12} + 5Cl_2 = 10KCl + 5K_6Fe_2Cy_{12}$ . The action of the bromine is so slow that a portion of it escapes in the free state, and, actually, it is found that the solution smells strongly of bromine if the acid is used at considerable concentration. Replacement of

hydrochloric by sulphuric acid gives unsatisfactory results as the reaction proceeds very slowly even in concentrated solution.

Direct titration of ferrocyanides with potassium permanganate (without external indicator) does not give good results, since the colour due to a slight excess of the oxidising agent is not readily perceived. The use of an outside indicator is to be preferred. Bollenbach's method (A., 1908, ii, 996), in which an excess of permanganate is added and the titration completed by addition of ferrocyanide solution until a permanent blue coloration of Prussian blue is obtained, gives excellent results, but an attempt to apply a similar method with potassium bromate fails, since the blue tint which immediately forms does not disappear; Prussian blue, therefore, does not appear to react with bromic acid in the same manner as with permanganate.

H. W.

**Colorimetric Estimation of Creatine.** E. BAUR and G. TRÜMLER (*Zeitsch. Nahr. Genussm.*, 1914, 27, 697—713).—The authors have investigated Jaffé's method for the estimation of creatine (A., 1886, 1056; 1904, ii, 375), particularly as regards the influence of time, temperature, and concentration of acid on the conversion of creatine into creatinine, and find that, in the case of meat extracts, the creatine is converted completely when 10 grams of the extract are heated with 100 c.c. of *N*/1-hydrochloric acid for four hours at 97°. The actual estimation of creatine in meat extracts is carried out as follows: Ten grams of the extract are dissolved in water to give 100 c.c. of solution; 5 c.c. of this solution are then treated with 15 c.c. of saturated picric acid solution and 5 c.c. of 10% sodium hydroxide solution, and, after seven minutes, the mixture is diluted to 500 c.c., and the coloration compared with that exhibited by a definite depth of *N*/2-potassium dichromate solution (compare A., 1904, ii, 375). The result gives the quantity of pre-formed creatinine. A second portion of 10 grams of the sample is then heated with hydrochloric acid as described above; after cooling, 5 c.c. of the solution are neutralised, treated with picric acid and sodium hydroxide, diluted to 500 c.c., and the coloration is compared. The amount of creatine plus creatinine is thus obtained. The comparisons should be made while the solutions are at a temperature of 17°. Liebig's meat extract was found to contain from 9.76 to 3.72% of creatinine and from 2.09 to 5.58 per cent. of creatine. Meat extracts prepared by the authors (1 kilo. of flesh yielded 30—35 grams of extract) contained from 7.5 to 8.9% of creatine plus creatinine.

W. P. S.

**The Non-interference of "Ptomaines" with Certain Tests for Morphine.** II. JACOB ROSENBLUM (*J. Biol. Chem.*, 1914, 18, 131—132).—The products of putrefaction present in a year-old body do not give reactions tending to confusion with morphine, or with coniine, nicotine, atropine, strychnine, digitalin, veratrine, colchicine and delphinine. After addition of morphine, however, the morphine reactions were readily obtained.

R. V. S.

**Qualitative Differentiation of Vegetable Tannins.** E. STIASNY [with C. D. WILKINSON] (*Collegium*, 1914, 76—81).—The author has examined Lauffmann's method of precipitating tannin solution with ammonium molybdate and ammonium chloride, and confirms the conclusion that quebracho extracts containing no pyrogallotans (formaldehyde test) and no wood pulp (aniline test) may be regarded as adulterated with mangrove if the molybdenum number obtained (weight of precipitate from 100 grams of tannin) is higher than 30—40. The test may also be employed for the detection of mangrove in sulphited quebracho, although the variations of the number in the case of quebracho and sulphited quebracho diminish the value of the test. A scheme is also described for the distinction of vegetable tannins, depending on the complete, partial, or non-precipitation of the substances on boiling with formaldehyde and hydrochloric acid. W. P. S.

**Estimation of the Percentage of Albumin in Blood Serum by means of the Refractive Index and Density.** G. B. ZANDA (*Chem. Zentr.*, 1914, i, 917—918; from *Arch. Farmacol. speriment.*, 1913, 16, 513—528).—The specific gravity, and especially the refractive index, of blood serum are influenced to a certain extent by carbamide, dextrose, salt, and such normal constituents of the fluid, but the albumin content has most control over these constants. Useful valuations of albumin in serum may therefore be obtained by physical measurements. J. C. W.

**Chemical Reaction for Blood.** DOMENICO GANASSINI (*Boll. chim. farm.*, 1914, 53, 36—39).—Polemical (compare A., 1913, ii, 260). R. V. S.

**Estimation of Colloids in Beers.** ROBERT MARC (*Kolloid-Zeitsch.*, 1914, 14, 181—186).—The interferometer method for the estimation of colloids, which has been described in previous papers (compare A., 1912, ii, 745, 1150), has been applied to the estimation of colloids in beer.

After diluting in the ratio 1:10, 20 c.c. of the beer are mixed with 10 grams of finely divided barium sulphate or carbonate, and the mixture shaken for half an hour. The change in the refractive index affords a measure of the colloid content of the beer.

The results obtained in the examination of a number of light and dark beers indicate that the change in the refractive power is very nearly proportional to the content of total solids, and also that the percentage change in the refractive power is approximately constant. H. M. D.  $\bar{f}$



## General and Physical Chemistry.

**Refractive Index at the Critical Point.** MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1914, **12**, 282—288).—The refractive index at the critical point ( $n_c$ ) has been calculated from the equation  $(n_c^2 - 1)/(n_c^2 + 2) = R d_c$ , in which  $R$  is the refractivity and  $d_c$  the critical density. For aliphatic esters, alcohols, hydrocarbons, etc., the value of  $n_c$  obtained in this way is practically constant = 1.117. Benzene and its derivatives give a somewhat higher value,  $n_c = 1.160$ . For these two groups of substances, the value of  $(n_c^2 - 1)/(n_c^2 + 2)$ , which represents the fraction of the total volume actually occupied by the molecules at the critical point, is found to be equal to 0.077 and 0.103 respectively. These values are approximately one-third of the corresponding theoretical volume ratios.

In homologous series of aliphatic compounds and in the series of mono-halogen derivatives of benzene, the ratio of the density at the ordinary temperature to the critical density increases with increasing molecular weight. The value of  $(n^2 - 1)/(n^2 + 2)$  shows a similar variation.

H. M. D.

**The Dispersion of Ultra-violet Rays by Organic Substances.** VICTOR HENRI (*Compt. rend.*, 1914, **158**, 1892—1894).—The author has measured the refractive indices of methyl, ethyl, propyl, butyl, amyl and heptyl alcohols, of glycol and of pentane, hexane, heptane and cyclohexane for rays of wave-length  $\lambda = 4200$ —2150, and from his results has calculated the molecular refractive powers for  $\cdot\text{CH}_2\cdot$ , and  $\text{H}\cdot$  and  $\cdot\text{O}\cdot$  of the hydroxyl group. Up to  $\lambda = 2600$  the refractive power of  $\cdot\text{CH}_2\cdot$  is perfectly additive, as in the visible spectrum, whilst for rays of shorter wave-lengths the additivity is only a first approximation. For the substances examined, the variation of the refractive indices can be accurately represented by the formula (I)  $n^2 = a + b\lambda_0^2/(\lambda^2 - \lambda_0^2)$ , and the molecular refractive power by the formula (II)  $[(n^2 - 1)/(n^2 + 2)]M/d = \alpha + \beta\lambda_0^2/(\lambda^2 - \lambda_0^2)$ . The values calculated from formula (I) and found for methyl, ethyl and propyl alcohols agree closely.

The values of the constants  $\alpha$ ,  $\beta$  and  $\lambda_0$  for formula (II), which hold good from  $\lambda = 6563$  to 2150, are:

	$\alpha$ .	$\beta$ .	$\lambda_0$ .
Methyl alcohol .....	8.0195	5.1132	1063
Ethyl „ .....	12.707	7.1734	1239
Propyl „ .....	17.112	10.148	1114
Amyl „ .....	26.083	6.792	1502
Pentane .....	24.727	11.62	1205
Hexane .....	29.223	25.45	965

W. G.

**The Application of Spectrum Analysis to the Study of Chemical Equilibria.** GUSTAV F. HÜTTIG (*Zeitsch. physikal. Chem.*, 1914, **88**, 172—190).—The first part of the paper deals theoretic-

ally with the relationships which exist between the changes of the absorption spectrum of a system in equilibrium and the changes in the equilibrium constants of the system. Mathematical relationships are derived for the connexion between the variable components of the absorption spectrum of the system and the number of participating molecules in the reaction, the reaction equation, and the reaction constants. Four types of problems which can be dealt with by this method are indicated. (1) Those in which the reaction constant is known and in which the number of molecules and the reaction equation can be calculated. In cases of this kind, the optical method serves only as a confirmatory one. (2) Those in which the reaction equation is known and the number of molecules can be calculated. In this case the reaction constant can be deduced by the optical method. (3) Those in which the number of reacting molecules is known; here the reaction equation and constant can be determined by the optical method; and (4) those cases in which nothing is known or calculable; here all three quantities, the reaction constant and equation and the number of molecules reacting, can be determined by the optical method.

The method is applied to the determination of the second and third dissociation constants of purpurin. The measurements consist in photographing the absorption spectrum of solutions of purpurin in pyridine, ammonia solution, normal sodium hydroxide solution, and in an excess of very concentrated sodium hydroxide solution. From the measurements the dissociation constants are calculated to  $2 \times 10^{-11} > k'' > 2 \times 10^{-10}$  and  $1 \times 10^{-15} < k''' < 5 \times 10^{-15}$ . The first and second dissociation constants of alizarin are also determined, and the values  $k' = 4.8 \times 10^{-3}$  and  $k'' = 1.15 \times 10^{-12}$  obtained. By another method (this vol., i, 701) the author has found these values to be  $k' = 5.0 \times 10^{-3}$  and  $k'' = 1.10 \times 10^{-12}$ . From the results obtained by Niggemann (*Diss.*, Leipzig, 1913), the absorption spectra of nitric acid in various states of dilution the author shows that the equilibrium  $\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 \cdot \text{H}_2\text{O}$  or  $2\text{HNO}_3 + 2\text{H}_2\text{O} \rightleftharpoons (\text{HNO}_3 \cdot \text{H}_2\text{O})_2$  exists in these solutions. J. F. S.

**Direct Spectrum Analysis by means of the Secondary Rays of Röntgen Rays.** MAURICE DE BROGLIE (*Compt. rend.*, 1914, 158, 1785—1788).—A study of the secondary spectra emitted by substances struck by primary Röntgen rays places the elements in the same position in the periodic classification as is obtained by calculation from Moseley's formula. Elements with an atomic weight of less than 28 have not shown any secondary radiation, whilst with elements of atomic weight between 30 and 50 special precautions are necessary to make the radiations apparent.

W. G.

**Oxygen in the Sun.** K. W. MEISSNER (*Physikal. Zeitsch.*, 1914, 15, 668—670).—The three red lines  $\lambda$  7772, 7774, and 7775, which are emitted by the iron arc only at the anode, have been attributed by Runge and Paschen to oxygen (compare *ibid.*, 1913, 14, 1267). According to the author's observations, the oxygen

doublet  $\lambda 8446$  is also observable in the anode spectrum of the arc. Both the triplet and the doublet are shown by the solar spectrum, and an accurate comparison of the wave-lengths has been made for the iron arc and the solar spectra.

The fundamental triplet of the principal and second subordinate series of sulphur has also been found in the anode spectrum in the arc discharge between an iron pyrites anode and an iron cathode. The wave-lengths of these three lines were found to be  $\lambda 9212\cdot80$ ,  $9228\cdot17$ , and  $9237\cdot71$  in terms of the international normals.

H. M. D.

**High-frequency Spectra and the Periodic Table.** W. M. HICKS (*Phil. Mag.*, 1914, [vi], 28, 139—142).—A discussion of the grouping of the elements suggested by Rydberg (compare succeeding abstract) in reference to the high-frequency spectra. Certain modifications of the table given by Rydberg are proposed in accordance with spectroscopic evidence.

H. M. D.

**The Ordinals of the Elements and the High-frequency Spectra.** J. R. RYDBERG (*Phil. Mag.*, 1914, [vi], 28, 144—149).—In a previous paper (*Lunds. Univ. Arsskrift*, 1913, 9, No. 18) the author has suggested that the elements fall naturally into quadratic groups consisting of  $4p^2$  elements ( $p$  being the number of the group). The two short series correspond with  $p=2$ , and give a group of sixteen elements, extending from helium to chlorine. The two recognised long series correspond with  $p=3$ , and give a group of thirty-six elements, extending from argon to iodine. The next group, corresponding with  $p=4$ , is supposed to contain sixty-four elements, and commences with xenon. In this system the elements are characterised by a succession of integral numbers (ordinals) which determine the properties of the various elements.

The fact that Moseley (this vol., ii, 326) has shown the existence of a relation between the "atomic numbers" and the frequencies of the X-ray spectra of the different elements, and that the "atomic numbers" are practically identical with the "ordinals," is supposed to afford strong support for the arrangement of the elements into quadratic groups.

H. M. D.

**Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin.** I. (Hon.) R. J. STRUTT (*Proc. Roy. Soc.*, 1914, A, 90, 364—372).—In a previous paper (A., 1913, ii, 279) it was shown that mercury vapour, allowed to distil from the arc, in a vacuum, into a cooled lateral tube, remains luminous for a considerable distance away from the region of discharge. Methods have now been devised which permit of the observation of luminous jets of the vapours of other metals.

As the luminous vapour moves away from the region of the arc discharge, the rate at which the different lines in the spectrum die out is not always the same. In general, the lines belonging to any given series die out at the same rate, but other series of

lines may be extinguished more or less rapidly than the first. In the case of sodium, the lines of the two subordinate series die away at the same rate, but the principal series is extinguished less rapidly. Differences in the duration of the spectral constituents have also been observed with potassium, magnesium, and zinc.

In some cases the luminous jet shows a band spectrum. For the alkali metals, this continuous spectrum lies beyond the limit of the subordinate series. H. M. D.

**Emission Spectra of the Common Gases.** F. CROZE (*Ann. Physique*, 1914, [ix], 1, 35—134. Compare A., 1912, ii, 613; 1913, ii, 85; 1914, ii, 2).—A detailed account is given of wave-length measurements and of observations on the Zeeman effect in the emission spectra of hydrogen, oxygen, and nitrogen. The apparatus employed was designed so as to facilitate the investigation of the ultra-violet region, and photographic records have been obtained which afford information in regard to the emission spectra up to about  $\lambda$  8000.

A number of new lines and bands have been discovered. These include ninety-eight lines in the second hydrogen spectrum between  $\lambda$  6852 and  $\lambda$  8029, thirty-one lines in the elementary spectrum of oxygen between  $\lambda$  5316 and  $\lambda$  7152, sixteen bands in the first nitrogen group, the least refrangible having the wave-length  $\lambda$  9108, and two bands in the cathodic spectrum of oxygen at  $\lambda$  6853 and  $\lambda$  5007.

The negative bands of oxygen and the most intense bands in the first nitrogen group have been resolved into lines, for which wave-length measurements are recorded. The arrangement of these lines in series is also discussed.

The mode of distribution of the lines in the second hydrogen spectrum, which do not show the Zeeman effect, has been investigated, with the result that the vibration frequencies are found to correspond with eight arithmetic series.

The Zeeman effect has been measured in the first hydrogen spectrum, for the most intense lines in the second spectrum, the whole of the lines in the elementary spectrum of oxygen and all the lines in the first nitrogen spectrum. The bands of the second positive and the negative nitrogen groups, of the "Swan" and the carbon monoxide spectra and of the cyanogen group  $\lambda$  3883, do not exhibit the Zeeman effect. This effect is, however, shown by the resolved bands of the first positive nitrogen group, although the unresolved bands have been previously stated to be unacted on by a magnetic field. H. M. D.

**The Spectra given by Carbon and some of its Compounds; and, in particular, the "Swan" Spectrum.** W. MARSHALL WATTS (*Phil. Mag.*, 1914, [vi], 28, 117—128).—The views put forward by different observers in explanation of the "Swan" spectrum are summarised, and an account is given of experiments in which the author has observed this spectrum under conditions which seem to preclude the presence of oxygen.

The experiments were made with a spark-discharge apparatus consisting of a rectangular block of transparent fluorspar in which a cylindrical cavity was bored. The lower end of this cavity was closed by a copper electrode ground into the spar. A platinum wire served as the upper electrode, and the discharge vessel was contained in a large glass tube which could be exhausted. Various oxygen-free carbon compounds were distilled over phosphoric oxide into the fluorspar vessel whilst the glass tube was kept exhausted, and the spectrum emitted by the spark discharge within the liquid was observed. Carefully purified materials were employed in all cases. Heptane, hexane, octane, carbon tetrachloride, and chlorobenzene all gave a brilliant "Swan" spectrum. On account of the rapid separation of carbon, only a few seconds were available for observation, and the spectrum could not be photographed.

The numerical relations between the wave-lengths of the lines of the spectrum are discussed, and it is shown that the experimental data may be more accurately represented by the formula  $F = 2407.015 - 19.6(p + 0.00309)^2 + 11.6422(m + 0.834291)^2$ , where  $p=45, 44, 43$ , and  $m=63, 64, 65, 66, 67, 68, 69$ , than by Deslandres' formulæ.

Special reference is made to the three lines  $\lambda 4381.93, 4371.31$ , and  $4365.01$ , which were attributed by Deslandres to hydrocarbons, whereas in the author's opinion there can be little doubt that these three lines form a part of the "Swan" spectrum. H. M. D.

**Influence of Solvents on the Optical Activity of Methyl Hydrogen, ortho- and allo-Camphorates, and Normal Camphorate.** J. MINGUIN and R. BLOC (*Compt. rend.*, 1914, 158, 1997—1999).—An extension of the work previously described (compare this vol., ii, 403), a large number of different organic solvents having been used. All solvents containing a benzene nucleus considerably increase the optical activity of the ortho-ester, but have a much less marked effect on the allo-ester. The lists obtained by arranging the solvents in the order of increasing optical activity of the ortho- and allo-esters, respectively, are quite different. Solvents of the same series with the same functional group have the same influence on the optical activity of either the ortho- or the allo-ester, the influence exerted being apparently related to the chemical nature of the solvent. The values obtained for the normal ester are intermediate between those for the ortho- and allo-esters, and in some cases are very close to their arithmetic mean. W. G.

**Thermodynamic Consideration of Photochemical Equilibria.** A. SCHIDLOF (*Arch. Sci. phys. nat.*, 1914, [iv], 37, 493—511).—A theoretical paper in which the author applies thermodynamic reasoning and Planck's theory of absorption of radiant energy to the discussion of photochemical equilibria. This leads to the view that there are three groups of photochemical reactions. In those which belong to the first group, radiant energy is liberated, and an increase in the frequency of the incident radiation is unfavour-

able to the photochemical change. Those belonging to the second group are endo-energetic, and an increase in the frequency favours the photochemical reaction. In the case of reactions which belong to the third group, the equilibrium is independent of the frequency of the radiation. The action of the light consists simply in increasing the velocity of the opposing reactions, after the manner of a catalyst.

H. M. D.

**Photochemical Decomposition of Hydrogen Peroxide. II.** J. HOWARD MATHEWS and HARRY A. CURTIS (*J. Physical Chem.*, 1914, **18**, 521—537. Compare this vol., ii, 255).—Several substances have been added to solutions of hydrogen peroxide, the mixtures submitted to ultra-violet light, and the effect of these substances on the rate of decomposition investigated. The method of investigation is the same as that previously adopted (*loc. cit.*). It is shown that acetamide (0·037%), carbamide (0·05%), boric acid (0·044%), and barium chloride (0·037%) have no action on the rate of decomposition; acetic acid, tartaric acid (0·096%), phosphoric acid (0·152%), sulphuric acid (0·0086%) (0·086%) (0·171%), potassium nitrate (0·031%), potassium chloride (0·023%), and sodium chloride (0·011%) (0·05%) exercise a slight retarding action on the rate of decomposition; benzoic acid, calcium hydroxide (0·002%), sodium hydroxide (0·053%), and barium hydroxide (0·007%) exercise a strong retarding action, and barium nitrate (0·037%) increases the rate of decomposition. The same catalysts do not effect the thermal decomposition and the photolytic decomposition of hydrogen peroxide in the same way. There is no general relationship between the chemical nature of a compound and its catalytic effect on the photolysis of hydrogen peroxide. The magnitude of the catalytic effect and the concentration of the catalyst vary in the same direction, but there is no direct proportionality between the two. Neither the change in the light absorption nor the change in the surface tension of a hydrogen peroxide solution, brought about by the addition of a small amount of a catalyst, seems adequate to explain the marked catalytic effect produced.

J. F. S.

**The Different Methods of Photolysis of Oxalic Acid by Ultra-violet Rays of Different Wave-lengths.** DANIEL BERTHELOT (*Compt. rend.*, 1914, **158**, 1791—1793. Compare A., 1911, ii, 170; 1913, ii, 819).—The photolysis of oxalic acid consists in a primary decomposition into carbon dioxide and formic acid, followed by a secondary decomposition of the formic acid in the nascent state, the products of the secondary reaction being carbon monoxide and water for rays of long wave-length and carbon dioxide and water for waves of short wave-length.

W. G.

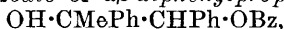
**Chemical Action of Light. XXX.** GIACOMO CIAMICIAN and P. SILBER (*Ber.*, 1914, **47**, 1806—1814; *Atti R. Accad. Lincei*, 1914, [v], **23**, i, 859—867).—Many of the photochemical reactions previously

described are confirmed, and the results recently communicated by Paternò and others (this vol., ii, 234) are criticised.

Benzaldehyde and benzophenone give the compound  $C_{27}H_{32}O_3$ , m. p.  $245^\circ$  (A., 1911, i, 647), and not a trimeric benzaldehyde (Paternò).

Whereas acetone and ethyl alcohol yield, among other substances,  $\beta$ -methylbutylene  $\beta\gamma$ -glycol (A., 1911, i, 513), acetophenone is only changed into the isomeric pinacones (compare A., 1901, i, 330). No combination takes place between benzophenone or acetophenone and isopropyl alcohol, the pinacones and acetone being the products. Phenyl ethyl ketone does not react with alcohol like methyl ethyl ketone (A., 1912, i, 537); the transformation of the ketone is not complete after some months, and the products can only be separated with difficulty into the isomeric *phenyl-ethylpinacones*,  $C_{18}H_{22}O_2$ , leaflets, m. p.  $138$ — $139^\circ$ , and large, well-developed crystals, m. p.  $113^\circ$ , respectively.

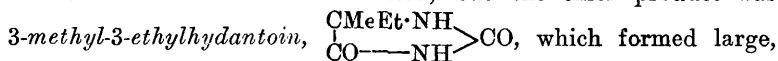
It was previously found that benzophenone and benzyl alcohol gave hydrobenzoin, benzopinacol, and also triphenylethylene glycol (A., 1903, i, 562). Paternò exposed a mixture of acetophenone and benzyl alcohol to light, but the only product which he described was  $\alpha\beta$ -diphenylpropanediol. The authors had also left such a mixture for some months, and now describe the examination of the product. After removing the unchanged reagents by steam, the residue was extracted with a mixture of much light petroleum with a little benzene. The extract deposited acetophenonepinacol, and the syrup which remained on evaporation of the mother liquor was benzoylated. The product was crystallised from much alcohol, which deposited dibenzoylhydrobenzoin, leaving the *monobenzoate* of  $\alpha\beta$ -diphenylpropanediol,



in solution. The latter was isolated in white needles, m. p.  $147$ — $148^\circ$ , but the *monobenzoate* obtained directly from Tiffeneau and Dorlencourt's  $\alpha\beta$ -diphenylpropanediol (*Ann. Chim. Phys.*, 1909, [viii], **16**, 252) had m. p.  $139$ — $140^\circ$ , and may therefore be an isomeride.

Paternò also illuminated a mixture of acetaldehyde and alcohol, and believed that he had obtained thereby butane- $\beta\gamma$ -diol. The authors had already found this glycol in the case of alcohol and acetone, and had expressed the opinion that its formation was due to a reaction between alcohol and acetaldehyde, the latter being formed during the experiment (A., 1911, i, 514).

The products obtained when methyl ethyl ketone and dilute hydrocyanic acid are exposed to sunlight are quite analogous to the products obtained from acetone (A., 1905, i, 414). In this case, however, the reaction also proceeds in the dark. Ammonium oxalate and oxamide were isolated, but the chief product was



colourless prisms, m. p.  $146^\circ$ , and was hydrolysed by hydrochloric acid in a sealed tube to  $\alpha$ -amino- $\alpha$ -methylbutyric acid (Slimmer,

A., 1902, i, 206). The amino-acid itself was not found among the products. In addition,  $\alpha$ -hydroxy- $\alpha$ -methylbutyramide,  $C_5H_{11}O_2N$ , m. p. 160°, was isolated and hydrolysed by baryta to the acid.

J. C. W.

**Oxidations with Bromine under the Influence of Light.** R. CIUSA and A. PIERGALLINI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 821—825).—When a mixture of lactic acid and bromine water is exposed to light for a day, pyruvic acid is formed. Tartaric acid in similar circumstances yields formylglyoxylic acid. Mandelic acid yields benzoic acid, benzaldehyde, and phenylglyoxylic acid. In the dark the same products are obtained, but benzoic acid is produced only in small quantity. Glycerol is oxidised to glycerose by bromine water when exposed to light. Mannitol in similar circumstances yields mannose. Citric acid yields pentabromoacetone. In all cases, except that of mandelic acid mentioned above, control experiments carried out in the dark gave either no oxidation products at all or only traces of them.

R. V. S.

**The Transformation of Radiant Energy into Chemical Energy.** S. C. LIND (*Le Radium*, 1914, 11, 108—111).—The author has shown by the study of eight reactions in gases and three in liquids that the number  $N$  of pairs of ions produced under the influence of  $\alpha$ -rays is approximately equal to the number  $M$  of molecules entering into the reactions brought about by the rays. In the electric discharge in gases the chemical action is frequently a thousand times greater than would be the case if this application of Faraday's law were followed, which is to be explained on the view that the great proportion of ions produced by collision recombine and produce their chemical effect before reaching the electrodes. The hypothesis of Warburg on the calculation of the quantity of ozone produced by the  $\alpha$ - and  $\beta$ -rays of radium is discussed, and shown to lead to a value too low on this account. From the ratio  $N/M$  found previously for several endothermic gaseous reactions, the proportion of the radiant energy converted into chemical energy is calculated to be of the same order—about 2%—as has been found in other chemical reactions effected by radiant energy. In exothermic reactions the proportion is of the same order, but reaches 10% in the case of the decomposition of water. The velocity of the reactions obeys the uni-molecular law, not because they are uni-molecular, but because the absorption of radiant energy is proportional to the concentration in the gaseous system. It is suggested that the ions play the part of intermediaries in the chemical reactions.

F. S.

**The Ultimate Rays of Elements in Different Luminous Sources.** ARNAUD DE GRAMONT (*Compt. rend.*, 1914, 159, 5—12).—A critical résumé of the author's work and that of other observers on this subject (compare A., 1907, ii, 517; 1908, ii, 645; 1910, ii, 85, 811; 1912, ii, 875; Hartley and Moss, A., 1912, ii, 821; Runge and Precht, A., 1903, ii, 346, 621; 1904, ii, 461), in which the



author deduces the following rules: (1) If, in sources of different temperatures the rays of an element do not maintain the same sensibility, the ultimate rays will, in every case, consist of a very small number of lines of great sensibility in the condensed spark. (2) The rays of maximum sensibility will be less refrangible as the temperature of the luminous source is lower. W. G.

**The Coefficient of Diffusion of X-Rays by Substances with Slight Atomic Weights (Organic Substances in particular).** H. GUILLEMINOT (*Compt. rend.*, 1914, 159, 56—59).—The author has deduced a formula for calculating the secondary radiation emitted by the emergent face of a paraffin filter, knowing the intensity of the initial ray and the thickness of the filter, and has tested its validity in the case of the paraffin filter and also for aluminium. W. G.

**The Passage of  $\alpha$ -Particles through Photographic Films.** H. P. WALMSLEY and W. MAKOWER (*Proc. Physical Soc., London*, 1914, 26, 261—263).—A flat metal plate was exposed to a fraction of a millicurie of radium emanation for a few seconds, and laid on an Ilford process plate. The darkening of the plate, due to the  $\alpha$ -rays of radium-A, was just visible to the naked eye after development, and was examined under the microscope and microphotographs taken. These showed the tracks of the single  $\alpha$ -particles through the film, with many of the characteristics demonstrated by C. T. R. Wilson's cloud photographs. The method is exceedingly simple, and lends itself to the study of the scattering of  $\alpha$ -particles by heavy atoms such as silver. Plates are reproduced, at a magnification up to 1800 diameters, showing the single darkened haloid grains in the track of the  $\alpha$ -ray. F. S.

**Fitful Point Discharges and the Electric Method of Counting  $\alpha$ -Particles.** H. GEIGER (*Ann. Physik*, 1914, [iv], 44, 813—815. Compare this vol., ii, 236).—Polemical. The results obtained by Myssovski and Nesturch are in part to be explained by secondary  $\beta$ -rays generated from the walls of the chamber under the action of the  $\gamma$ -rays. That the discharges in question are caused by individual  $\alpha$ -particles, and not by natural disturbances, is proved by sending the  $\alpha$ -particles through two counting chambers placed one behind the other, when, almost without exception, the discharges take place simultaneously in the two chambers. The criticism shows that the right experimental conditions for counting the  $\alpha$ -particles were not realised. F. S.

**Absorption and Reflexion of  $\beta$ -Particles Measured by Direct Counting.** ALOIS F. KOVARIK and LOUIS W. MCKEEHAN (*Physikal. Zeitsch.*, 1914, 15, 434—440).—Using Geiger's method for the direct counting of  $\beta$ -particles, by the fitful discharges from a sharp point kept at high potential, the number of  $\beta$ -particles reflected and transmitted through various substances was determined. The number transmitted of the  $\beta$ -particles of radium-*B*

and the active deposit of thorium, respectively, did not follow an exponential law with increasing thickness of matter, although the ionisation follows this law in these cases. The fraction of the whole number transmitted in each similar layer usually becomes less instead of remaining constant. The reflected and transmitted rays are more strongly absorbed than the initial rays. The number reflected by different elements of increasing atomic weight increases in the same way as the ionisation due to the reflected rays, which shows that the loss of velocity of the rays by reflexion is nearly independent of the nature of the reflecting material. Very thin foils increase the number of  $\beta$ -particles, and in certain circumstances the direction of the new  $\beta$ -particles generated is nearly normal to that of the thin foil. F. S.

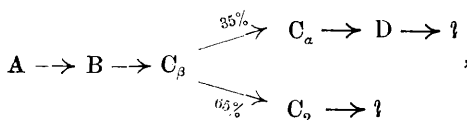
**Disintegration of Radium Emanation in a Helium Atmosphere.** W. MARCKWALD (*Physikal. Zeitsch.*, 1914, 15, 440—441).—No difference in the normal rate of disintegration of the radium emanation was observed when the emanation was allowed to decay in an atmosphere of helium, such as might have been expected to occur were the reaction at all reversible. F. S.

**The Electrochemical Properties of Radium-*B* and Thorium-*B*.** Z. KLEMENSIEWICZ (*Compt. rend.*, 1914, 158, 1889—1891).—In an endeavour to find some method of distinguishing between the isotopic elements lead, radium-*B*, and thorium-*B*, the author has proceeded as follows. An amalgam of lead (1 gram of lead in 5—10 c.c. of mercury) was shaken for several minutes with 5 c.c. of *N*/10-lead nitrate solution, acidified with *N*/50-nitric acid, which had been in contact with 0.1 curie of radium emanation for several hours, and then boiled. After the shaking, the amalgam was removed and washed with a solution of *N*/10-mercurous nitrate and *N*-nitric acid. This and the original solution were then evaporated to dryness with hydrochloric acid and heated at 125° for fifteen minutes, leaving two fractions of lead chloride crystals. In order to remove any radium-*C*, the two fractions were dissolved in warm *N*/100-nitric acid, and a plate of nickel plunged into each solution. The solutions were then evaporated to dryness again with hydrochloric acid, and the crystals powdered and spread on two equal brass disks. The total radiation was then measured by means of a quartz piezo-electrometer. Similar measurements were made with thorium-*B*. In neither case was there any difference in activity between the two fractions of crystals, thus proving that the electrolytic potentials of radium-*B* and thorium-*B* are equal to those of lead, the differences observed being much less than those which are obtained with specimens of the same metal which have undergone different mechanical treatment. W. G.

**Volatility of Thorium Active Deposit.** T. BARRATT and A. B. WOOD (*Proc. Physical Soc., London*, 1914, 26, 248—260).—The thorium active deposit, on platinum or quartz plates, was heated in an electric furnace, usually for fifteen minutes, to

accurately known temperatures, and the percentage of thorium-*B* and of thorium-*C* respectively volatilised was determined by examination of the decay curves prior to and after heating. The  $\alpha$ -ray measurements showed that both the *B*- and *C*-members begin to volatilise at 750°, and volatilisation is complete at 1200°, but at intermediate temperatures a greater proportion of the *B*- than of the *C*-member is volatilised. There is an inflexion on the curve showing the proportion of the *C*-member volatilised, at a point where about 35% of the  $\alpha$ -ray activity has been removed and at about 900°. The  $\beta$ -ray curves, on the other hand, showed that the *C*-member does not begin to volatilise until 900°. With films deposited from solutions of the active deposit in strong acids volatilisation occurred at the same temperatures as stated for the nitric acid solution, but for a hydrochloric acid solution volatilisation commences at 300°. Thorium-*D* was found to begin volatilising at 500° in the case of a film not dissolved in acid.

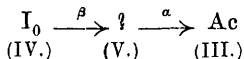
In order to explain the results, a new member of the disintegration series is assumed to exist, according to the following scheme:



in which branching occurs at the member  $\text{C}_\beta$ , which has a half-period of 60.3 minutes, and gives  $\beta$ -rays. In the minor branch the product is supposed to be a new member,  $\text{C}_\alpha$ , of period one minute or less, giving the  $\alpha$ -rays of range 5.0 cm.  $\text{C}_\beta$  is volatile at 900°, and  $\text{C}_\alpha$  at 750°. The product  $\text{C}_2$  of the above scheme (often called *C'*) is that which gives the  $\alpha$ -rays of 8.6 cm. range, and is usually supposed to have a period of  $10^{-11}$  second. This scheme agrees with the facts better than any other that can be devised. The range of the  $\alpha$ -rays of  $\text{C}_\alpha$  corresponds, by the Geiger-Nuttall relation, with a period of one minute or less. F. S.

**The Magnetic Spectrum of the  $\beta$ -Rays of Uranium-*X*.**  
O. VON BAEYER, O. HAHN, and L. MEITNER (*Physikal. Zeitsch.*, 1914, 15, 649—650).—The magnetic spectrum of the more penetrating  $\beta$ -rays of uranium-*X* consists of a broad, indistinct band which affords evidence of intensity maxima at velocities corresponding with 0.96 and 0.82 of the velocity of light. The less penetrating rays give rise to a shallow band at the velocity ratio 0.59, and to two sharp lines at 0.52 (weak) and 0.48 (strong). An attempt to resolve the spectrum of the high-speed rays into lines gave a negative result with the comparatively weak preparations of uranium-*X* which were available for the experiments. Since the  $\gamma$ -radiation of uranium-*X* is very weak in comparison with the  $\beta$ -radiation, the continuous character of the magnetic spectrum would appear to be in agreement with Rutherford's theory, according to which the emission of  $\gamma$ -rays is connected with the discontinuous character of the  $\beta$ -ray spectrum. H. M. D.

**The Origin of Actinium.** C. GÖHRING (*Physikal. Zeitsch.*, 1914, 15, 642—645).—A strong ionium preparation, four years old, was examined for the presence of an "eka tantalum," acting as the parent of actinium, according to the scheme:



by precipitating tantalic acid in the solution. The product was very active, but by repeated solution of the tantalic acid by fusion with potassium hydroxide, and reprecipitation by acid, the activity was removed. It was probably due to ionium. A search for the parent of actinium in pitchblende was made by precipitating tantalic acid in the solution and purifying as above. The product was again practically inactive. Lastly, the uranium-Y separated from 1500 grams of uranyl nitrate was examined for a residual activity, and none was found. It is possible that the method of purification of the tantalic acid adopted may have separated the substance sought. F. S.

**The Distribution of the Radio-elements in Rocks. I. Monazite Sand.** M. BALUCH and G. WEISSENBERGER (*Zeitsch. anorg. Chem.*, 1914, 88, 88—102).—The separation of the minerals in monazite sand may be effected magnetically, magnetite being first removed, then ilmenite, by using an electromagnet, and then monazite, by using a strong field. Zircon is then separated from quartz and feldspar in a centrifugal apparatus. The quartz and feldspar can only be imperfectly separated by using heavy liquids.

Brazilian monazite sand is thus found to contain 75% monazite, 12.4% ilmenite, 8.8% zircon, about 3% quartz, and the remainder magnetite and feldspar.

The other minerals are freed from any adhering traces of monazite by treatment with hot concentrated sulphuric acid. Zircon is found to be coloured violet, as if by the action of radium, and this coloration is not removed by the acid treatment. The quartz is not coloured.

The quantities of radium and thorium have been determined by electrometric measurements, with the exception of the thorium in monazite, which is estimated analytically. The following values for the ratio Th:Ra are found: monazite,  $3.10 \times 10^8$ ; zircon,  $1.51 \times 10^6$ ; magnetite,  $1.49 \times 10^6$ ; ilmenite,  $1.10 \times 10^7$ ; feldspar,  $1.94 \times 10^6$ ; quartz,  $2.13 \times 10^6$ , the total quantity in the last two minerals being very small. Uranium is present in monazite in sufficient quantity to be recognised chemically. Two analyses give 0.062 and 0.065% U, the ratio Ra:U being thus  $3.22 \times 10^{-7}$ . The mesothorium preparations from the sand contain 0.25% mesothorium, 25.00% radium, and 74.75% barium, and it is not possible to alter the ratio in any considerable degree by separating the component minerals. C. H. D.

**Radioactivity of the Rocks of the Kolar Gold-fields.** HERBERT EDMESTON WATSON and GOSTABEHARI PAL (*Phil. Mag.*, 1914, [vi], 28, 44—51).—A modification of Joly's fusion method of

estimating radium in rocks by means of the emanation liberated is described, in which 10 grams of the powdered rock are heated with 2 grams of sodium carbonate and 50 grams of unfused stick potassium hydroxide in a copper flask, previously exhausted by a Fleuss pump. The rocks of the Kolar gold-fields in Mysore, 80 kilometres east of Bangalore, and extending to a depth of 1.2 kilometres, were found to contain only very minute quantities of radium. A source of error was found in the hydrogen liberated in the reaction, which causes the leak produced by a given quantity of radium emanation to be considerably reduced. It was necessary to pass the gas through heated copper oxide before introducing it into the electroscope. The mean amount of radium in the gold-bearing schists was  $0.19 \times 10^{-12}$  gram per gram of rock, and was approximately the same throughout the whole of the workings, independently of the depth. The temperature gradient in the Kolar mines is quite abnormally small, just as the radium content of the rock is extraordinarily low. Other specimens of different rocks of later geological age from the same locality gave amounts of radium varying from 0.8 to 6.9 ( $\times 10^{-12}$  gram per gram).

F. S.

**Radioactivity of the Waters of Saratoga Springs, New York.** RICHARD B. MOORE and C. F. WHITEMORE (*J. Ind. Eng. Chem.*, 1914, 6, 552—553).—The total activity of these waters, with one exception, was found to be low. A large proportion of the activity is due to the presence of dissolved radium salts. Many of the springs contain barium hydrogen carbonate, and, to some extent, there is a relation between the quantity of radium and that of this salt. A connexion could not be traced between the activities and the quantities of the other salts in solution.

W. P. S.

**Analysis of Radioactive Substances by Sublimation.** C. RAMSAUER (*Le Radium*, 1914, 11, 100—107).—An apparatus is described, consisting of a surface of platinum foil, electrically heated, inside a closed desiccator attached to a rubber balloon to allow for the expansion of the gas. Above the heated surface is a tray containing ice, and charged negatively to 220 volts. Radioactive substances are heated on the foil, and the active deposit products, sublimed on the cold surface, are employed to determine the relative proportions of radium, thorium, and actinium present. The heating is maintained for four minutes at  $1150^\circ$ , and measurements of the decay curves are started five minutes from the commencement of heating. The theoretical curves for the pure substances are calculated, and the experimental curves are shown to agree. An analysis by this method of the thermal sediment of Kreuznach gave 1.75 mg. of radium per 1000 kilos., in good accord with the result of the emanation method, 1.84 mg. per 1000 kilos. The amounts of thorium-X and actinium-X present were also estimated.

F. S.

**Distribution of Solvents between Solutes. III. Electrical Conductivity of Mixtures of Salts in Organic and Mixed Solvents.** A. G. DOROSCHEVSKI and S. V. DVORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 453—459. Compare this vol., ii, 419).—The fact that the conductivities of mixtures of potassium and tetraethylammonium iodides in water, methyl or ethyl alcohol, methyl ethyl ketone, acetonitrile and nitromethane, are in agreement with Barmwater's formula (compare Philip and Courtman, T., 1910, **97**, 1261), in conjunction with the authors' conclusions (A., 1913, ii, 1014), indicates that solutions of the two above iodides in all these solvents are isohydric at equivalent concentrations. This is, indeed, found to be the case, as nearly as can be expected in view of the difficulties attending measurement of the conductivity in the solvents employed.

Deviations from this rule might be expected with feeble electrolytes and with solvents exhibiting strongly marked chemical functions and slight ionising capacity. The authors have investigated the conductivities of sodium and potassium iodides and their mixtures in water and in absolute methyl and ethyl alcohols. In absolute methyl alcohol,  $\lambda_{64}$  has the values 74.92 and 80.30 respectively for sodium and potassium iodides, and in absolute ethyl alcohol 28.73 and 29.50. With mixtures of the iodides, the results obtained are analogous to those of Philip and Courtman.

Further measurements of the conductivity were made on sodium and potassium chlorides and their mixtures, and on barium chloride and nitrate and their mixtures, in aqueous ethyl alcohols of different strengths. The results obtained lead to the conclusion that strong electrolytes in organic and mixed solvents form solutions which are isohydric at equivalent concentrations.

T. H. P.

**Dielectric Constant of Gases.** L. VERAIN (*Ann. Physique*, 1914, [ix], **1**, 255—296, 523—590).—Measurements have been made of the dielectric constants of air, carbon dioxide, and sulphur dioxide by a method involving the comparison of the capacity of a condenser containing the gas under examination as dielectric with that of a standard condenser. The influence of temperature was determined by measurements between 0° and 70°, and the pressure was varied from about 1 to 6.5 atmospheres for air and carbon dioxide, and up to 2.4 atmospheres for sulphur dioxide.

The results obtained for air are in excellent accord with the requirements of Maxwell's relation  $K = n^2$ , where  $K$  is the dielectric constant and  $n$  the refractive index. For the other two gases, the agreement is much less satisfactory.

The Mossotti-Clausius relation  $(K - 1)/(K + 2)d = \text{constant}$ , which for gases at low pressures may be written in the form  $(K - 1)/d = \text{constant}$ , is satisfied by the data for air and carbon dioxide within the limits of experimental error, but a much greater divergence is shown by the numbers for sulphur dioxide.

Measurements were also made of the dielectric constant of liquid carbon dioxide and of its saturated vapour at temperatures

between  $-4^{\circ}$  and the critical temperature ( $31.4^{\circ}$ ). In this case Drude's method was employed. If the values of the dielectric constant are plotted as a function of the temperature, an apparently continuous curve is obtained, the tangent at the critical temperature being perpendicular to the temperature axis.

H. M. D.

**The Thermoelectric Force of Tin Selenides.** H. PÉLABON (*Compt. rend.*, 1914, 158, 1897—1900. Compare this vol., ii, 521).—The author has determined the thermoelectric force of couples consisting of platinum with tin-selenium alloys of varying composition at various temperatures, and has plotted the curves, showing the relationship between the thermoelectric force and the percentages of tin and selenium in the alloys. The form of the curves varies with the temperature, but all show an angular point corresponding with the selenide  $\text{SnSe}$ . The selenide  $\text{SnSe}_2$  is not indicated by any particular change in direction of the curve. At the hot junction the current passes from platinum to the alloy for  $\text{Pt-SnSe}$ , and from the alloy to platinum for  $\text{Pt-SnSe}_2$ . A couple formed by platinum and an alloy of composition intermediate between that of the two selenides, and varying slightly with the temperature, will have no thermoelectric force. W. G.

**Application of the Theory of Allotropy to Electromotive Equilibria.** A. SMITS and A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 37—54. Compare this vol., ii, 165).—If the equilibrium at the surface of contact between a metal and a solution of one of its salts is disturbed by anodic dissolution or cathodic deposition, a difference of potential will be set up between the electrode and a "normal" auxiliary electrode. For very small current densities, the external equilibrium will not, in general, be sensibly disturbed, but as the current density increases, it is to be expected that the departure from the normal condition of equilibrium will become evident, and that the resulting difference of potential between the electrode and the auxiliary electrode will increase. If the internal equilibrium is set up very quickly, the potential difference in question will be very small, but much larger values are to be expected if the adjustment of the internal equilibrium is comparatively slow.

Experiments have been made in which currents of varying intensity were passed between rods of silver, copper, lead, nickel, cadmium, bismuth, iron, and aluminium, immersed in solutions of the corresponding salts, and in which the anodic and cathodic polarisation was determined by the aid of an auxiliary electrode of the same metal.

The results obtained lead the author to the conclusion that the internal equilibrium is very quickly set up in silver, copper, and lead, very slowly in nickel, and at an intermediate rate in cadmium. The behaviour of bismuth, iron, and aluminium suggests that catalytic agencies play a considerable part in connexion with the polarisation phenomena.

H. M. D.

**Stability and Oxidation Potential of Hypochlorites.** Contributions to Catalysis and a Hypochlorite-Carbon Cell. K. A. HOFMANN and KURT RITTER (*Ber.*, 1914, **47**, 2233—2244).—The authors have compared the behaviour of calcium hypochlorite, free from chloride, with that of bleaching powder and of a mixture of calcium hypochlorite and calcium chloride towards various reagents (compare Taylor, T., 1910, **97**, 2541). Towards carbon dioxide-free, dry air, calcium hypochlorite and bleaching powder show very little difference in behaviour at 90°, there being only a very slight loss of chlorine in both cases. When exposed to moist air containing carbon dioxide at the ordinary temperature, the bleaching powder loses a greater proportion of its available chlorine than does the calcium hypochlorite; a mixture of calcium hypochlorite and calcium chloride behaves similarly to the bleaching powder. In an atmosphere of dry carbon dioxide, calcium hypochlorite loses a small percentage of its available chlorine after five hours' exposure; the mixture of hypochlorite and chloride loses a slightly greater percentage, whilst the bleaching powder loses all its available chlorine. In a current of moist carbon dioxide, both calcium hypochlorite and bleaching powder lose all their active chlorine, but whilst the latter evolves only chlorine, the former evolves both chlorine and hypochlorous acid; a mixture of hypochlorite and chloride behaves similarly to bleaching powder. In a solution of calcium hypochlorite a stream of carbon dioxide gives the ratio: free chlorine: chloride chlorine: chlorate chlorine = 2: 1: 1, the hypochlorous acid formed in solution decomposing in accordance with the equation  $4\text{HOCl} = \text{HClO}_3 + \text{HCl} + \text{Cl}_2 + \text{H}_2\text{O}$ . In a solution of bleaching powder the free chlorine is increased at the expense of the chlorate chlorine, the ratio being 3: 1. Both calcium hypochlorite and bleaching powder behave in the same way towards ammonia, there being an almost quantitative evolution of nitrogen.

Solutions of calcium hypochlorite and of bleaching powder are decomposed catalytically to the same extent by cobalt, nickel, and iridium oxides, whereas the oxides of chromium, iron, manganese, uranium, bismuth, palladium, osmium, thallium, and vanadium are inactive. Calcium hypochlorite solutions are more stable towards ruthenium and rhodium salts, whereas bleaching powder solutions are more stable towards copper sulphate and lead nitrate.

It has been supposed that the oxidising power of hypochlorites and other oxidising agents can be increased by the addition of oxygen-evolving catalysts. Experiments with solutions of sodium hypochlorite and hydrogen peroxide show that this is not the case; oxygen-evolving catalysts, such as iridium powder and cobaltic oxide, simply evolve their oxygen without exerting any appreciable oxidising effect on any oxidisable substances present, for example, anthracene, whereas oxygen carriers, such as osmium tetroxide, increase the oxidising power, that is, raise the oxidation potential of the hypochlorite or hydrogen peroxide. This result can be predicted from thermochemical considerations.

Measurement of the oxidation potentials of solutions of calcium



hypochlorite and of bleaching powder, each saturated with calcium hydroxide, using platinum, magnetite, or gold electrodes, showed they are approximately the same; the potential depends very little on the dilution, but is affected by the alkalinity of the solutions. The bleaching-powder solutions are, however, too unstable for use.

Of various cells which were built up in order to make use of the oxidising powers of hypochlorites, the following gave the highest *E.M.F.*, namely, 2.24 volts, corresponding with a 92.2% yield on the used oxygen: Platinum-sodium hypochlorite solution made alkaline with sodium carbonate | 20% solution of sodium chloride | 10% sodium hydroxide, zinc oxide, zinc.

It was found possible to construct cells with carbon electrodes. Thus the cell: Platinum-sodium hypochlorite, sodium carbonate solution | 2*N*-sodium hydroxide | 2*N*-sodium hydroxide, beechwood charcoal in platinum wire gauze, gave an initial voltage of 0.76—0.91 volt. Quantitative measurements showed that the current yield from this cell was 76% of the oxygen used from the hypochlorite. With a somewhat similar cell it was shown that the electromotively active oxygen was almost completely transformed into carbon dioxide.

It follows that with alkaline hypochlorite solutions at unattackable electrodes a sufficiently strong oxidation potential is obtained to oxidise boxwood charcoal, opposed to it in a galvanic cell; also, from such a cell current may be taken continuously. Before these results are of practical value, however, further investigations are necessary.

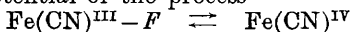
T. S. P.

### The Potential of the Ferricyanide-Ferrocyanide Electrode.

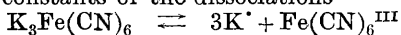
ERICH MÜLLER (*Zeitsch. physikal. Chem.*, 1914, 88, 46—56).—The potential of a number of mixtures of potassium ferrocyanide and potassium ferricyanide in the presence of potassium hydroxide, hydrochloric acid, and potassium chloride has been determined at 0°. The electrode used was either of gold or platinised platinum. The results obtained have been compared with those of Lewis and Sargent (*A.*, 1909, ii, 369) and Fredenhagen (*A.*, 1902, ii, 238). It is shown that the figure which has hitherto been regarded as the potential of the ferrocyanide-ferricyanide electrode is an undetermined and indefinite quantity, which depends not only on the ratio of the concentration of the two salts, but also on the concentrations of the salts themselves. In the presence of *N*-potassium chloride the potential at 0° is expressed by

$$e = 0.232 + 0.0546T \log i/o \text{ volts (against } NE),$$

where *i* and *o* are the total concentrations of the ferricyanide and ferrocyanide respectively, and *NE* represents the normal electrode. The electrolytic potential of the process



is at 0° approximately 0.14 volt (against *NE*), and the ratio of the dissociation constants of the dissociations



and  $\text{K}_4\text{Fe(CN)}_6 \rightleftharpoons 4\text{K}^+ + \text{Fe(CN)}_6^{IV}$  is approximately 68. The influence of potassium hydroxide and acids on the potential of the

$\text{Fe}(\text{CN})_6^{\text{III}}/\text{Fe}(\text{CN})_6^{\text{IV}}$  electrode is due to a shifting of the dissociation ratio. At small concentrations of potassium ferri- and ferrocyanides, the dependence of the potential on the concentration of potassium hydroxide and potassium chloride at  $0^\circ$  is given by the equation  $\epsilon = 0.24 + 0.0546T \log i/o. \text{K}^+$  volts (against  $NE$ ), and on the concentration of free acid by the equation

$$\epsilon = 0.45 + 0.0546T \log i/o. \text{H}^+ \text{ (against } NE),$$

where  $\text{K}^+$  and  $\text{H}^+$  respectively are the concentrations of the potassium and hydrogen ions. J. F. S.

**Electromotive Behaviour of Soluble Sulphides.** ROGER C. WELLS (*J. Physical Chem.*, 1914, 18, 510—520).—The single potentials of acid solutions of hydrogen sulphide and of solutions of sodium hydrogen sulphide, sodium sulphide, and sodium polysulphides have been measured against a calomel electrode. It is shown that solutions of polysulphides behave electromotively in the same way as other oxidation and reduction elements. It is generally impossible to represent their behaviour mathematically without assuming that several polysulphides are present in a rather complicated equilibrium. For mixtures which contain sufficient sulphur to form  $\text{Na}_2\text{S}_2$  and  $\text{Na}_2\text{S}_3$  the normal electrode potential can be obtained by calculation from the relative concentrations of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_4$  by means of the equation

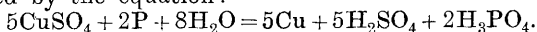
$$E = E_0 - 0.059/6 \log (S^{--})^4/(S_4^{--}),$$

when the value of  $E_0$  is found to be  $-0.208$  volts. On reaching a sulphur concentration corresponding with  $\text{Na}_2\text{S}_4$  there is a sudden shift in the  $E_0$  value which points to a higher polysulphide. On the other hand, solutions which are easily saturated with sulphur have as the expression for their potential the equation:

$$E = -0.26 - 0.029 \log (S^{--}).$$

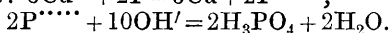
J. F. S.

**Positive Ions from Non-metallic Elements. I. Precipitation of Metals from Solutions of their Salts by Yellow Phosphorus.** R. M. BIRD and S. H. DIGGS (*J. Amer. Chem. Soc.*, 1914, 36, 1382—1392).—The products obtained by the action of yellow phosphorus on aqueous solutions of copper sulphate are copper and phosphoric acid, together with smaller quantities of copper phosphide and phosphorous acid. The metallic copper was deposited in the form of tubes surrounding the sticks of phosphorus, each tube being covered on the inside with a layer of black copper phosphide. It is probable that the phosphide is formed by the subsequent action of the precipitated copper on the phosphorus, and that the phosphorous acid is due to the interaction of the phosphorus and the phosphoric acid formed in the principal reaction. The quantitative measurements indicate that approximately five atoms of copper are precipitated by two atoms of phosphorus, as represented by the equation:

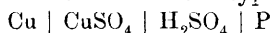


Since the copper is formed only on the surface of the phosphorus or on the surface of conductors connected with the phosphorus, it is

probable that the action is electrolytic in character, as represented by the equations:  $5\text{Cu}^{++} + 2\text{P} = 5\text{Cu} + 2\text{P}^{\cdots\cdots}$ ;



According to this, the primary action consists in the transfer of positive charges from the copper to the phosphorus. In support of this view, it is found that a cell of the type

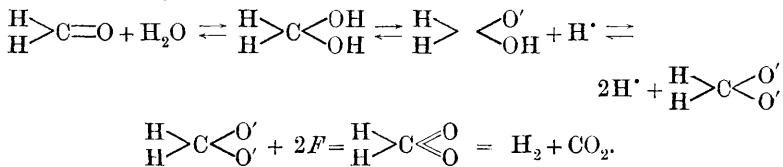


yields a current which passes from the phosphorus to the copper through the solutions. The *E.M.F.* of the cell is about 0.35 volt, and little or no difference is found by varying the concentration of the sulphuric acid solution or by replacing this by distilled water, or by solutions of sodium and magnesium sulphate.

According to these experiments there is no essential difference between the metallic and non-metallic elements in respect of their tendency to form positive ions.

H. M. D.

**Evolution of Hydrogen at the Anode during the Electrolysis of Methyl Alcohol and Formaldehyde.** ERICH MÜLLER and FRIEDRICH HOCHSTETTER (*Zeitsch. Elektrochem.*, 1914, **20**, 367—369).—Equal volumes of 4*N*-sodium hydroxide and methyl alcohol were electrolysed in a divided cell using a platinum anode and a current density of 0.1 ampere per 15 sq. cm. The anode products were formic acid and formaldehyde and 135 c.c. of a gas consisting of 97.4%  $\text{H}_2$ , 1.2%  $\text{O}_2$ , and 1.4%  $\text{CO}$ . The amount of gas produced increased as the electrolysis proceeded. The substitution of formaldehyde or formic acid for the methyl alcohol gave no gas evolution at the anode. On substituting a copper anode for the platinum gas, evolution did not take place with methyl alcohol or formic acid, but with formaldehyde pure hydrogen was evolved at the anode, and in amounts equal to that at the cathode. It is shown that in this case the total current can be used in effecting the reaction  $\text{H}_2\text{C}=\text{O} + \text{O}'' + 2\text{F} = \text{H}_2 + \text{CO}_2$ , and this reaction probably consists in the discharge of the ion  $\text{H}_2\text{CO}_2''$ , since formaldehyde behaves as a dibasic acid in alkaline solution. The whole change is represented by the scheme:



J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. III. Attempts to Prepare Zirconium, Aluminium, Antimony and Chromium Bronzes.** R. KREMAN, JOSEF LORBER, and RUDOLF MAAS (*Monatsh.*, 1914, **35**, 581—602. Compare this vol., ii, 96, 422).—Attempts to deposit zirconium electrolytically from (1) an alkaline solution of zirconium hydroxide and tartaric acid, with platinum electrodes,

(2) with a mercury cathode, and (3) from an alkaline solution of zirconium oxychloride and tartaric acid to which a small quantity of an iron salt had been added, all led to negative results; in the last case iron was deposited in the passive condition. Attempts to deposit zirconium along with tin, zinc, and copper respectively from mixed alkaline solutions also failed to give a deposition of zirconium. The deposition of copper from aluminium solutions in tartaric acid or potassium cyanide gave deposits of copper containing several per cent. of cuprous oxide. Antimony and copper could be simultaneously deposited from a solution of copper sulphate containing tartar emetic, aluminium sulphate, and alkaline tartrate. The alloys were examined, and it is shown that the tendency to form mixed crystals is small, but that rather the two metals separate out as individuals. The electrolysis of a chromium containing copper solution gave no deposit of metallic chromium copper alloy; a copper is deposited which contains about 2.2% of chromium, but this is in all probability present as hydroxide.

J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. IV. Experiments on the Deposition of Iron-Magnesium Alloys from Aqueous Solutions.** ROBERT KREMANN and JOSEF LORBER (*Monatsh.*, 1914, 35, 603—634. Compare preceding abstract).—A series of solutions of ferrous sulphate and magnesium chloride, with and without the addition of potassium chloride, have been electrolysed with the object of in this way obtaining alloys of iron and magnesium. The deposits obtained with current densities varying from 0.6 to 3.3 amperes per sq. dcm. contained metallic iron and a solid solution of iron and magnesium, together with ferrous hydroxide and magnesium hydroxide. The maximum percentage of magnesium in any case being 3.0%, and in all cases where the magnesium approaches this value the oxygen content of the deposit also increases, rising in the stated case to 10.37%. The product oxidises very rapidly in the air, and on slowly drying in a desiccator it becomes heated. On warming the deposit to 200—300° it oxidises so rapidly that it glows. A series of potential measurements were made with the products, and also with electrolytic iron; in all cases the potential against ferrous sulphate solution shows that the iron is passive. The metallographic investigation shows that alongside with the iron deposit there is a silver-white deposit, probably of iron-magnesium alloy and oxides. The determination of the hardness of the deposits leads to the same conclusion. When the dried deposits are placed in water at 94°, an evolution of pure hydrogen occurs, which increases with the magnesium content of the deposit.

J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. V. Nickel-Iron Alloys Deposited from Sulphate Solutions at High Temperatures.** ROBERT KREMANN and RUDOLF MAAS (*Monatsh.*, 1914, 35, 731—753. Compare preceding abstracts).—In a previous com-

munication (this vol., ii, 97) iron-nickel alloys deposited at ordinary temperature were shown to be brittle, and this was supposed to be due to the presence of hydrogen. The present paper deals with the production of similar alloys at higher temperatures, the object being to obtain less brittle alloys, which are to be expected if the presence of hydrogen is the cause of the brittleness. Experiments were carried out with (1) solutions of iron and nickel sulphates without additions, (2) in the presence of potassium oxalate, and (3) in the presence of citric acid. In comparison with the results obtained at the ordinary temperature (*loc. cit.*) it is shown that the nickel content of the deposit increases enormously with increasing temperature. With regard to the relationship between the composition of the solution and that of the deposits, it is shown that the same sort of relationships are found as at ordinary temperatures. (1) The nickel content of the deposit increases at first rapidly and then more slowly with an increasing concentration of the nickel in the solution. (2) Addition of potassium oxalate or citric acid increases the nickel content of the deposition. In the case of citric acid the amount of increase depends on the original concentration of the acid. An improvement in the consistency of the deposit by working at higher temperatures is not effected, but the increased percentage of nickel in the deposits (70—80%) is to be regarded as a disadvantage from the point of view of the preparation of nickel steels. When iron cathodes were employed in the electrolysis of the metal there is a great tendency to the formation of spongy deposits, but the use of carbon cathodes leads to a deposit of greater consistency. The concentric ring structure of the alloys found at lower temperatures is obtained in the present work, but much more strongly marked. It is supposed to be due to the formation of hydrogen bubbles on the surface of the deposit round which the further deposition takes place. The hardness of the alloys is greater than that of the alloys obtained at lower temperatures, and from this the authors draw the conclusion that the formation of solid solutions has taken place to a far greater extent at higher temperatures than at lower temperatures. The increased hardness also offers a confirmation to the hypothesis put forward in the earlier paper that the presence of hydrogen cannot be regarded as the cause of the increased hardness of the electrolytic deposits. The *E.M.F.* of the various deposits have been measured against solutions of nickel sulphate and ferrous sulphate. It is shown that both those obtained at 75° and at the ordinary temperature give a potential which is much nobler than the usual potential, and on remaining in the solution slowly approach the normal value. The conclusion is drawn from this that iron-nickel alloys are deposited in the passive condition. This is explained by the assumption of a local alkalinity in the neighbourhood of the electrode.

J. F. S.

**Electrolytic Deposition of Brass on a Rotating Cathode.**  
C. W. BENNETT and A. W. DAVISON (*J. Physical Chem.*, 1914, 18, 488—509).—Since the deposition of brass electrolytically from

mixed solutions of cyanides of zinc and copper only yielded unsatisfactory results, a series of experiments were made with other solutions of salts of these metals with the object of obtaining brass electrolytically. As a preliminary the deposition voltages of zinc and copper, at various current densities, were determined against an oxygen electrode for solutions of the sulphate, formate, fluoride, silicofluoride, and cyanide of these metals with various additions of acid, ammonium chloride, and potassium cyanide, and deposition voltage curves drawn. Pairs of substances which had similar curves were then employed for the production of brass electrolytically. It is shown that in no case save that of the mixed cyanides could a deposit of brass be obtained, and since this is not satisfactory the reasons for the non-success were studied. It is shown that the deposition of brass from cyanide solutions depends probably on two factors: (1) the tendency of the potentials of copper and zinc to become the same in cyanide solutions, and (2) the increase in the potential of the more noble metal by impoverishment. The latter factor is practically eliminated by using a rapidly rotating cathode. A satisfactory brass has not been deposited from cyanide solutions on a rotating cathode; the alloy obtained is brittle, and the brittleness is probably due to occluded impurities which arise from the cyanide, and therefore cannot be removed. The ratio of the metals in the solutions for the deposition of a brass varies with the amount of free cyanide and the rate of rotation of the cathode. J. F. S.

**Magneto-chemical Phenomena.** A. SCHÜKAREV (*Physikal. Zeitsch.*, 1914, 15, 670—673).—If two platinum plates are immersed in a solution containing 0.1*N*-ferric chloride and 0.1*N*-potassium iodide, a current is obtained when the two plates are connected through a galvanometer. The phenomenon is independent of the stirring of the solution, and if the plates are of unequal size the current flows from the larger to the smaller plate.

If two plates equal in size are employed, and the solution is exposed to the action of a magnetic field in such a way that the two plates are unsymmetrically situated in reference to the magnetic lines of force, a further polarisation current is set up, which flows from the plate which is in the more intense part of the field to the plate in the less intense region. This magneto-chemical effect is not observed if the plates are symmetrically situated with reference to the transverse field or if the plates are at right angles to the lines of force. Similar effects have been obtained with other solutions.

Other experiments are described which show that similar magnetic effects may be observed at the electrodes during the electrolysis of aqueous solutions of certain salts. A table is given in which the results obtained with a larger number of different electrolytes are recorded. H. M. D.

**The Diamagnetic Properties of the Elements follow a Periodic Law.** PAUL PASCAL (*Compt. rend.*, 1914, 158, 1895—1897).—By plotting the coefficients of magnetisation of the elements

against their atomic weights a series of curves are obtained, similar to Lothar Meyer's atomic volume curves, on which elements belonging to the same natural family occupy similar positions on the curves.

W. G.

**Qualitative Method for the Study of the Magnetic Susceptibility of Solutions.** A. QUARTAROLI (*Nuovo Cim.*, 1914, [vi], 7, i, 159—164).—By means of truncated conical poles a field is obtained in which a zone of great intensity is separated sharply from one of feeble intensity. The solution to be examined is introduced into a glass tube of 8—10 mm. diameter, and above it is placed, carefully and without mixing, coloured water. The tube is then arranged between the poles so that the surface of separation of the two liquids corresponds with the lower point where the poles begin to diverge. When the magnet is excited, the water bulges out into the magnetic solution below without sensibly mixing with it, and, if the field is sufficiently intense, a globule of the water becomes detached and remains suspended in the magnetic liquid. The phenomenon is visible with weak fields and dilute solutions, which yield scarcely perceptible indications by Plücker's or the U-tube method. Naturally, the results become more marked as the specific gravities of the two liquids approach equality. T. H. P.

**The Manner in which the Susceptibility of Paramagnetic Substances Depends on the Density.** W. H. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 110—122. Compare this vol., ii, 335).—By application of the quantum theory, the author has deduced equations from which it is possible to calculate the susceptibility of paramagnetic substances. The calculated values for oxygen are in satisfactory agreement with the data obtained by Perrier and Onnes (*loc. cit.*) in their measurements of the susceptibility of liquid mixtures of oxygen and nitrogen. It was previously pointed out that these results could be explained on the basis of Langevin's theory by the assumption of negative molecular fields, and the experiments in question do not therefore afford an experimentum crucis in respect of the two theories.

H. M. D.

**Is the Duhem-Margules Equation Dependent on the Ideal Gas Laws?** M. A. ROSANOFF (*J. Amer. Chem. Soc.*, 1914, 36, 1408—1411).—It is shown that the Duhem-Margules equation connecting the partial pressures and the proportions of the components in a binary mixture is a purely thermodynamic relationship, and is applicable to all mixtures independently of whether the vapours satisfy or deviate from the simple gas laws.

H. M. D.

**Laws of Raoult and Henry and the Constants of Ebullioscopy and Cryoscopy.** M. A. ROSANOFF and R. A. DUNPHY (*J. Amer. Chem. Soc.*, 1914, 36, 1411—1418).—The authors show that Raoult's and Henry's laws may be deduced in a simple manner from the Duhem-Margules equation (compare preceding abstract). It is further shown that expressions for the ebullioscopic and cryo-

scopic constants may be obtained from Raoult's law in combination with the gas laws. The molecular rise of the boiling point is given by  $E = RT/100v dP_1/dT$ , in which  $v$  is the specific volume of the vapour at the boiling point and  $dP_1/dT$  is the variation of the vapour pressure with the temperature at the boiling point. From the available data it would seem that both these quantities can be measured with considerable accuracy, and the formula is recommended for the evaluation of boiling-point constants. These constants have been calculated for thirty-three liquids, and it is estimated that the probable error attaching to the values obtained in this way is in general less than 2%.

The expression derived for the freezing-point constant is similar, and may be written  $E = RT/100v(dp_i/dt - dp_w/dt)$ , where  $v$  is the specific volume of the vapour at the freezing point, and  $dp_i/dt$  and  $dp_w/dt$  are the slopes of the vapour-pressure curves for ice and water respectively at this temperature. On account of the experimental difficulty attached to the measurement of these quantities, the equation is only of theoretical interest.

Since Raoult's law follows from the Duhem-Margules equation, in which the molar fractions are based on the molecular weights of the vapours, it is suggested that the molecular weights obtained from boiling-point and freezing-point measurements may have reference to the substances in vapour form, and not to the substances in the liquid solution. H. M. D.

**Application of the New Heat Theorem to Gases.** W. NERNST (*Zeitsch. Elektrochem.*, 1914, 20, 357—360).—The Nernst heat theorem has hitherto only been applied to condensed systems of crystallised substances, amorphous substances, mixtures, and dilute solutions. The present paper deals with the application to gaseous systems. Three fundamental hypotheses are made: (1) Every gas which is cooled at constant volume without liquefying reaches eventually a condition in which it possesses a vanishing heat capacity. (2) The decrease in the specific heat of a gas occurs earlier the greater the density of the gas; and (3) every physical or chemical change which takes place with the production of the maximum work  $A$  in gases of finite density, occurs in accordance with the expression  $\lim_{T \rightarrow 0} dA/dT = 0$  ( $T = 0$ ). The heat theorem is then applied to the vapour-pressure curve of gases, and the expression  $A = -Tf(\lambda_v/T^2)dT$  evolved. It is shown that every gas which is constantly cooled at constant volume (assuming that liquefaction does not take place) must eventually reach a condition in which it presents resemblances to the amorphous condition. Strong compression of a gas at constant temperature will bring the same condition about. Confirmation of these two statements is found in the results of seismic researches on the conduction of transverse vibrations through the interior of the earth. J. F. S.

**Specific Volumes of Nickel Steels.** P. CHEVENARD (*Compt. rend.*, 1914, 159, 53—56).—A study of the dilatation curves of nickel steels with varying nickel content at  $-195^\circ$ ,  $0^\circ$ , and  $750^\circ$ . At  $0^\circ$



there is an irregularity in the curve for alloys between Fe and  $\text{Fe}_2\text{Ni}$ , the alloys corresponding with this portion of the curve undergoing an irreversible transformation, the amplitude of which is proportional to the content of free iron in the alloy. For alloys between  $\text{Fe}_2\text{Ni}$  and  $\text{FeNi}_2$  there is a reversible irregularity, the amplitude of which is directly proportional to the amount of the compound  $\text{Fe}_2\text{Ni}$  in the alloy. W. G.

**Calorific Conductivity and Viscosity of Monatomic Liquids.** LÉON BRILLOUIN (*Compt. rend.*, 1914, 159, 27—30).—A mathematical discussion of the subject. W. G.

**The Limits of Inflammability of Fire-damp.** F. LEPRINCE-RINGUET (*Compt. rend.*, 1914, 158, 1793—1796).—The composition of the combustible gases has been determined, in each case, by Lebreton's apparatus, by Le Chatelier's apparatus, and by the eudiometric method. Using the first apparatus, three factors have to be taken into account, namely, the temperature, the percentage of water vapour, and the solubility of the gases in the water with which they are shaken, the influences of which can be calculated. The results show (1) that pressure exerts no appreciable influence on the limit of inflammability. (2) The limit varies with the diameter of the tube used, and is the limit of propagation relative to the diameter of the orifice. (3) The limit of propagation from the bottom upwards is inferior to the limit from the top of the tube downwards. W. G.

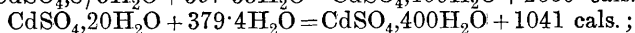
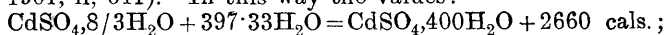
**The Inflammability of Mixtures of Methane and Different Gases.** F. LEPRINCE-RINGUET (*Compt. rend.*, 1914, 158, 1999—2001).—A study of the inferior and superior limits of inflammability of mixtures of methane and oxygen and nitrogen; and methane, oxygen, and carbon dioxide. The curves obtained, showing in the first  $y = \text{CH}_4/\text{O}_2$  and  $x = \text{N}_2/\text{O}_2$ , and in the second case  $y = \text{CH}_4/\text{O}_2$  and  $x = \text{CO}_2/\text{O}_2$  are the same curves, the abscissæ in the second being multiplied by 0.56. Thus a mixture containing several incombustible gases behaves as though each incombustible element was replaced in a definite ratio by one other of these gases. W. G.

**Pressure Regulators. II.** ERNST BECKMANN and OTTO LIESCHE (*Zeitsch. physikal. Chem.*, 1914, 88, 13—21. Compare A., 1912, ii, 534).—Several modifications are described which make the pressure regulator for ebullioscopic determinations more trustworthy and easier to manipulate. Slight changes are made in the method of admitting small quantities of air, and in the automatic regulation of the pressure. Instead of one large flask as compensating volume, two are used in the modified apparatus. A single electrical circuit and relay replaces two such in the original apparatus. By means of this apparatus the pressure can be kept constant to within 6 mm. at pressures down to 100 mm. This constance of pressure implies a constancy in the boiling point of about 0.01°. J. F. S.

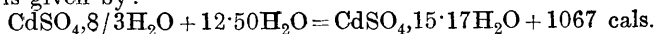
**Ebullioscopic Behaviour of Solvents at Various Pressures. I. Benzene, Chloroform and Ethyl Alcohol.** ERNST BECKMANN and OTTO LIESCHE [with JULIUS VON BOSSE] (*Zeitsch. physikal. Chem.*, 1914, 88, 23—34).—The ebullioscopic constants have been determined for the solvents benzene, chloroform, and ethyl alcohol at a series of pressures from 1371 mm. to 40 mm., using a number of substances of known molecular weight in the determinations. The apparatus used was electrically heated, and the pressure was maintained by the manostat previously described (see preceding abstract). The value of the constant falls parallel with the pressure. The constants obtained agree well with those obtained by Drucker (A., 1910, ii, 929), and the values are compared with the values calculated from a number of formulæ which were discussed by the authors (this vol., ii, 170), and in general a satisfactory agreement is found. The newly-determined constants for atmospheric pressure are: benzene, 25·7; chloroform, 38·8; ethyl alcohol, 12·0. Curves are given of the change of the constant with pressure.

J. F. S.

**The Theoretical Heat of Solution of  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  and the E.M.F. of the Weston Normal Element.** H. VON STEINWEHR (*Zeitsch. physikal. Chem.*, 1914, 88, 229—254).—The work of Holsboer (A., 1901, ii, 226) and that of Kohnstamm and Cohen (A., 1898, ii, 495) on the heat of solution and the solubility minimum of cadmium sulphate are criticised, and the results, in part, recalculated. A series of new determinations of the heat of solution and its temperature-coefficient are made by the method of taking a saturated solution and determining the heat change when successive small quantities of water are added to it. The apparatus and experimental details are the same as that described by the author (A., 1901, ii, 641). In this way the values:



and  $\text{CdSO}_4 \cdot 15\cdot17\text{H}_2\text{O} + 5\cdot43\text{H}_2\text{O} = \text{CdSO}_4 \cdot 20\cdot6\text{H}_2\text{O} + 552 \text{ cal.}$  are obtained, and from these the integral heat of solution of the solid hydrate in 12·5 mols. of water, that is, the number of mols. of water required to give a saturated solution of  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  at 18°, is given by:



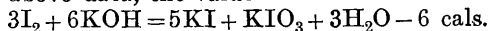
The temperature-coefficient of the heat of solution at 18° is found to be  $-63\cdot15 \text{ Cal.}$  From the thermal experiments the total energy of the Weston Element is found to be  $U = 47201 \text{ cal.}$ , and from electrical data the E.M.F. is calculated to 1·028675 volt at 18° and  $U$  to 47427 cal. It is thus shown that the energy measured calorimetrically is not independent of the temperature, as was asserted by Cohen (*loc. cit.*), and that the temperature-coefficient is not small enough to be neglected, and the value of this coefficient determined calorimetrically agrees well with that determined electrically.

J. F. S.

The Hypohalogenous Acids and the Hypohalogenites.  
**VII. Heat Changes in Reactions of Iodine Solution.** ANTON SKRABAL and FRIEDRICH BUCHTA (*Monatsh.*, 1914, 35, 697—730).—Compare A., 1907, ii, 448; 1909, ii, 224; 1911, ii, 382; 1912, ii, 33, 340).—The heat changes accompanying the reactions of iodine in alkali solutions have been determined calorimetrically, using a calorimeter of the Thomsen pattern, in which the usual gold-plated vessels are substituted by glass vessels. The following thermal data has been obtained:

- (1)  $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} = 3\text{I}_2 + 3\text{H}_2\text{O} + 6\text{KCl} + 829 \text{ cal.}$
- (2)  $\text{KIO}_3 + 8\text{KI} + 6\text{HCl} = 3\text{KI}_3 + 6\text{KCl} + 3\text{H}_2\text{O} + 804 \text{ cal.}$
- (3)  $3\text{KI}_3 + 6\text{KOH} = 8\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} + 25 \text{ cal.}$

From the above data, the value



was deduced, together with the heat of solution of iodine in potassium iodide and in water.

The following reaction, (4)  $\text{KI}_3 + \text{KOH} = 2\text{KI} + \text{HIO} - 43 \text{ cal.}$ , was also determined. In this connexion, note is made of the fact that reactions (3) and (4) occur simultaneously, and the most suitable conditions for each determination were evolved from a knowledge of the kinetics of the reactions. J. F. S.

**Principles of the Distillation of Alcohol.** E. CHENARD (*Bull. Soc. chim.*, 1914, [iv], 15, 592—595).—The vapour formed by distillation of aqueous alcohol tends to separate into layers of different density, affording a means of mechanical separation. Fractionating columns need not be vertical. It is suggested that partial separation of substances boiling at the same temperature might be effected by taking advantage of the difference in density of the vapour in various parts of the condenser. A. J. W.

**The Quantitative Effect of Rapid Cooling on the Constitution of Binary Alloys.** II. G. H. GULLIVER (*J. Inst. Metals*, 1914, 11, 252—272).—Methods are given for calculating the proportions of liquid and solid present in rapidly cooled alloys, even in cases in which the liquidus and solidus lines are considerably curved. The methods are illustrated by application to alloys of copper with zinc, tin, and nickel. C. H. D.

**Fluidity as a Function of Volume, Temperature, and Pressure. The Equation of State and the Two Kinds of Viscous Resistance. So-called "Slipping" of Gases.** EUGENE C. BINGHAM (*J. Amer. Chem. Soc.*, 1914, 36, 1393—1408).—According to Batschinski (A., 1913, ii, 26), the fluidity of a liquid is proportional to the "free volume," and the author shows that this relation also holds for suspensions of solids in liquids. It follows from this connexion between the fluidity and the "free volume" that the variation of the fluidity of a liquid with temperature and pressure may be represented by an equation resembling that of van der Waals. Empirical equations, which may be regarded as

simplified forms of the modified van der Waals equation, have already been shown to represent the experimental data for liquids with considerable accuracy. The equations do not apply, however, to gases, and the large discrepancy between the calculated and observed values is attributed to a special type of viscous resistance which does not come into play in the case of liquids. This resistance has its origin in the diffusion of the gas which carries with it translational motion, and is termed "diffusional viscosity." In liquids, the resistance to flow caused by diffusion is negligibly small in comparison with the "collisional viscosity," which is due to the collisions of molecules of one layer with those of an adjacent layer moving at a slightly lower velocity. In this case, the transfer of momentum is not accompanied by transfer of material.

According to the above views, the viscosity of a gas or liquid is the sum of the diffusional or collisional viscosities. By combining the formulæ for these two types of viscosity, the author arrives at the equation  $\phi = (v - w) / \{A + BT(v - w)\}$  for the connexion between the viscosity  $\phi$ , the specific volume  $v$ , and the absolute temperature  $T$ . In this equation,  $A$ ,  $B$  and  $w$  are constants,  $w$  representing the limiting volume corresponding with zero fluidity (compare Batschinski, *loc. cit.*). It is shown that the fluidity of carbon dioxide in both the liquid and gaseous states can be represented with a fair degree of approximation by means of this formula.

The case of a rarefied gas is also considered in accordance with the above views, and the author draws the conclusion that the viscosity at constant temperature is directly proportional to the density, and at constant volume is directly proportional to the square root of the absolute temperature. At constant temperature and pressure, the viscosity is directly proportional to the square root of the molecular weight, and is independent of the other physical or chemical properties of the gas.

It is supposed that the above deductions from the kinetic theory are also applicable to the explanation of phenomena observed in connexion with the elastic properties of solids. H. M. D.

**Relation of the Internal Pressure of a Liquid to its Dielectric Capacity and Permeability.** W. C. McC. LEWIS (*Phil. Mag.*, 1914, [vi], 28, 104—116).—The minimal values of the internal pressure of a number of liquids at 0° have been calculated from the equation  $\pi = RT/(v - v_l)$ , in which  $v_l$  is the limiting volume at absolute zero. This limiting volume has been derived from the critical volume by the relation  $v_l = 0.27v_c$  (Guldberg). In general, the pressures obtained in this way are approximately half as large as the values given by the latent heat of vaporisation.

A comparison of the internal pressures with the corresponding dielectric constants shows that these are not directly proportional, although it is probable that they are related in a less direct manner. On the assumption that the forces of molecular attraction are electromagnetic in character, a relation connecting the internal pressure with the dielectric capacity is deduced, and it is shown

that substances with larger internal pressures have correspondingly smaller permeabilities.

By application of the electron theory to the question of cohesion, it is further shown that the validity of Pascal's relation, according to which the product of the susceptibility and the specific volume is independent of the temperature and the state of aggregation of a substance, involves the conclusion that the orbits of the electrons are constant, and that the frequencies of the absorption bands in the visible and ultra-violet should be the same for both the liquid and gaseous states, which is approximately, but not strictly, in agreement with experiment.

The diminution of cohesion with rise of temperature is in accord with the view that the intermolecular forces are electromagnetic in character.

H. M. D.

**The Variation of the "Gold Value" and the Viscosity of Colloidal Solutions with the Temperature.** L. LICHTWITZ and A. RENNER (*Zeitsch. physiol. Chem.*, 1914, **92**, 113—118).—The power of colloidal solutions to prevent the precipitation of gold increases slightly with the temperature. The viscosity diminishes with rise of temperature, and increases again when the temperature falls. The colloidal solutions employed were prepared from gelatin, serum-albumin, and human blood-serum, and the results are in accord with those obtained by previous investigators (compare White, A., 1912, ii, 61).

H. W. B.

**The Viscosity of Protein Solutions. II. Pseudoglobulin and Euglobulin (Horse).** HARRIETTE CHICK (*Biochem. J.*, 1914, **8**, 261—280. Compare Chick and Lubrzynska, this vol., ii, 248).—The previous study of the influence of concentration and temperature on the viscosity of solutions of egg and serum albumins has been repeated in the cases of  $\psi$ -globulin and euglobulin, and a general survey of the results is given. In all cases, increase in protein concentration is accompanied by a disproportionately great increase in the viscosity of the solution. The effect is least marked in the case of serum albumin, and is greatest with euglobulin, solutions of which exhibit a high viscosity with a comparatively low protein content. Euglobulin dissolved (dispersed) in alkali has greater viscosity than when dissolved in salt solution. The euglobulin in horse serum is in the condition of salt globulin.

The viscosity of protein solutions is decreased with rise of temperature, frequently to a degree far in excess of that displayed by water or solutions of crystalloids. The greater the viscosity of the solution, the greater is the temperature effect, being most marked in the case of euglobulin solutions.

An interpretation of the results is found in the two-phase nature of the systems studied. The observed disproportionate increase in viscosity of protein solutions with increase in concentration of the protein is explained on the ground that the volume of the disperse phase increases at the expense of the continuous phase.

By means of Hatschek's formula, the amount of water required

for the colloidal solution of 1 gram of these proteins is calculated to be 2.1, 3.8, and 5.8 c.c. for serum albumin,  $\psi$ -globulin, and salt-euglobulin respectively at 25°. Hence, by the withdrawal of water in any salting-out process, the euglobulin, requiring most water, is the first, and serum albumin the last, to be precipitated.

The effect of temperature on the viscosity of protein solutions is explained as being due to a less degree of hydration of the colloid at the higher temperature. H. W. B.

**Palladium and Hydrogen. I.** ADOLF SIEVERTS (*Zeitsch. physikal. Chem.*, 1914, 88, 103—127).—The absorption of hydrogen by palladium wires of various thicknesses and purity, by palladium sponge, palladium black, and molten palladium has been determined over a range of temperature 100—1500°. It is shown that the absorption by palladium wire decreases with increase of temperature very rapidly up to 600°, and then much more slowly to 800°, and between 800—1500° only very slightly. The quantity of hydrogen absorbed by a given weight of palladium is independent of the area of the palladium surface; consequently, the absorption of hydrogen by palladium is to be regarded as a simple solution. Commercial palladium wire absorbed rather less hydrogen than chemically pure palladium. At the melting point, 1550°, molten palladium absorbed less hydrogen than the solid metal, and consequently there is no formation of bubbles or spitting when molten palladium which is charged with hydrogen solidifies. The absorption of hydrogen by palladium black was investigated with three different specimens between the temperatures 0° and 220°, and the absorption curves were plotted; they were also similar, and showed a very rapid fall in the amount of hydrogen absorbed above 100°. The amount of hydrogen absorbed is different in all the three cases, but the amount absorbed above 137° is larger than that absorbed by palladium wire at the same temperature. On heating, palladium black passes over into palladium sponge, and at the same time there is an increase in the amount of hydrogen absorbed, which at low temperatures approaches that of palladium wire. At temperatures above 600° the absorption of all varieties of palladium is practically identical. An explanation of this is offered in the assumption that platinum black, depending on its method of preparation, is made up of variable quantities of amorphous and crystalline particles. The amorphous variety has a greater power of absorption than the crystalline variety. The change in the absorption by heating is therefore explained as due to the change of the amorphous variety into the crystalline variety. It is supposed that the absorption by the amorphous variety is a simple adsorption, whilst that by the crystalline variety is solution. It is also shown that hydrogen which has been ionised by the action of Röntgen rays or by  $\beta$ - and  $\gamma$ -rays from radium will not diffuse through a palladium plate at the ordinary temperature. J. F. S.

**Adsorption by Hydrated Zirconium Oxide.** E. WEDEKIND and H. RHEINOLDT (*Ber.*, 1914, 47, 2142—2150).—The hydrated

zirconium oxide was obtained by precipitating a cold, saturated solution of pure zirconium oxychloride with ammonia; the precipitate was collected on a linen filter, washed until the disappearance of the chlorine reaction, and then dialysed to remove the last traces of ammonia. The adsorption of iodine and ammonia by this hydrated zirconium oxide does not follow the ordinary adsorption equation; the absolute content of the adsorbed iodine or ammonia increases with the concentration of the solution, but there is no approximation to a constant value, even in the presence of large excess of the adsorbed substance.

The adsorption of boric acid and phosphoric acid follows the ordinary adsorption law. No salts of zirconium with boric acid are known, but a zirconium hydrogen phosphate exists, namely,  $\text{Zr}(\text{HPO}_4)_2$ ; this phosphate, however, behaves differently from the adsorption compound of hydrated zirconium oxide and phosphoric acid.

Details are given of the qualitative behaviour of hydrated zirconium oxide towards colloidal ferric hydroxide, molybdenum-blue, starch iodide solution, Congo-red, safranine, etc. The solution of Congo-red is rapidly decolorised, with the formation of a blue adsorption compound, which, on warming, is transformed into the red salt.

T. S. P.

**Adsorption of Dextrose.** II. PETER RONA and KOLOMAN VON TÓTH (*Biochem. Zeitsch.*, 1914, **64**, 288—295. Compare A., 1909, ii, 384).—It has been shown that the disappearance of sugar from solutions when the latter are shaken with animal charcoal, for the purpose of clearing, can be avoided by the addition of acetic acid and other substances to the solution. Experiments show that in the case of acetic acid this is due to the undissociated molecules, and is not a function of the hydrion concentration. Experiments with the urethane series of substances show, furthermore, that the more readily a substance is adsorbed, the more readily it sets free sugar from its state of adsorption with the charcoal. The action of various substances in the sugar-charcoal mixture is due, therefore, to their mechanical adsorbability.

S. B. S.

**Sorption of Certain Acids and Non-electrolytes by Wool.** A. DIETL (*Kolloid. Zeitsch.*, 1914, **14**, 319—321).—The absorption of various substances from aqueous solution by wool has been investigated by experiments at different concentrations. The relation between the quantity of substance  $c_f$  removed by a fixed weight of wool, and the equilibrium concentration  $c_w$  of the aqueous solution, is expressed by the equation  $\sqrt{c_w}/c_f = \text{constant}$ . For phosphoric acid  $n=2$ , benzoic acid  $n=1.77$ , salicylic acid  $n=2.15$ , acetone  $n=1.47$ , sucrose  $n=1.1$ . The low values of  $n$  for the two non-electrolytes are supposed to indicate the formation of a solid solution.

H. M. D.

**The Dissociation Pressures of Some Nitrides.** R. E. SLADE and G. I. HIGSON (*Rep. Brit. Assoc.*, 1913, 451).—The following

nitrides dissociate, at the given temperatures, at pressures which are not greater than the given values: vanadium, 1203°, 0.2 mm.; 1271°, 1.5 mm.; tantalum, 1170°, 0.4 mm.; boron, 1222°, 9.4 mm.

C. H. D.

**Dissociation Pressures of Ammonium and Tetramethylammonium Haloids and of Phosphonium Iodide and Phosphorus Pentachloride.** ALEXANDER SMITH and ROBERT PEYTON CALVERT (*J. Amer. Chem. Soc.*, 1914, **36**, 1363—1382).—The dissociation pressures were measured at a series of temperatures by means of the static isoteniscope. In the case of phosphorus pentachloride, the dynamic isoteniscope was employed, on account of the difficulty of finding a suitable confining liquid. The limiting temperatures and pressures are indicated in the following summary, which also shows (in brackets) the temperatures at which the dissociation pressure is equal to 760 mm.: ammonium bromide, 300—403°, 35—935 mm. (394.6°); ammonium iodide, 310—410°, 48—857 mm. (404.9°); ammonium chloride, 250—350°, 50—1063 mm. (337.8°); tetramethylammonium chloride, 190—233.3°, 120—760 mm. (233.3°); tetramethylammonium iodide, 240—307°, 81—799 mm. (305.5°); phosphonium iodide, 19.2—65.7°, 50—900 mm. (62.6°); phosphorus pentachloride, 90—167°, 18—919 mm. (162.8°). The experimental data can be satisfactorily represented by the Kirchhoff-Rankin-Dupre formula,  $\log p = -A/T + B \log T + C$ , in which  $A$ ,  $B$ , and  $C$  are constants. The values of the constants for each of the substances are recorded in the paper. H. M. D.

**The Ludwig-Soret Phenomenon.** AUGUST EILERT (*Zeitsch. anorg. Chem.*, 1914, **88**, 1—37).—A glass apparatus is described, of 20 sq. cm. horizontal cross-section, for containing the liquid. The upper part is heated by a flat glass spiral near the surface, containing mercury and conveying a current. The lower part is cooled by a similar spiral of silver tube, through which cold water circulates. It is possible to keep the upper layer at a temperature constant within 0.5° for twelve hours. The solutions are separated after the experiment by cautiously opening a tap in the lower part of the apparatus.

The apparatus ensures the presence of a narrow zone quite free from convection currents. About eighteen hours are required for the system to reach the stationary state. The ratio of concentrations in the upper and lower zones,  $c_o/c_u$ , is then determined by analysis. Equilibrium may also be reached from the other side by using two solutions, the initial ratio of concentrations being greater than the ratio to be expected. Diffusion then takes place from the colder to the hotter region. These two methods are employed in each experiment, the equilibrium thus being reached from both sides.

For solutions of sodium, potassium, and strontium chlorides, acetic acid, and sucrose in water, and of benzil in benzene and lithium chloride in acetone, the ratio  $c_o/c_u$  is greater the greater the concentration, whilst for solutions of lithium chloride in water



and of acetic acid in nitrobenzene it is nearly independent of the concentration, and for hydrochloric acid it increases with diminishing concentration. In the case of the chlorides examined, the ratio increases with the molecular weight of the solute. Increasing the difference of temperature between the two layers increases the ratio of concentrations for solutions of acetic acid or sucrose in water, diminishes it for solutions of acetic acid in nitrobenzene, and is almost without influence for solutions of lithium chloride in water.

The explanation of the Ludwig-Soret phenomenon given by van't Hoff (A., 1888, 778) is thus incorrect. The results may be qualitatively explained, but only for concentrated solutions, by Tammann's hypothesis of the internal pressure. C. H. D.

**Counter Diffusion in Aqueous Solution.** WILLIAM ALEXANDER OSBORNE and LILIAS CHARLOTTE JACKSON (*Biochem. J.*, 1914, 8, 246—249).—The authors have found that if there are two solutions, one vertically placed above the other in a tall cylinder and in contact over a relatively small surface, and if both contain  $N/10$ -sodium chloride, and the lower of them contains in addition ammonium sulphate, dextrose, or some other substance, then, after some days' diffusion, the concentration of sodium chloride in the upper fluid is greater than it is in the lower. No satisfactory explanation of these results is offered. H. W. B.

**The Relation between Ionic Mobility and Ionic Volume.** RICHARD LORENZ (*Kolloid. Zeitsch.*, 1914, 14, 322).—A claim for priority against Mines (compare this vol., ii, 418) in respect of the view that the abnormally high mobility of the hydrogen and hydroxyl ions may be due to interaction between the ions and the solvent water molecules (compare A., 1913, ii, 281). H. M. D.

**Processes Operative in Solutions. XXIX. Disturbance of the Equilibrium in Solutions by "Strong" and "Weak" Interfering Agents.** H. E. ARMSTRONG and E. E. WALKER (*Proc. Roy. Soc.*, 1914, A, 90, 375—393. Compare A., 1913, ii, 368).—Further experiments have been made in which the change in the rotatory power of *lævulose* on the addition of foreign substances has been investigated. On the assumption that the change in rotation is due to an alteration in the proportion of the  $\alpha$ - and  $\beta$ -forms, the results obtained indicate that monohydric alcohols and most weak solutes (hormones) favour the formation of  $\alpha$ -*lævulose*, whilst polyhydric alcohols, sugars, salts, phenols, and basic substances (anhormones) are favourable to the formation of  $\beta$ -*lævulose*.

In connexion with the effects which are produced by interfering agents, an attempt is made to distinguish between (1) a purely mechanical screening effect, which causes dissociation of the water complexes, of the complex molecules of the solute, and of the hydrates of the solute, and (2) an action of opposite character, which is proportional to the attractive powers or residual affinities of the admixed substances, and promotes association. It is claimed that the hypothesis is justified by the explanation which it affords of interference effects in general. H. M. D.

**Rhythmic Crystallisation.** Liesegang's Rings and Related Phenomena. III. ERNST KÜSTER (*Kolloid. Zeitsch.*, 1914, 14, 307—319. Compare A., 1913, ii, 893).—A detailed description is given of the microscopic structures which are obtained when a small quantity of an aqueous solution is allowed to evaporate in contact with a layer of solidified gelatin solution. The structure varies markedly with the nature of the dissolved substance, as may be seen by comparison of the microphotographs obtained with solutions of trisodium phosphate, copper sulphate, ferrous sulphate, ammonium sulphate, and potassium ferrocyanide. On the one hand, the microphotographs afford evidence of simple ring-formation, similar to that exhibited by the precipitation layers in the interaction of silver nitrate with a solidified layer of gelatin containing small quantities of potassium chromate, whilst others exhibit a net-like or grating structure. In the author's opinion, the cause of the formation of the structures is the same, although specific influences come into play in the different cases. Although the development of the micro-structure is facilitated in presence of a gelatin or other gel, it is improbable that the gel plays a fundamental rôle in the phenomenon.  
H. M. D.

**Ring Formation and Crystal Structure.** P. GROTH (*Ber.*, 1914, 47, 2063—2067).—Although the results of recent experiments with Röntgen rays have clearly proved that molecules do not exist in crystals, yet it is evident from the frequent occurrence of close morphotropic relationships between chemically related substances, especially in the case of benzenoid compounds, that some of the interatomic linkings of the molecule must persist in the crystal. In view of the special rôle apparently played by the ring system of benzene, an inquiry has been started to ascertain whether aliphatic ring compounds, such as anhydrides and imides of dibasic acids, will behave similarly.

It is found that there is a close structural resemblance between crystals of the anhydrides of succinic and maleic acids, whereas the acids themselves show no such relationship. There is also a close similarity revealed, when their topic parameters are calculated, between the imides of succinic and *cis-s*-dimethylsuccinic acids.

E. H. R.

**Manipulation of the Immersion Ultramicroscope.** R. ZSIGMONDY and W. BACHMANN (*Kolloid. Zeitsch.*, 1914, 14, 281—295).—A new form of ultramicroscope is described in which the immersion objectives of both the illuminating and observing systems are of large aperture. In comparison with the slit ultramicroscope, the new instrument affords a much greater intensity of illumination and facilitates appreciably the investigation of the ultramicroscopic particles of hydrosols. The method of setting up the apparatus and the manipulation involved in ultramicroscopic observations are described in detail.  
H. M. D.

**A Modification of the Ultra-filtration Apparatus.** P. KIRSCHBAUM (*Biochem. Zeitsch.*, 1914, 64, 495—498).—The apparatus,

which is illustrated by figures, is essentially a modification of Elfer's, and consists of a metal bell-jar screwed on to a metal underpart supported on a tripod which bears the sieve support for the filter. This is made of silver, as is also a hollow cylinder which is placed in the upper bell-jar and fixes on to the sieve. Into this the liquid to be filtered is brought, and it is the most essential modification of the apparatus.

S. B. S.

[The Preparation of Colloidal Solutions by Electric Disintegration]. RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1914, 88, 22. Compare Zavriev, this vol., ii, 444).—It is shown that Bredig (A., 1900, ii, 278) had previously prepared colloidal solutions of cadmium and zinc by electric disintegration. His method, however, differs essentially from that of Zavriev (*loc. cit.*) in many particulars.

J. F. S.

Behaviour of Gels towards Liquids and the Vapours Thereof. II. L. K. WOLFF and E. H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 92—101. Compare A., 1913, ii, 568).—According to von Schroeder (A., 1903, ii, 721), a gelatin plate which has taken up the maximum quantity of water in contact with the liquid, loses water when introduced into a space saturated with water vapour at the same temperature. Although the authors' earlier experiments (*loc. cit.*) seemed to confirm this observation, further experiments by an improved method, in which the swollen gelatin plate was exposed to the influence of a current of air saturated with water vapour at the temperature of swelling, show that the weight of the gelatin plate remains unchanged. Under the conditions of the previous statical method of experimentation, it has been shown that pure liquid water loses weight by evaporation, and although the static method has been modified so as to eliminate to a large extent the errors which are incidental to this method, it is much inferior to the dynamic method of observation. The results obtained with gelatin have been confirmed by experiments with agar-agar and with celloidin swollen in ethyl alcohol.

It would seem that the vapour pressure of gelatin which has taken up a relatively small amount of water is practically equal to that of pure water. In consequence of the very small difference in vapour pressure, the absorption of water from the saturated vapour is extremely slow, and a condition of equilibrium is apparently reached when this is not really the case. There is consequently no discrepancy between the phenomena associated with the swelling of gelatin and the second law of thermodynamics, as was previously supposed.

H. M. D.

Silver Chromate Rings and Spirals. RAPHAEL ED. LIESEGANG (*Zeitsch. physikal. Chem.*, 1914, 88, 1—12).—The author shows that the production of a rhythmic precipitation of silver chromate in gelatin jellies is best effected when silver nitrate is allowed to diffuse into potassium chromate jellies which contain definite

small quantities of acid and gelatose. The commoner commercial varieties of gelatin contain these substances in practically the necessary concentration, but gelatin which has been washed with water must have the necessary quantity of acid, either citric acid or nitric acid, added to it, and hard gelatin must be mixed with gelatose for the purpose of showing the formation of rings. The presence of a large hydrogen-ion concentration in rich chromate jellies causes the rings to be formed at greater distances from one another, the reason for this being the increased solubility of the silver chromate. Small disturbances cause the precipitation to occur in spirals instead of concentric rings, and often portions of a spiral are formed in isolated positions, which later join up with the main system. The Ostwald supersaturation theory (*Zeitsch. physikal. Chem.*, 1897, **23**, 365) can be applied to the formation of spirals in the same way as in the case of the formation of rings.

J. F. S.

**Structure of Silicic Acid Gels.** JOHN S. ANDERSON (*Zeitsch. physikal. Chem.*, 1914, **88**, 191—228).—A quantity of silicic acid gel was prepared and dried until the weight was constant by keeping over concentrated sulphuric acid. It was found that it contained 5.5% of water, which was not removable at the ordinary temperature. The dried gel was then placed in contact with the vapour from sulphuric acid-water mixtures in an exhausted apparatus, and in each case the increase in weight noted. The reverse process was then carried out; the gel, saturated with water, was placed in contact with sulphuric acid of increasing concentration up to pure sulphuric acid, and in each case the weight determined. In this way a series of values of the amount of water absorbed or given up at different vapour pressures was obtained. Curves were plotted, and it is shown that the absorption and drying curves do not coincide over their whole length, there being a decided hysteresis shown in the sense that water is given up at lower pressures than those at which it is absorbed. In this way measurements were obtained over the pressure range for the water vapour of 12.7—0 mm. Similar experiments were made with alcohol and benzene. In the case of alcohol, mixtures of alcohol and glycerol were employed to obtain alcohol vapour pressures from 32.6—0.0 mm., and in the case of benzene, mixtures of benzene and paraffin oil gave benzene vapour pressures from 60—0 mm. Curves of exactly the same type were obtained as in the case of water. The water experiments were repeated by the van Bemmelen method (*A.*, 1908, ii, 838; 1909, ii, 234), which consisted in hydrating and dehydrating the gels in a desiccator in the presence of air. Curves of almost the same type were obtained, except that by this method the curve in the region where hysteresis is shown is horizontal. This is not the case in the absence of air, and points to the fact that the gel is made up of pores of varying sizes, which are largest at the point where hysteresis begins and smallest where it ceases on the dehydrating curve. From measurements of the lowering of the vapour pressure of water, alcohol,

and benzene in the gel, the values of the diameter of the pores are calculated to the following figures: (a) largest diameter,  $5.49\ \mu\mu$ ,  $5.17\ \mu\mu$ , and  $5.98\ \mu\mu$ ; (b) smallest diameters,  $2.75\ \mu\mu$ ,  $2.42\ \mu\mu$ , and  $2.70\ \mu\mu$  in the three cases respectively. The dimensions of these values are in agreement with those obtained by Zsigmondy from other properties of the gel (A., 1911, ii, 880). The specific gravities of the gel substance ( $\text{SiO}_2$ ), the dried gel, and the gel saturated with water have also been obtained, and found to be 2.048, 0.980, and 1.500 respectively. The velocity at which the three substances water, alcohol, and benzene are absorbed and given up by the gel were determined and compared. Very similar curves are obtained for all three cases. It is shown that the absorption and expulsion of liquids from gels, as well as the turbid appearance at certain stages, are to be explained by capillary phenomena, and that there is no evidence of hydrate formation. J. F. S.

**Swelling of Vulcanised Caoutchouc.** F. KIRCHHOF (*Kolloidchem. Beih.*, 1914, 6, 1—22. Compare Posnjak, A., 1912, ii, 912).—The swelling of plantation Para-caoutchouc has been examined by measuring the increase in weight of thin disks of the material after immersion in benzene, carbon tetrachloride, carbon disulphide, and benzene (D 0.74) for measured intervals of time.

The results show that the maximum swelling of the caoutchouc decreases as the extent of the vulcanisation increases. The maximum swelling was attained after twenty-four hours. The specific influence of the various liquids runs parallel with the solvent capacity for caoutchouc. The rate at which swelling takes place is approximately in agreement with the equation for a unimolecular change. The swelling velocity increases with rise of temperature, but the temperature-coefficient is very small (1.1). The relation between the extensibility and the vulcanisation-coefficient is similar to that existing between the swelling capacity and the degree of vulcanisation. Although the swelling is in part due to capillary absorption, the observed increase in weight is mainly due to solution of the solvent in the caoutchouc.

Some experiments were also made on the swelling of the caoutchouc disks in the vapours of the boiling liquids. This effect is very much smaller, and is practically independent of the degree of vulcanisation. H. M. D.

**Dynamic Isomerism.** H. E. ARMSTRONG, T. M. LOWRY, SYDNEY YOUNG, C. H. DESCH, J. J. DOBBIE, and M. O. FORSTER (*Rep. Brit. Assoc.*, 1913, 141—143).—A report on work published during 1913. C. H. D.

[The Condition Diagram of Water.] G. TAMMANN (*Zeitsch. physikal. Chem.*, 1914, 88, 57—62. Compare Bridgman, this vol., ii, 254).—Polemical; an answer to Bridgman's criticism (*loc. cit.*) of the author's paper (A., 1913, ii, 935), in which the existence of

two forms of ice II is described. The author has repeated his experiments, with results which confirm the original work.

J. F. S.

**Equilibria in Ternary Systems. XV.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 70—85. Compare this vol., ii, 548).—A further examination of types of equilibrium in ternary systems, the assumption being made that the vapour contains only one or two of the three components.

H. M. D.

**Equilibrium Distribution of Certain Neutral Narcotics.** ALFRED DORNER (*Chem. Zentr.*, 1914, i, 1453—1454; from *Sitzungsber. Heidelberger Akad. Wiss.*, 1914, [B], 1—12).—According to Warburg, it may be assumed that the concentrations of different narcotics of differing "external concentration" are the same or similar at the affected point in the cell when a similar action is produced. The author's investigations on the equilibrium distribution of acetone, heptyl alcohol, and octyl alcohol, using intact "vogelerythrocytes" and their stomata, lead to the following conclusions: The stomata, after being freed from fat, are able to fix considerable quantities of narcotics, the amount being greater for the more powerful narcotics than for the weaker ones. The stomata which have not been treated with alcohol and ether fix considerably more octyl alcohol than the extracted substance. The difference may either be attributed to the fixative power of the fatty constituents of the stomata as compared with that of the nucleohistone, or to a possible alteration of the latter by treatment with alcohol and ether in such a manner that it can fix less of the alcohol. The fixation of narcotics by the stomata is not a chemical process, and the equilibria measured are more closely allied to adsorption than to distribution equilibria.

H. W.

**Conditions of Formation and Existence in Equilibrium with Solutions of Basic, Acid and Complex Salts.** E. I. SCHPITALSKI (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 566—576).—The author applies the considerations previously discussed (A., 1907, i, 695) to the investigation of complex equilibria in solutions, with special reference to chromates.

From the facts known concerning the dependency of the composition of a precipitated salt on the degree of acidity of the solution, the conclusion is drawn that, for each salt, there exist two definite concentrations of acid between which the given salt may exist in the solid state in equilibrium with the solution. The conversion of a basic salt into a normal one, or the latter into an acid one, may be regarded as a reversible reaction of combination with a molecule of acid,  $M_1 + A \rightleftharpoons M_2$ . From this it follows that, for saturation of the solution simultaneously with the two salts,  $M_1$  and  $M_2$ , there should exist the relation  $S = M_2/M_1 = \text{constant}$ . The constancy of  $S$  is related to the non-dissociated molecules of acid, and  $S$  will correspond with the hydrolytic tension of the mutual

transformation of the salts, the simultaneous existence of which is possible only for the particular magnitude of  $S$ . For any solution saturated with respect to two hydrolysable salts, capable of inter-conversion, the concentration of the non-dissociated acid depends only on the temperature. It is shown, further, that the possibility of formation of each salt is defined by two quite definite magnitudes, termed "stability products," characteristic of the particular salt.

T. H. P.

**Equilibria of Reduction of Oxides by Carbon.** R. E. SLADE and G. I. HIGSON (*Rep. Brit. Assoc.*, 1913, 450—451).—The equilibrium pressures have been determined when certain oxides are heated with carbon, the free metal being present in excess. With three components, M, C, and O, there are four phases, CO, M, MO, and either C or  $M_2C$  (M being two equivalents of the metal). Equilibrium is reached from both sides. The following values are obtained:

Vanadium .....	1340°	1.5 mm.
Tantalum .....	1270	< 0.1 "
Chromium .....	1292	6.2 "
" .....	1339	9.2 "
Tin.....	750	> 760 "
Tin, in presence of silica .....	753	670 "

C. H. D.

**Equilibrium in the System Arsenic Tribromide and Naphthalene.** N. A. PUSCHIN and J. F. KRIGER (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 559—565).—Thermal analysis of the system arsenic tribromide-naphthalene shows that these components form a definite yellow compound,  $C_{10}H_8 \cdot 2AsBr_3$ , m. p.  $19.8^\circ$ . There are two eutectic points: (1) one at  $17.2^\circ$  occurring in the stable region and corresponding with 19.5 mol. %  $C_{10}H_8$ ; (2) the other in the unstable region at  $10^\circ$ , corresponding with 27 mol. %  $C_{10}H_8$ . A transition point occurs at  $19.8^\circ$ , the corresponding composition being 33 mol. %  $C_{10}H_8$ . On reciprocal dissolution the two components retain their normal molecular weights.

T. H. P.

**Freezing-point Curves of Volatile Systems.** GEORGES BAUME (*J. Chim. Phys.*, 1914, 12, 206—215. Compare A., 1912, ii, 329, 1039).—General observations in reference to the author's investigation of the freezing-point curves of a large number of volatile binary systems.

H. M. D.

**Quantitative Investigation of Volatile Systems. Freezing-point Curve of the System Sulphur Dioxide-Water.** GEORGES BAUME and (Mlle.) ALINE TYKOCINER (*J. Chim. Phys.*, 1914, 12, 270—275).—Sulphur dioxide and water are only partly miscible at low temperatures. The region covered by the two-liquid system extends from about 11 to 97 mols. % of sulphur dioxide. The data obtained for systems containing less than 11 mols. % of sulphur dioxide agree with those recorded by Roozeboom (*Rec. trav. chim.*,

1884, **3**, 44; A., 1886, 117). The eutectic at which ice and the compound  $\text{SO}_2 \cdot 7\text{H}_2\text{O}$  co-exist in equilibrium lies at about  $-3^\circ$ . The freezing-point curve of this compound is intercepted at  $+12.1^\circ$  by the straight line which corresponds with one of the above-mentioned liquid phases. The freezing temperature of the second liquid is  $-74^\circ$ , and the corresponding straight line on the diagram intercepts the curve for sulphur dioxide (m. p.  $-72.3^\circ$ ) at about 97 mols. % of sulphur dioxide.

Some observations relating to the systems  $\text{HCl} + \text{H}_2\text{O}$ ,  $\text{NH}_3 + \text{H}_2\text{O}$  are also included in the paper. H. M. D.

**Quantitative Investigation of Volatile Systems. Freezing-point Curves for the Systems formed by Hydrogen Chloride and Methyl Alcohol with Methyl Chloride and by Methyl Alcohol with Water.** GEORGES BAUME and WACŁAW BOROWSKI (*J. Chim. Phys.*, 1914, **12**, 276—281).—The freezing-point data for mixtures of methyl alcohol and water correspond with the intersection of two curves at  $-139^\circ$  and about 67 mols. % of methyl alcohol. Mixtures which contain from 55 to 75 mols. % of methyl alcohol yield non-crystalline glasses on cooling. The previous results obtained by Pickering for mixtures containing 0—50 mols. % of alcohol are in agreement with the authors' data.

Hydrogen chloride and methyl chloride also afford the simplest possible thermal diagram. The eutectic lies at  $-161^\circ$  and 27.3 mols. % of methyl chloride.

Methyl alcohol and methyl chloride behave in exactly the same way, the eutectic temperature being  $-112^\circ$ , and the composition corresponding with 24.2 mols. % of methyl chloride. H. M. D.

**The System  $\text{CaSiO}_3$ — $\text{MnSiO}_3$ .** ST. KALLENBERG (*Centr. Min.*, 1914, 388—394).—The freezing-point curve for mixtures of calcium and manganese silicate is continuous, and shows a minimum at  $1150^\circ$  for a mixture containing 10 mols. % of calcium silicate. Within the limits of experimental error the results are in agreement with those obtained by Ginsberg (A., 1908, ii, 842). Since artificial wollastonite is either hexagonal or monoclinic, whilst rhodonite is triclinic, it is probable that the mixed crystals form an *isodimorphous* series.

Although the crystalline form of synthetic rhodonite is very similar to that of the naturally occurring rhodonites, it differs from the minerals in the positive character of its double refraction. Synthetic rhodonites containing iron and magnesium silicate are optically similar to the pure manganese silicate, but in presence of 5% of calcium silicate the positive double refraction changes to negative. Since the natural rhodonites generally contain calcium silicate in greater proportion than this, the apparent discrepancy in the optical behaviour of synthetic rhodonite and the minerals is readily explained. H. M. D.

**Mixed Crystals in the Ternary Systems Formed by Strontium Chloride, Barium Chloride, and Sodium Chloride or Potassium Chloride.** ERHARD VORTISCH (*Jahrb. Min. Beil.-Bd.*, 1914, **38**, 185—272).—The equilibrium relations in the binary and



ternary systems have been determined by freezing-point measurements combined with the investigation of the microscopic structure of the products of crystallisation.

Strontium chloride and barium chloride form a complete series of regular ( $\beta$ ) mixed crystals, which on cooling are transformed into monoclinic ( $\alpha$ ) crystals. These two series correspond with the  $\alpha$ - and  $\beta$ -forms of barium chloride, which co-exist in equilibrium at  $922^\circ$ . The freezing-point curve shows a minimum at  $847^\circ$ , at which point 30 mols. % of barium chloride are present.

Sodium chloride and strontium chloride are immiscible, and the two freezing-point curves meet at  $565^\circ$  and the composition 50 mols. % of strontium chloride. Sodium chloride and barium chloride behave similarly, the eutectic in this case being at  $654^\circ$  and 40 mols. % of barium chloride.

The corresponding ternary system is characterised on the space model by means of which the experimental data are summarised, by the existence of three surfaces of saturation, the solid phases corresponding with which are sodium chloride,  $\alpha$ -mixed crystals, and  $\beta$ -mixed crystals of strontium and barium chloride respectively.

Potassium chloride combines with strontium chloride to form the compounds  $2\text{KCl}, \text{SrCl}_2$ , melting at  $597^\circ$ , and  $\text{KCl}, 2\text{SrCl}_2$ , melting at  $638^\circ$ . With barium chloride it forms the compound  $2\text{KCl}, \text{BaCl}_2$ , melting at  $660^\circ$ . The compounds  $2\text{KCl}, \text{SrCl}_2$  and  $2\text{KCl}, \text{BaCl}_2$  are isomorphous, and rhombic crystals containing both compounds separate out from certain fused ternary mixtures. Mixed crystals of the type  $\text{KCl}, 2(\text{SrBa})\text{Cl}_2$  are also formed.

By reason of the fact that this system gives rise to four series of mixed crystals, the equilibrium relations are much more complicated than those exhibited by the ternary system, in which the potassium chloride is replaced by sodium chloride. The spacial model showing the equilibrium relations is characterised by five surfaces which determine the conditions under which crystallisation of  $\alpha(\text{SrBa})\text{Cl}_2$ ,  $\beta(\text{SrBa})\text{Cl}_2$ ,  $\text{KCl}, 2(\text{SrBa})\text{Cl}_2$ ,  $2\text{KCl}, (\text{SrBa})\text{Cl}_2$ , and  $\text{KCl}$  occur. For a detailed account of the relationships between the various systems the original must be consulted. H. M. D.

**Natural Fats from the Point of View of the Phase Rule. III. The Ternary System: Tristearin-Stearic Acid-Palmitic Acid.** ROBERT KREMANN and RICHARD KROPSCH (*Monatsh.*, 1914, 35, 561—580. Compare A., 1912, ii, 1152; 1913, ii, 922).—Of the three binary systems making up the above-mentioned ternary system, one, that between tristearin-palmitic acid, has been investigated by de Visser (A., 1898, i, 560) and Carlinfanti and Levi-Malvano (A., 1910, i, 5). The fusion curves for the remaining binary systems are determined in the present work. The system tristearin-stearic acid is simple, and possesses a single eutectic point at  $54^\circ$  for the mixture 90% tristearin, 10% stearic acid. The system tristearin-palmitic acid gives a fusion curve which rises rapidly from tristearin and passes through a flat maximum at 7% palmitic acid, and at 16% palmitic acid has a eutectic point at  $63^\circ$  (not sharp); then passes along a very flat maximum to a second eutectic

point at 50% palmitic acid at 55°, and then rises linearly to the melting point of palmitic acid. A series of other fusion curves are then determined for ternary mixtures, taking a series of constant ratios of two constituents, and varying the third; in this way some fourteen series are determined, tables and curves are given for each of these, and the separate curves are combined in a triaxial diagram to give the ternary system. From these results it follows that of the hard fats, *i.e.*, those which are free from oleic acid and triolein, those which correspond with the system tristearin-palmitic acid, and particularly those with a small palmitic acid content, will have the highest melting points. J. F. S.

**Velocity of Absorption of Hydrogen and Oxygen by Solutions of Metallic Salts.** JOHN EGGERT (*Zeitsch. Elektrochem.*, 1914, 20, 370—381).—The velocity of absorption of hydrogen and oxygen by reducible and oxidisable salt solutions respectively has been determined at 17°. It is shown that the reduction and oxidation of ter- and bi-valent iron by hydrogen and oxygen took place with its maximum velocity when the platinum which served as stirrer and catalyst was brought into contact with the gaseous atmosphere above the solution. It is shown that the maximum velocity is proportional to the surface of the platinum and the time during which it is in contact with the gas space, but is independent of the number of times per minute it is raised into the gas space and lowered into the liquid. The initial velocity of absorption, under uniform conditions, is constant and independent of the nature of the dissolved metal salt; as the reaction approaches completion a decrease in velocity of absorption occurs, which is generally exponential. The meaning of this phenomenon is explained on the basis of a separation of the process into a velocity of occlusion and a velocity of "activation" of the occluded gas towards the solution. The beginning of the process appears to be governed by occlusion, that is, by the nature of the platinum, whilst at the end of the process the different powers of "activation" of the various metals make themselves noticeable. The velocity of occlusion has a temperature-coefficient of 1.8—3.3%, and is independent of the concentration. A decrease in the absorption is to be noticed, which runs parallel with the increased viscosity of the solution. The effects are also not independent of the nature of the anions and the hydron concentration. Solutions of  $\text{Fe}^{\text{III}}$ ,  $\text{U}^{\text{VI}}$ ,  $\text{V}^{\text{IV}}$ ,  $\text{Ti}^{\text{IV}}$ ,  $\text{Mo}^{\text{VI}}$ , and *p*-benzoquinone are reversibly reduced by hydrogen and reoxidised by oxygen. The velocity of autoxidation of solutions in alkali, to which quantities of tartrate have been added, increases in the order  $\text{V}^{\text{III}}$ ,  $\text{Mo}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Sn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ , and  $\text{Mn}^{\text{II}}$ . J. F. S.

**Kinetics of Chemical Reactions. IX.** E. I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 535—559).—In the oxidation of hypophosphorous acid by means of iodine, the value of the velocity-constant, calculated on the assumption that the reaction is one of the first order, continually increase with the time; the initial value of the constant is, however, approximately proportional

directly to the concentration of the sodium hypophosphite, and inversely to that of the iodine. The results have therefore been calculated according to the equation  $dx/dt = k(A-x)(B+x)$ . If the concentration of hypophosphite remains constant, increase of the concentration of iodine is accompanied by increase of  $B$  and decrease of  $k$ , but is not proportional to  $B$ . A similar result has been obtained in other instances where the above equation is applicable.

When the quantity of iodine used is larger than is required for oxidation of the hypophosphorous to phosphoric acid, the early observations are in agreement with a reaction of the first order, whereas later the value of the constant begins to fall, and the formula  $dx/dt = k(A - mx)$  becomes applicable. These results are discussed in relation to the equation

$$dx/dt = k_1(A - x) + k_2x(A - x) - k_3x(A - x),$$

previously deduced by the author (A., 1913, ii, 681).

The results obtained cannot be explained according to the formula  $O:PH_2 \cdot OH$ , for hypophosphorous acid, which initially unites with the iodine. It is therefore assumed that in acid solution the above form exists in equilibrium with  $OH \cdot PH \cdot OH$ , the latter not being found in alkaline solution, in which oxidation by iodine does not take place. The course of the reaction is explained on the assumption that the complex  $HI_3$  or  $I_2 \cdot HI$  under-

goes partial dissociation in an aqueous medium into



and  $H^+$ .

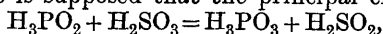
Unlike hypophosphorous acid, phosphorous acid is only slowly oxidised by iodine, and the reaction does not proceed to an end. The numerical results show that the oxidation takes place according to the equation  $dx/dt = k(A - kx) - k_1x$  or

$$dx/dt = k(A - mx).$$

The magnitude of  $k_1$  depends on the concentrations of the phosphorous acid and of the iodine, but that of  $k$  is approximately constant. Here, too, the author assumes the existence of molecules of the two structures  $O:PH(OH)_2$  and  $P(OH)_3$ , only the latter undergoing oxidation by means of iodine into phosphoric acid.

Investigation of the reduction of sulphurous acid to sulphur by hypophosphorous acid shows that the separation of sulphur occurs only after the lapse of some time, and that if an aqueous solution of safranine or indigotindisulphonic acid is added to a solution of hypophosphorous and sulphurous acids containing sulphuric acid, the liquid becomes decolorised appreciably earlier than the sulphur is deposited. The conclusion is therefore drawn that this reduction of sulphurous acid takes place by way of intermediate products, such as hyposulphurous acid, to which is due the decolorisation of the safranine or indigotindisulphonic acid. The formation of sulphur requires the accumulation of a certain quantity of hyposulphurous acid, which in an acid medium undergoes change according to the equation  $2H_2SO_2 = H_2SO + H_2SO_3$ , this being followed rapidly by  $H_2SO = H_2O + S$ . Calculation of the velocities of the

reduction by means of the formula  $Ak = x/t(A - x)$  shows that, after the lapse of a certain time, and subsequent to the initial precipitation of sulphur, the magnitude of  $Ak$  remains constant. The amount of sulphurous acid which disappears during the early stage of the reaction is greater than that calculated for a reaction of the second order. It is supposed that the principal change,



is at first accompanied by the formation of a product of combination of the two acids,  $\text{O}:\text{PH}_2\cdot\text{OH} + \text{HSO}_2\cdot\text{OH} = \text{OH}\cdot\text{SO}_2\cdot\text{PH}_2(\text{OH})_2$ , this compound existing in solution for some time, and then decomposing into its original constituents. Of the three reactions,  $\text{H}_3\text{PO}_2 + \text{H}_2\text{SO}_3 = \text{H}_3\text{PO}_3 + \text{H}_2\text{SO}_2$ ,  $2\text{H}_2\text{SO}_2 = \text{H}_2\text{SO} + \text{H}_2\text{SO}_3$ , and  $\text{H}_2\text{SO} = \text{H}_2\text{O} + \text{S}$ , it is the first which determines the second order of the reaction, the other two occurring very rapidly.

The reduction of safranin in a solution of sulphurous and hypophosphorous acids takes place according to the equation

$$dx/dt = k(A - x)(B + x),$$

and that of indigotindisulphonic acid according to

$$dx/dt = k(A + x)(B + x).$$

T. H. P.

**The Velocity of Solution of Zinc-Blende and Galena in Dilute Sulphuric Acid.** FELIX ROSENKRÄNZER (*Zeitsch. anorg. Chem.*, 1914, **87**, 319—334).—The crushed ores (galena from Claustal, and four varieties of blende) are sifted and graded, and treated with dilute sulphuric acid by shaking in a flask, after which the dissolved hydrogen sulphide is estimated colorimetrically by the method based on the formation of methylene-blue (this vol., ii, 380).

The experiments show that the velocity of solution is constant throughout an experiment, and is proportional to the concentration of the sulphuric acid and to the surface of the particles. The concentrations employed are 1.25, 0.125, and 0.0125%. The influence of temperature is independent of the size of the particles, and is represented by an exponential function. The temperature-coefficient is the same for blende and galena, although the velocities are very different. The difference of velocities, and the fact that rapid shaking is without influence on the velocity, are opposed to the view that the velocity of a heterogeneous reaction is merely a diffusion velocity. A chemical process must precede the actual solution.

C. H. D.

**Kinetics of the Thermal Bleaching of Colouring Matters.** S. VAVILOV (*Zeitsch. physikal. Chem.*, 1914, **88**, 35—45).—The velocity at which the dyes cyanine, lepidine-cyanine, quinaldine-cyanine, and pinaverdol are bleached by the action of heat has been investigated at temperatures from 60° to 110°, and the results are compared with the photochemical bleaching of the same substances obtained by Lasarev (*A.*, 1912, ii, 219, 513). The dyes were mixed with collodion and poured on thin squares of glass, and subjected to the action of heat in a specially constructed thermostat. They were investigated from time to time by means of a König-Mertens

spectrophotometer. The bleaching of lepidine-cyanine takes place in accordance with the equation for a bimolecular reaction, and that of cyanine with the unimolecular equation. The order of the reaction in the other cases could not be determined. The temperature-coefficient of all the reactions approximates to 3, whereas that for the photochemical reaction is only slightly larger than unity. The solid, coloured products of the thermal bleaching show little difference optically from that of the products of the photochemical bleaching, and the difference can be explained by changes in the collodion. The gaseous products of the reaction and atmospheric air are shown to influence a strong catalytic action on the process. Experiments on the thermal bleaching of the dyes in the absence of collodion led to no positive results.

J. F. S.

**Catalysed Ester Formation in Mixed Solvents by means of Hydrogen Chloride.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1914, **88**, 65—102).—The velocity of esterification of benzoic acid, succinic acid, tartaric acid, and malic acid has been determined in alcoholic hydrogen chloride, and in mixtures of alcohol-benzene, alcohol-ether, and alcohol-carbon tetrachloride. Experiments were made also in the same mixtures to which known amounts of water had been added. The equivalent conductivity of the hydrogen chloride in all the solutions used for the kinetic experiments was also determined. It is shown that the velocity of esterification in absolute alcohol is reduced by the addition of the other solvents, most in the case of ether and least in the case of carbon tetrachloride. The retarding influence of water is approximately the same in the alcohol-ether mixture as in the case of absolute alcohol, and greater in the alcohol-carbon tetrachloride mixture. The constants calculated to a constant quantity of alcohol, in the cases of mixtures of aqueous alcohol and the ether-absolute alcohol mixture, are smaller than those for mixtures to which a second solvent has not been added, but in the cases of mixtures of alcohol and carbon tetrachloride and those containing more than 25% benzene they are larger, and increase with an increasing amount of the second solvent. The influence of the addition of benzene to alcohol in the esterification of succinic, malic, and tartaric acids is similar to that observed in the case of benzoic acid, and the irregularities lie in the opposite direction to that which they should lie if the esterification in these cases is termolecular, that is, does not take place in steps. Just as in absolute alcohol, so in the various mixtures, the esterification proceeds as a reaction of the first order. It is also shown that the equivalent conductivity of hydrogen chloride in absolute alcohol and in aqueous alcohol is reduced by the addition of the other three solvents. If it is assumed that the catalytic action of the hydrogen ion is greater than that of the undissociated hydrogen chloride, then it follows that the addition of these other solvents to the alcohol has an accelerating influence on the esterification. If, however, it is assumed with Snethlage (*A.*, 1912, ii, 947; 1913, ii, 1044) that the undissociated hydrogen chloride molecule is twice as active as the hydrogen ion, then it

follows that the addition of benzene and carbon tetrachloride alone acts in an accelerating manner, and that only when they are present in large quantity and when only traces of water are present. If it is assumed that the concentration of the unimolecular alcohol is determinative of the velocity of esterification, then this would explain the accelerating influence of the other solvents, although the specific action of these solvents and that of the acid itself would also play some part in the acceleration. J. F. S.

**Catalytic Influence of Copper Oxide on the Combination of Oxygen and Hydrogen.** JACQUES JOANNIS (*Compt. rend.*, 1914, 159, 64—67. Compare this vol., ii, 260).—Pure iron wire at 300° does not act as a catalyst on an explosive mixture of oxygen and hydrogen. It becomes coated with a film of black oxide, which is not reduced under the given conditions. Electrolytic copper at 300° or even at 200° is at first oxidised in the explosive mixture, and the oxide formed acts as a catalyst for the combination of the oxygen and hydrogen. Copper oxide itself undergoes no reduction, but at 300° produces practically complete combination of the hydrogen and oxygen. The catalytic action is, however, apparently largely controlled by the vapour tension of the water formed.

W. G.

**Catalytic Actions of Colloidal Metals of the Platinum Group. X. The Reduction of the Oxides of Heavy Metals.** C. PAAL [with WILHELM HARTMANN and GUSTAV BRÜNJES] (*Ber.*, 1914, 47, 2202—2216).—When a colloidal solution of cupric hydroxide is reduced by means of colloidal palladium, prepared according to Paal's method, and hydrogen, a colloidal solution of copper is obtained. A similar solution results when precipitated copper hydroxide is used instead of the colloidal solution, in this case reduction and peptonisation occurring at the same time. The colloidal copper solution is ruby-red in transmitted light, and black in reflected light (compare Paal and Leuze, A., 1906, ii, 356). In one case where only a small quantity of colloidal palladium was used, colloidal cuprous oxide was obtained as an intermediate product. In order to increase the stability of the solutions, it is best to add some sodium protalbate to the reaction mixture, to act as a protective colloid. In a similar manner colloidal nickel can be obtained from a colloidal solution of nickel hydroxide, or from the precipitated hydroxide, but with the latter the reduction is not complete. The metal hydrosol is a brilliant, chestnut-brown colour in transmitted light, and black in reflected light; the reversible gel forms blackish-brown, brittle lamellæ.

Cobaltous and lead hydroxides could not be reduced similarly to those of copper and nickel.

Experiments on the reduction of solutions of ammonium chromate, metavanadate, and molybdate gave respectively the colloidal solutions of chromic hydroxide, vanadium trihydroxide, and molybdenum tetrahydroxide. The first is a blackish-green, the second a brown, and the last a reddish-brown hydrosol; all give

reversible gels. Ammonium tungstate is not reduced by colloidal palladium and hydrogen. T. S. P.

**The Quantum Theory and the Rotation-energy of Molecules.** EVA VON BAHR (*Phil. Mag.*, 1914, [vi], 28, 71—83).—The author discusses the application of the quantum theory to phenomena associated with the rotational energy of molecules, and shows that considerable support for the assumption of discontinuity in the distribution of the rotation-frequencies is afforded by the results which have been obtained in experiments on the ultra-red absorption of gases (compare A., 1913, ii, 810). These results are summarised with special reference to their significance for the quantum theory. H. M. D.

**Atomic Structure and the Spectrum of Helium.** J. W. NICHOLSON (*Phil. Mag.*, 1914, [vi], 28, 90—103. Compare this vol., ii, 325).—The theory of atomic structure put forward by Bohr (A., 1913, ii, 689, 943, 1045) must, in the author's opinion, stand or fall according to its capacity to give an account of the spectra of hydrogen and helium. It is shown that the theory cannot explain the helium spectrum or any other series spectrum by any modification which retains the simpler theory of hydrogen and the Pickering series, if it is assumed that forces act between bound electrons. The assumption that such forces do not exist is also shown to lead to conclusions which are incompatible with the helium spectrum. From these results the author infers that Bohr's theory cannot be developed in the manner which its earlier success in the interpretation of spectra appeared to foreshadow. It is to be admitted, however, that the connexion between the Rydberg constant and Planck's constant is so close that it is difficult to believe that this connexion is not real. Such reality does not, however, involve a corresponding reality in the process by which the form of the hydrogen spectrum is derived on the basis of Bohr's theory. H. M. D.

**Presidential Address to Section B (Chemistry).** W. P. WYNNE (*Rep. Brit. Assoc.*, 1913, 408—424).—A review of the following subjects: residual valency; substitution in the paraffin series; the structure of the benzene molecule; substitution in the benzene series; symmetric and asymmetric syntheses. C. H. D.

**Quantity of Residual Valencies Possessed by Various Molecules.** A. P. MATHEWS (*J. Physical Chem.*, 1914, 18, 474—487).—A theoretical paper in which the amount of residual valency of a number of non-associated liquids and gases has been calculated by subtracting the number of valencies known to be acting in the molecule from the calculated total number of valencies. The difference between the two values is regarded as the residual valency. The total number of valencies is calculated from the molecular cohesion by means of the formula  $a = C(M \times N)^{2/3}$ , in which  $a$  is the van der Waals factor,  $C$  a constant which is calculated to

$3.2015 \times 10^{-37}$  expressed in dynes from Millikan's new determination of the number of molecules in a gram-molecule,  $M$  the molecular weight, and  $N$  the total number of valencies. The value of  $a$  was obtained from the formula  $a = \{(S^2 - S + 2)/(S - 2)\} P_c V_c^2$ , in which  $S$  is the critical coefficient,  $P_c$  and  $V_c$  the critical pressure and volume respectively (compare A., 1913, ii, 674). The constant  $C$  for a pair of molecules was assumed to be equal to  $(m^2 k)^{2/3}$ , in which  $m$  is the gravitational mass of a molecule of unit molecular weight, and  $k$  the gravitational constant. The assumption is made that at a given moment only a small percentage of the molecules are exhibiting residual valencies, so that the figures calculated really give mean values. The numbers obtained vary between 0.195 for hydrogen and 9.08 for *n*-octane. J. F. S.

**The Solidification of Metals from the Liquid State.** CECIL H. DESCH (*J. Inst. Metals*, 1914, 11, 57—118).—A report and summary under the following heads: the cellular structure of metals; crystallisation from centres and the formation of crystallites; foam-structures and Quincke's hypothesis; cellular structures in cooling liquids; liquid crystals; the influence of surface tension; undercooling and the existence of a metastable limit; changes of volume on solidification; the thrust exerted by growing crystals.

C. H. D.

**The Influence of Time in the Rapid Deformations of Metals.** GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1914, 158, 1969—1973).—By varying the height of fall of the weight producing deformation in metal bars by shock, from 6 metres to 1 metre, a variation in the time of deformation from 0.001 to 0.01 of a second has been obtained. This variation produces practically no difference on the work absorbed by rupture of the bar as measured by its resilience. Grooved bars were used, and care was taken in their preparation to ensure that the results obtained in the experiments came between two well-defined limits, which did not differ much from one another. W. G.

**Simple Extraction Apparatus.** MICHAEL FREUND (*Chem. Zeit.*, 1914, 38, 802).—The apparatus consists of a small, wide-mouthed bottle closed with a cork, through which pass a tube connected with a reflux apparatus and a siphon tube; the former tube is provided with a side-tube, and this and the outer end of the siphon are bent downwards, and pass through a cork closing a flask containing the solvent. The material to be extracted is placed in the bottle, and the condensed solvent from the reflux apparatus falls through the material; when the bottle is full of solvent the siphon comes into operation, and the solution is returned to the solvent flask.

W. P. S.

**Simple Fat Extractor.** G. A. STOKES (*Analyst*, 1914, 39, 295).—The substance to be extracted is placed in a paper thimble, covered with a layer of cotton-wool, and the thimble is then inserted



in the flask containing the solvent by means of a wire, the lower part of which is bent into the form of a spiral so as to fit tightly into the thimble. The upper part of the wire passes through the cork closing the flask, and the latter is attached directly to a reflux apparatus. At the commencement of the extraction the lower part of the thimble is immersed in the boiling solvent, but after a time it is raised by means of the wire and the extraction continued.

W. P. S.

**Apparatus for the Extraction of Powdery Material.** ERNST BORNEMANN (*Chem. Zeit.*, 1914, **38**, 833. Compare A., 1913, ii, 855).—A central tube made from porous material is placed down the centre of the thimble holding the substance to be extracted and contained in a Soxhlet apparatus; the lower end of the tube passes through the bottom of the thimble, and extends into the stem of the apparatus; the latter is not provided with a siphon. The top of the tube is plugged with cotton-wool, and the condensed solvent from the reflux apparatus is distributed over the thimble by means of a perforated glass bulb and ring fitted above the central tube.

W. P. S.

**Modification of Golodetz's Rectifying Apparatus for Mixtures of Low Boiling Point.** W. NEUBERGER (*Chem. Zeit.*, 1914, **38**, 823. Compare A., 1912, ii, 626).—A reflux apparatus is provided above the side-tube of the jacket surrounding the still-head of the apparatus; the condensed liquid passes back through the still-head into the flask, while the less volatile vapours escape into the condenser.

W. P. S.

**Non-uniformity of Drying Oven Temperatures.** LORIN H. BAILEY (*J. Ind. Eng. Chem.*, 1914, **6**, 585).—Thermometric readings of the temperatures at different parts of various drying ovens (electrically-, gas-, and steam-heated ovens) showed that only those surrounded by boiling water and steam are capable of maintaining even approximately uniform temperatures.

W. P. S.

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### Inorganic Chemistry.

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**The Taste of Hard Water.** ALEXANDER FRIEDMANN (*Chem. Zentr.*, 1914, i, 1515—1516; from *Zeitsch. Hyg. Infekt. Krankh.*, 77, 125—142).—In connexion with the supposed superiority in taste of a hard water when compared with a soft water, the author has carried out experiments with carbon dioxide dissolved in distilled water. Less than 116 mg. of carbon dioxide per litre can never be tasted; between 116 and 246 mg. give different effects with differ-

ent persons, whilst more than this quantity is distinctly tasted. The temperature of the solutions varied between 15° and 17°. In the case of hard water, bicarbonate-carbon dioxide and total carbon dioxide were examined by Winkler's method. Carbon dioxide in hard water can be tasted at lower concentrations than in distilled water. In one case, the presence of 52.5 mg. of carbon dioxide per litre in a water of 36.4° hardness at 14.2° was recognised, whilst a water containing 173 mg. of free carbon dioxide per litre was found to be distinctly acidic. Above this concentration, carbon dioxide is practically invariably detected by taste. In distilled water, on the other hand, suspicion is first aroused by 126 mg., and the uncertainty persisted in one case up to 252 mg.; more than 264 mg. per litre is detected by taste with certainty. Below this concentration, the free acid is not tasted as such, but can nevertheless cause the sensation termed "refreshing." The possible reason of this property is discussed. H. W.

**Physical Analysis of Some Springs at Evaux-les-Bains.** CLUZET and TH. NOGIER (*Compt. rend.*, 1914, 159, 92—93).—The authors have determined for some five of the springs at Evaux-les-Bains the following physical constants: (a) Temperature at the source; (b) density; (c) freezing point, (d) electrical resistance; (e) radioactivity measured in millimicrocuries of radium emanation from one litre of water at the source. The gases evolved from the Caesar spring have a high radioactivity, and there is a large evolution of gas in one year (262,000 litres). W. G.

**Composition of the Water of the "Limans" of Odessa.** ET. BARRAL (*Bull. Soc. chim.*, 1914, [iv], 15, 630—634).—Complete analyses of the water of three salt lakes on the shore of the Black Sea are given. The number of grams per litre of residue at 120° from each lake is as follows: Konialnick, 82.684; Kadjibeiski, 45.410; Klein-Liebenthal, 21.674. A. J. W.

**Influence of the Current Frequency and Temperature on the Yield of Ozone.** N. PUSCHIN and M. KAUCHTSHEV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 576—590).—With constant periodicity, up to 800 per second, the yield of ozone increases with increase of the voltage from 6500 to 8000. When the frequency is varied, but the voltage and other conditions kept constant, the yield of ozone increases as the frequency is increased to 1240 periods per second at 6500 volts, to 950 at 7000 volts, and to 660 at 8000 volts; if the rate at which the air passes through the ozoniser remains the same, increase of the frequency beyond these limits is accompanied by diminution of the yield of ozone. Continued increase of the air current displaces the maximum yield towards continually increasing frequencies. Rise of temperature from 0° to 28° causes the yield of ozone to increase, but further rise diminishes it.

T. H. P.

**Theory of the Lead Chamber Process.** WALTHER HEMPEL (*Zeitsch. angew. Chem.*, 1914, **27**, 407—408).—A reply to Wentzki (this vol., ii, 558), in which it is pointed out that the objection that no account had been taken of the thermal dissociation of nitrogen peroxide, and that the gas had been led into the reaction chamber at the ordinary temperature in the experiments on the velocity of the formation of sulphuric acid (*A.*, 1914, ii, 455), is quite groundless. The entry and exit tubes of the reaction chamber were wound with electrically heated wires, and thereby maintained at a temperature slightly higher than that of the chamber itself, and condensation of the sulphuric acid in the tubes was likewise prevented by this arrangement. G. F. M.

**Two New Modifications of Phosphorus.** P. W. BRIDGMAN (*J. Amer. Chem. Soc.*, 1914, **36**, 1344—1363).—During the course of experiments on the effect of high pressure on white phosphorus it was found that this is transformed into a new modification. The transition temperature is a linear function of the pressure, and varies from  $-76.9^{\circ}$  at a pressure of 1 kilogram/cm.<sup>2</sup> to  $64.4^{\circ}$  at a pressure of 12,000 kilogram/cm.<sup>2</sup>. The results obtained in the dilatometric measurements were confirmed at atmospheric pressure by thermometric observations. By crystallisation of solutions of white phosphorus in carbon disulphide at low temperature, the new modification was obtained in the form of microscopic crystals belonging to the hexagonal system.

In an attempt to convert white phosphorus into red by the application of high pressure, a black modification of phosphorus was obtained. The conversion, which is irreversible, takes place quite readily at  $200^{\circ}$  under a pressure of 12,000 kilogram/cm.<sup>2</sup>. Black phosphorus is characterised by its high density. By the suspension method this was found to be 2.691 at the ordinary temperature, whilst the density of white phosphorus is 1.83, and that of red phosphorus varies from 2.05 to 2.34 according to the method of preparation. It is not spontaneously inflammable, and may be heated to about  $400^{\circ}$  in the air without igniting. When heated in a closed tube, it vaporises and condenses in the colder parts to red and white phosphorus. In this behaviour it closely resembles red phosphorus, and it would seem that the vapours of black and red phosphorus are identical. In its general chemical behaviour it is also very similar to red phosphorus. In contrast with the white and red modifications, black phosphorus is a fairly good conductor of heat and electricity. The resistivity at  $0^{\circ}$  was found to be 0.711, and this diminishes as the temperature rises. On account of the porous character of the substance, the true value of the specific resistance is probably considerably less than this number would indicate. Between  $30^{\circ}$  and  $100^{\circ}$  the specific heat was found to be 0.170, which is appreciably less than the recorded values for red phosphorus over the same interval of temperature. The relationship between the specific heats would seem to show that black phosphorus is more stable than red. This conclusion is supported

by the vapour-pressure data, according to which the black modification is much less volatile than the red.

By heating white phosphorus to a dull red heat under a pressure of about 1000 kilogram/cm.<sup>2</sup> it is transformed into red phosphorus, the density of which (2.387) is greater than that of "metallic" phosphorus (2.34), which represents the densest form of red phosphorus previously obtained.

The connexion between the different modifications is discussed, with special reference to the nature of red phosphorus, and the relation between this and the black and white forms. H. M. D.

**Preparation of Phosphorus Pentachloride.** SAMUEL PEACOCK (Fr. Patent, 463497).—When calcium phosphate and sodium or potassium chloride, in the proportions  $\text{Ca}_3\text{P}_2\text{O}_8 + 10\text{KCl}$ , are heated together in a closed vessel at, say,  $1100^\circ$ , and the small amounts of phosphorus trichloride and chlorine formed are removed by an aspirator so that their partial pressures in the vessel remain below atmospheric pressure, a rapid and almost complete reaction occurs, giving  $3\text{CaO} + 5\text{K}_2\text{O} + 2\text{PCl}_5$ . The phosphorus pentachloride may be collected, but is preferably passed into hot water, and so converted into phosphoric and hydrochloric acids, the latter being then separated by evaporation. From the residue potassium hydroxide is obtainable. T. H. P.

**The Melting Point of Arsenic.** W. HEIKE (*Intern. Zeitsch. Metallographie*, 1914, 6, 168—171).—By using a sealed porcelain vessel, as for the lead-arsenic alloys (this vol., ii, 464), and enclosing this in an outer vessel packed into sand, it has been found possible to determine the melting and freezing points of arsenic. The value found is  $830^\circ$  (compare Goubau, this vol., ii, 198; Jolibois, *ibid.*). Arsenic which has solidified in the porcelain vessel tarnishes readily in air, whilst the crystals condensed from vapour are very stable. C. H. D.

**Borates. II and III. The System  $\text{BaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  at  $30^\circ$ .** U. SBORGI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 717—721, 854—857. Compare this vol., ii, 562).—The author's experiments were carried out by determining analytically the equilibria reached at  $30^\circ$  by mixtures of various borates with water and boric acid or barium hydroxide. The borates taken had the compositions  $\text{BaO}, \text{B}_2\text{O}_3, 4\text{H}_2\text{O}$ ,  $2\text{BaO}, 3\text{B}_2\text{O}_3, 6\text{H}_2\text{O}$ , and  $\text{BaO}, 3\text{B}_2\text{O}_3, 7\text{H}_2\text{O}$ . The resulting solubility curves are represented on a triangular diagram. R. V. S.

**The Identification of Silicic Acids.** G. TSCHERMAK (*Zeitsch. anorg. Chem.*, 1914, 87, 300—318).—A reply to criticisms. Mügge (A., 1908, ii, 277, 688) gave experiments to show that the position of the break in the dehydration curve varied with the temperature. Some of these results show the break in the curve quite clearly at the point predicted by theory, when the velocity of dehydration is plotted, whilst others are useless for calculation, owing to the intervals of time being too large, and to other errors.

In many cases the mineral or synthetic product used as source of silicic acid is not homogeneous, so that mixtures of silicic acids are obtained. It is necessary to avoid preliminary treatments, such as pressing or prolonged washing, which alter the structure of the gel. The dehydration should be carried out over sulphuric acid of known concentration. Theile's experiments (this vol., ii, 138), when these fail to yield true results for the constitution of the silicates examined, are vitiated by errors of the kind described above. Control experiments, and an optical examination of Theile's preparations, show that some of the silicates were not homogeneous. The homogeneous products yield silicic acids, corresponding closely with the requirements of Tschermak's theory. The replacement of water in silicic acid gels by other liquids, although proving that the gels are adsorption compounds, does not disprove the original presence of definite hydrates.

C. H. D.

**Colloidal and Gelatinous Carbon.** N. L. SÖHNGEN (*Chem. Weekblad*, 1914, 11, 593—596).—Electrolysis of a solution of potassium hydroxide with a current of 4 amperes at 100 volts, using carbon electrodes, yields a substance containing about 81.2% C, 0.85% H, and 18% O. The product obtained by the action of sulphuric acid on a solution of sucrose contains about 55% C, 4.5% H, and 41% O. Colloidal carbon cannot be prepared by either method, or by any known process.

A. J. W.

**A Reduction of Carbon Monoxide by Hydrogen brought about by Radium Emanation.** OTTO SCHEUER (*Compt. rend.*, 1914, 158, 1887—1889).—A mixture of carbon monoxide and hydrogen submitted to the influence of radium emanation for nineteen days undergoes a diminution in volume of nearly 10%. The gas left at the end has no odour, and is shown to be a mixture of carbon monoxide and hydrogen with a small amount of methane and probably a trace of ethylene. The gas contains neither formaldehyde nor methyl alcohol. During the first few days a slight solid deposit was noticed on the walls of the experimental flask, but this had disappeared at the end of four days. On repeating the experiment, formaldehyde was detected in the flask at the end of two days. The action, therefore, probably takes place in two stages, the carbon monoxide being first reduced to formaldehyde, which is then in its turn reduced to methane and other hydrocarbons.

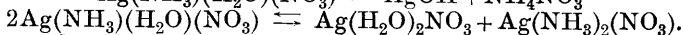
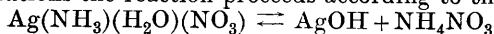
W. G.

**Preparation of Ammonium Sulphate.** BADISCHE ANILIN- & SODA-FABRIK (Fr. Patent, 463487).—The slow oxidation of ammonium sulphite to sulphate is considerably accelerated by keeping the solution alkaline with ammonia and by the presence of oxygen-carriers. The reaction proceeds well under pressure.

T. H. P.

**Does a Mono-ammoniacal Silver Nitrate Exist?** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, 28, 198—200. Compare A., 1904, ii, 403).—The amount of silver hydroxide precipitated from solu-

tions of silver nitrate containing various quantities of ammonia is determined for a number of solutions. The author considers that in dilute solutions the reaction proceeds according to the equations:



The reaction is examined by the law of mass action, and from the results it is shown that it is extremely probable that a mono-ammoniacal silver nitrate does exist.

J. F. S.

**The Dehydration of Gypsum.** C. GAUDEFROY (*Compt. rend.*, 1914, **158**, 2006—2008).—Anhydrous calcium sulphate as prepared by the dehydration of gypsum is much more soluble and less dense than the natural anhydrite. The last stage in the dehydration, passage from the hemihydrate to the anhydrous form, is reversible, each process only requiring a few minutes at 110° in a dry and humid atmosphere respectively. The temperature at which the anhydrous sulphate is produced therefore depends on the hygro-metric state of the air in the oven, thus explaining the variations in the results of different workers. Further, both the hemihydrate and the anhydrous form can absorb water vapour from the air at the ordinary temperature. The author considers that the two types of figures formed on gypsum by its dehydration are only modifications of one another, and are formed by the hemihydrate.

W. G.

**Glucinum Borates.** B. BLEYER and L. PACZUSKI (*Kolloid. Zeitsch.*, 1914, **14**, 295—306).—Experiments have been made to ascertain whether any glucinum borates are formed as the products of reactions in which water is involved, for theory indicates that borates can only be obtained in this way if the borates themselves are not very soluble and the corresponding oxides or hydroxides are readily soluble.

In the first series of experiments, the distribution of boric acid between water and glucinum hydroxide was investigated. On account of the rapidity with which the hydroxide ages and diminishes in its reactivity, it was found necessary to make the experiments with glucinum hydroxide precipitated *in situ* by the addition of ammonia to a solution containing boric acid and glucinum sulphate. The results obtained in this manner show that the ratio of distribution of the boric acid between the water and glucinum hydroxide is independent of the concentration of the boric acid. This constancy of the concentration ratio was found both in experiments at 20° and at 100°. From this behaviour, the authors draw the conclusion that no definite compounds are formed by the interaction of glucinum hydroxide with aqueous solutions of boric acid, and that the boric acid removed by the hydroxide forms a solid solution.

A further series of experiments, in which the products obtained by the interaction of glucinum sulphate and sodium borate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) in aqueous solution were investigated, confirms this con-

clusion. The composition of the solid solution, which separates out when these solutions are brought together, varies considerably with the concentration and with the relative proportions of the reacting substances. Precipitates containing the largest proportion of boric acid are obtained when the glucinum salt reacts with an equivalent quantity of sodium borate in a solution of the highest possible concentration. The addition of sodium or ammonium sulphate to the solution has no appreciable influence on the composition of the precipitate.

According to the results of this investigation, it is extremely probable that the glucinum borate,  $5\text{BeO} \cdot \text{B}_2\text{O}_3$ , described by Krüss and Mohrat (A., 1890, 697), is simply a solid solution of boric acid in glucinum hydroxide.

H. M. D.

**Magnesium Chloride. II. Influence of Magnesium Chloride on the Oxidising Action of Chlorates and Nitrates.** K. A. HOFMANN, FRITZ QUOOS and OTTO SCHNEIDER (*Ber.*, 1914, 47, 1991—1999).—In continuation of former experiments (Hofmann and Höschel, this vol., ii, 204), the authors have found that moist magnesium chloride considerably facilitates a number of technically important oxidation processes. When chlorates, nitrates, and nitrites are mixed with magnesium chloride, either in the form of the hydrate,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , or as carnallite mother liquors, their oxidising action takes place at remarkably low temperatures, the molten magnesium chloride keeping the mixture homogeneous, and the water preventing too great a rise in temperature. As an example, the oxidation of anthracene to anthraquinone may be cited. A mixture of 20 grams of anthracene, 23 grams of sodium nitrate, and 80 grams of magnesium chloride hexahydrate is heated in an open flask on the sand-bath. The fusion turns yellow already at  $125^\circ$ , owing to the formation of anthraquinone. The temperature is allowed to rise to  $145^\circ$ , 40 c.c. of water added, and the temperature slowly raised to  $300^\circ$ , stirring well meanwhile. The anthraquinone separates above the salt residues, and after being collected is mixed with 5 grams of magnesium oxide and sublimed. The yield is 91.5%.

Details are also given of the influence of moist magnesium chloride on the oxidation of aniline to aniline-black, of a mixture of aniline and paraphenylenediamine hydrochloride to indulines and paraphenylene-blue, of a mixture of *p*-tolylenediamine hydrochloride, aniline, and *o*-toluidine to safranine, and of the oxidation of sawdust and of molasses to oxalic acid. Considerable quantities of trimethylamine are first evolved in the oxidation of the molasses. Magnesium chloride also has a considerable influence on the introduction of nitroso-groups into phenols, and on the formation of induline from a mixture of aniline, aniline hydrochloride, and aminoazobenzene; the previous preparation of aminoazobenzene is not absolutely necessary; it also accelerates the liberation of iodine from potassium iodide solutions by means of potassium chlorate and dilute sulphuric acid.

Magnesium chlorate and nitrate also exert an oxidising action at



comparatively low temperatures in the presence of water of crystallisation, but the temperatures are not so low as with the mixture of magnesium chloride hexahydrate and sodium nitrate.

The experiments of the authors lead them to the conclusion that the effect of the hydrated magnesium chloride cannot be ascribed to its products of hydrolysis or to the ions formed. It is possible that additive products are formed, which are very reactive. Magnesium salts are known to give complex compounds very readily.

T. S. P.

**The Crystallographical and Optical Properties of Magnesium and Manganese Pyrophosphates.** O. ANDERSON (*J. Washington Acad. Sci.*, 1914, 4, 318—325).—The two salts are found to belong to a new monosymmetric isomorphous group. Crystals for examination were obtained from cavities in a rapidly crystallised fusion of each substance. The optical properties could only be determined on microscopic fragments.

$\text{Mg}_2\text{P}_2\text{O}_7$ :  $a:b:c = 0.7947:1:1.0880$ ;  $\beta = 75^\circ 49'$ ; optical character positive;  $D_4^{25} 3.058$ .

$\text{Mn}_2\text{P}_2\text{O}_7$ :  $a:b:c = 0.7834:1:?$ ;  $\beta = 74^\circ 9'$ ; optical character positive;  $D_4^{25} 3.707$ .

The two salts are perfectly miscible in the solid state, forming a system belonging to Roozeboom's Type I.

E. H. R.

**Allotropy of Zinc. II.** ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 59—60. Compare this vol., ii, 127).—The so-called "atomised" zinc obtained by Schoop's method has been found by dilatometric observations to consist of a mixture of two or more allotropic forms. The metal was found to contract at  $25^\circ$ .

H. M. D.

**Allotropy of Cadmium. II.** ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 54—58).—In a previous paper (this vol., ii, 52) experiments were described which seemed to show the existence of a transition temperature at  $64.9^\circ$ . Further dilatometric observations indicate, however, that this temperature varies with the previous thermal history of the metal, and the authors draw the conclusion that there are more than two allotropic forms which must be taken into account.

H. M. D.

**Allotropy of Cadmium. III.** ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 122—131. Compare preceding abstract).—According to dilatometric observations, electrolytically deposited cadmium is unstable at the ordinary temperature, and its nature has been further investigated by electromotive force measurements. The *E.M.F.* of the cell, electrolytic cadmium | cadmium sulphate solution | 12.5% cadmium amalgam, was found to be  $0.0503\text{ V}$  at  $25^\circ$ , but after standing for several weeks the *E.M.F.* fell to  $0.0475^\circ$ . The change in the *E.M.F.* is attributed to the transformation of unstable  $\gamma$ -cadmium into the stable  $\alpha$ -form. In support of this view, it was

found that the above difference in *E.M.F.* increases from 2.8 millivolt at 25° to 4.0 millivolt when the temperature is lowered to 0°. This is to be expected, for the difference in *E.M.F.* should increase as the interval between the temperature of the measurement and the transition temperature is increased.

In addition to the change in *E.M.F.* which is brought about by transformation of the electrolytic cadmium, a further change is found if the metal is deposited by passing a current through the above cell. This is due to the local transformation of the two-phase amalgam into a one-phase system. By diffusion of the cadmium, the two-phase equilibrium is, however, gradually restored, and the *E.M.F.* falls to its "normal" value after four or five days.

H. M. D.

**Atomic Weight of Lead of Radioactive Origin.** THEODORE W. RICHARDS and MAX E. LEMBERT (*J. Amer. Chem. Soc.*, 1914, **36**, 1329—1344; *Compt. rend.*, 1914, **159**, 248—250. Compare Soddy and Hyman, T., 1914, **105**, 1402).—According to the views put forward by Russell, Fajans and Soddy (A., 1913, ii, 274, 275, 276, 277), the nature of the end-product of the process of disintegration of a radioactive mineral will vary according to the proportion of the parent substances in the mineral. In order to test this theory, measurements have been made of the atomic weight of radioactive lead obtained from different sources.

The method adopted was very similar to that used by Baxter and Wilson (A., 1908, ii, 281), which involves the preparation and analysis of the chloride of the metal. The results obtained show that all the radioactive specimens of lead examined by the authors have a lower atomic weight than ordinary lead. The actual values and the source of the lead are indicated in the following summary: lead from uraninite (North Carolina), 206.40; from pitchblende (Joachimsthal), 206.57; from carnotite (Colorado), 206.59; from Ceylonese thorianite, 206.82; from English pitchblende, 206.86; ordinary lead, 207.15.

The fact that all analyses were carried out by the same method, and that each sample gave consistent results, excludes the possibility of analytical error, and the authors consider that the variability indicated by the above atomic-weight numbers is definitely established. A similar result was also obtained by Soddy and Hyman in the determination of the atomic weight of lead from Ceylon thorite (*loc. cit.*).

The ultra-violet spectrum of a typical radioactive lead was found to be practically identical with that of ordinary lead. It would seem, therefore, that the admixed substance cannot be identified by spectroscopic or by chemical methods.

H. M. D.

**Atomic Weight of Lead from Pitchblende.** O. HÖNIGSCHMID and (Mlle.) ST. HOROVITZ (*Compt. rend.*, 1914, **158**, 1796—1798. Compare Curie, this vol., ii, 563).—The results of atomic-weight determinations of lead, using lead chloride obtained from pitchblende residues and carefully purified, give the value 206.736 as

the atomic weight of lead, this being the mean of nine determinations by Baxter's method. This low value is in accord with the view that radium by the loss of five  $\alpha$ -particles passes into radium-G, an element inseparable by chemical methods from lead, but possessing a different atomic weight, the value for which, calculated theoretically from those of uranium and radium, should be 205.62.

W. G.

**Cause of the Oxidation of Type Metal.** S. ZINBERG (*Zeitsch. angew. Chem.*, 1914, 27, 436—437).—The formation of lead hydroxide and carbonate on the surface of type metal is due to the action of moisture in the atmosphere. Whilst distilled water readily attacks an alloy containing 82% of lead and 14% of antimony, it has no action on one containing 72% of lead and 24% of antimony. The presence of certain salts in water, such as those contained in drinking water, inhibits the action of the latter on the metal, and this water may be employed for cleaning type metal, but the use of turpentine or petroleum is to be preferred for the purpose.

W. P. S.

**Experiments on White Lead.** R. STUART OWENS (*J. Physical Chem.*, 1914, 18, 461—473).—Experiments have been carried out on the production of white lead, lead carbonate, and lead hydroxide with the object of ascertaining how the physical properties of these substances change with the conditions of precipitation. It is shown that lead hydroxide can be precipitated in a definite crystalline form, and by varying the conditions the size of the crystals can be varied between  $1 \times 10^{-3}$  and  $37.5 \times 10^{-3}$  mm. in diameter. Lead carbonate is not precipitated in any definite crystalline form. It is probable that the particles are aggregates of very small crystals; the size of the particles can be varied between  $1 \times 10^{-3}$  and  $3.7 \times 10^{-3}$  mm. in diameter. When a mixture of particles of lead carbonate and lead hydroxide is kept under a solution of sodium acetate, particles of white lead are formed which have a uniform size, no matter what the size of the particles of the reacting substances. When a mixture of sodium hydroxide and sodium carbonate solutions is added to a solution of lead acetate, white lead is precipitated, and the size of the particles can only be varied between narrow limits ( $0.2 \times 10^{-3}$ — $2.0 \times 10^{-3}$  mm.). White lead prepared in this way does not show any definite crystalline form, but seems to consist of rounded, translucent particles. Rapid precipitation gives smaller particles, and slow precipitation larger particles. The absorption of oil by white lead is greater with larger particles than with smaller particles. Paint made from small-particle white lead is superior to that made from large-particle white lead. Uniformity in the size of the particles is not necessarily an advantage in a paint.

J. F. S.

**Allotropy of Copper.** II. ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 60—62. Compare this vol., ii, 205).—Further observations indicate that the transi-

tion temperature  $71.7^{\circ}$  recorded in the previous paper is to some extent dependent on the previous thermal history of the metal. At  $69.5^{\circ}$  the volume was found to increase, and then to decrease in a further series of observations. This behaviour seems to show that the metal consists of more than two allotropic modifications.

H. M. D.

**The Oxidation and Reduction of Copper.** JACQUES JOANNIS (*Compt. rend.*, 1914, 158, 1801—1804. Compare Berger, this vol., ii, 564).—A study of the rate of oxidation of copper and reduction of its oxide at  $300^{\circ}$  under varying pressure. The copper used was prepared electrolytically, and was in the form of fine wire 1 mm. diameter. It was placed in a cylindrical tube, heated in an electric furnace, and connected through a stop-cock to a chamber fitted with a manometer and stop-cocks, through which hydrogen or oxygen could be introduced. The progress of the reactions was followed by means of the manometer readings. Pressure apparently plays no appreciable part in the oxidation of copper, but the coating of oxide formed considerably diminishes the velocity of oxidation, even if a fresh supply of oxygen is introduced. In the process of reduction, pressure has apparently no influence either, but in this case it is impossible to draw any definite conclusions, owing to the velocity of condensation of the water formed.

W. G.

**The Influence of Nickel on Some Copper-Aluminium Alloys.** A. A. READ and R. H. GREAVES (*J. Inst. Metals*, 1914, 11, 169—213).—The mechanical properties are chiefly considered. The corrodibility of alloys of copper and aluminium containing 5 and 10% Al is small when sea-water is used, and is still further reduced by the addition of nickel. In acids, the alloys containing nickel are more readily corroded than those from which it is absent.

C. H. D.

**Muntz Metal.** J. E. STEAD and H. G. A. STEDMAN (*J. Inst. Metals*, 1914, 11, 119—150. Compare Bengough and Hudson, A., 1908, ii, 186).—Muntz metal, the alloy containing about 60% of copper and 40% of zinc, is rendered most ductile by prolonged annealing at  $430^{\circ}$ . At this temperature the  $\beta$ -constituent almost completely disappears in the course of several months, the specimen then consisting almost entirely of  $\alpha$ , although without loss of zinc. There is no evidence that the  $\beta$  is resolved into  $\alpha$  and  $\gamma$  (compare Carpenter, A., 1912, ii, 764; 1913, ii, 138, 139). During heating in air, the copper is completely protected from oxidation, the scale consisting only of zinc oxide.

C. H. D.

**The Micro-chemistry of Corrosion. II. The  $\alpha$ -Alloys of Copper and Zinc.** SAMUEL WHYTE and CECIL H. DESCH (*J. Inst. Metals*, 1914, 11, 235—251. Compare this vol., ii, 367).—Using the method previously described, brass containing 70% of copper and 30% of zinc is slightly more corroded in the cast than in the

annealed state, owing to the presence of cores in the crystallites formed on solidification. When 1% of zinc is replaced by tin, the corrosion is at first stimulated, but is rapidly checked by the formation of an adherent layer of basic salts. A similar effect is produced by 2% of lead.

Spontaneous and electrically stimulated corrosion are completely similar, the first process in each case being one of dezincification, which proceeds along the boundaries of crystal grains and along twinning planes.

C. H. D.

**Reduction of the Oxides of Copper and Nickel by Hydrogen in the Presence of a Dehydrating Agent.** E. BERGER (*Compt. rend.*, 1914, 158, 1798—1801. Compare Sabatier and Espil, this vol., ii, 276).—The reduction of oxides of copper and nickel is very considerably accelerated by the presence of a dehydrating agent such as barium oxide. The curve showing the rate of reduction of copper oxide is continuous, whilst in the case of nickel oxide, NiO, there is a break, showing the intermediate formation of the oxide, Ni<sub>2</sub>O. In the case of nickel, completely reduced, absorption of hydrogen continues until at 209.5° in forty hours the metal has absorbed three hundred times its volume of the gas, and the absorption still continues.

W. G.

**Colloidal Cuprous Oxide.** C. PAAL and A. DEXHEIMER (*Ber.*, 1914, 47, 2195—2199. Compare Paal and Leuze, A., 1906, ii, 356).—If a colloidal solution of cupric oxide, prepared by the method of Paal and Leuze (*loc. cit.*) with either sodium protalbate or lysalbate, is treated with a solution of pure hydroxylamine, reduction, which is accelerated by heating, takes place, with the evolution of gas, and leads to the quantitative formation of colloidal cuprous oxide. From the hydrosol thus prepared, the solid, soluble hydrogel may be obtained when air is excluded to prevent oxidation. According as the hydroxylamine is used in the equivalent quantity, or in excess, the hydrosol and hydrogel show different stabilities towards atmospheric oxidation, the presence of excess of hydroxylamine making them much more stable.

The hydrosols are bright orange in colour in transmitted light, and have a yellowish-grey, milky appearance in reflected light.

T. S. P.

**Position of Cerium in the Periodic System and Complex Molybdates of Quadrivalent Cerium.** G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 805—812).—The constitution of the complex molybdates described in this paper is analogous to that of the complex molybdates of zirconium and thorium, and this fact supports the view that cerium occupies a place in the same group as these elements in the periodic system. The *neutral ammonium cerimolybdate*, (NH<sub>4</sub>)<sub>8</sub>[Ce(Mo<sub>2</sub>O<sub>7</sub>)<sub>6</sub>].8H<sub>2</sub>O, is a yellow, crystalline substance yielding yellow solutions, which are stable towards hydrogen peroxide, and give a precipitate with oxalic acid only after prolonged boiling. *Acid aniline cerimolybdate* is a yellow

substance, which becomes green in the light. *Acid ammonium cerimolybdate*,  $(\text{NH}_4)_6\text{H}_2[\text{Ce}(\text{Mo}_2\text{O}_7)_6]\cdot 10\text{H}_2\text{O}$ , is a pale yellow, crystalline substance. *Silver cerimolybdate*,  $\text{Ag}_8[\text{Ce}(\text{Mo}_2\text{O}_7)_6]$ , is an orange-yellow, crystalline substance.

R. V. S.

**The Separation of Yttrium from the Yttrium Earths. II.** H. C. HOLDEN and C. JAMES (*J. Amer. Chem. Soc.*, 1914, **36**, 1418—1423. Compare this vol., ii, 370).—The most efficient method for the separation of yttrium from the yttrium earth metals has been found to be the method of fractional precipitation with sodium nitrite. The oxides are dissolved in nitric acid, the solution diluted and boiled, and a quantity of sodium nitrite is added sufficient to precipitate the required fraction of the rare earth material. The yttrium concentrates in the later fractions. This method gives a larger yield, a more rapid separation, and is less expensive than the phosphate or chromate method. The method is not very effective, however, for the separation of yttrium from terbium.

H. M. D.

**The Chemical or Physical Nature of Colloidal Hydrous Aluminium Silicates.** R. GANS (*Centr. Min.*, 1914, 365—368. Compare this vol., ii, 469).—Further discussion and reply.

L. J. S.

**Some Physical Properties of Indium Tribromide in Water.** ADOLF HEYDWEILLER (*Zeitsch. anorg. Chem.*, 1914, **88**, 103—107).—The electrical conductivity, density, specific heat, and refractive index for three hydrogen lines have been determined for solutions of indium tribromide in water.

C. H. D.

**Metallic Bromides. VIII.** ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1914, **49**, 834—844. Compare A., 1913, ii, 692, 957; this vol., ii, 214, 379).—When heated, anhydrous manganese bromide decomposes, with liberation of bromine. The tetrahydrate softens at 70—80°, and melts to a transparent liquid at 110°; Kuznetsov (*J. Russ. Phys. Chem. Soc.*, 1897, **29**, 288) gave m. p. 64·3°. It loses 2H<sub>2</sub>O in a thermostat at 40°, or more readily at 50°, and 3H<sub>2</sub>O at 80°; the fourth molecule of water is expelled at 120°. In a desiccator over sulphuric acid it loses 2H<sub>2</sub>O rapidly, and a further H<sub>2</sub>O very slowly; over calcium chloride it gives up only 2H<sub>2</sub>O. Over sulphuric acid at 40 or 20 mm. pressure, it loses 3H<sub>2</sub>O, the residual monohydrate becoming anhydrous in an oven at 116°. In a current of dry air at 41°, the tetrahydrate gives up 2H<sub>2</sub>O rapidly, and the third H<sub>2</sub>O slowly, the fourth molecule of water being expelled only at 99°. Elimination of 1H<sub>2</sub>O from the tetrahydrate, with formation of  $\text{MnBr}_2\cdot 3\text{H}_2\text{O}$ , has not been effected.

When heated, hexahydrated magnesium bromide melts, and then loses water and hydrogen bromide, the dry residue giving up bromine on further heating. Under no conditions of heating was loss of water without decomposition observed.

When heated in moist air, glucinum bromide decomposes accord-

ing to the equations  $\text{GIBr}_2 + \text{O} = \text{GIO} + \text{Br}_2$  and  $\text{GIBr}_2 + \text{H}_2\text{O} = 2\text{HBr} + \text{GIO}$ .

Zinc bromide forms anhydrous crystals, and boils unchanged, but when heated with iodine it readily gives up bromine.

When heated near its boiling point, anhydrous cadmium bromide sublimes and gives up bromine, much of the latter being obtained if iodine is present. Its vapour density was found to be 9.22 and 9.28, instead of 9.40, at  $923^\circ$  and  $914^\circ$  respectively.

Tetrahydrated cadmium bromide is completely dehydrated in a thermostat at  $30^\circ$ , or over sulphuric acid at  $18\text{--}20^\circ$ .

Mercuric bromide forms anhydrous crystals, and even when heated rapidly sublimes without liberation of bromine, but this does occur in presence of iodine. Bromine is not set free when the bromide is heated with 50% chromic acid solution, but is eliminated copiously in the presence of a saturated solution of chromium trioxide. Bromine is also lost when the bromide is shaken with potassium iodide solution and then heated with 50% chromic acid solution.

Anhydrous cuprous bromide readily evolves bromine when heated.

T. H. P.

**Manganese Sulphide and the Estimation of this Metal.** A. VILLIERS (*Compt. rend.*, 1914, 159, 67—69. Compare Raab and Wessely, A., 1903, ii, 697).—A study of the conditions governing the formation of the pink and green forms of manganese sulphide. Precipitation in a neutral solution saturated with ammonium and alkali salts gives a pink precipitate which does not turn green, whereas precipitation in a neutral solution containing but a small amount of foreign salts gives a pink sulphide, which slowly changes at the ordinary temperature into the green form. In order to obtain the green sulphide in the cold, any excess of acid should be first boiled off, the solution diluted, made alkaline with ammonia, and ammonium hydrogen sulphide added. For the estimation of manganese, the precipitation should always take place at  $100^\circ$  after the addition of ammonia in quantity sufficient to make the solution alkaline. By this means a very dense, green precipitate is obtained, which can be easily collected and washed.

W. G.

**Preparation of Hydrates of Manganese Sulphate.** R. DE FORCRAND (*Compt. rend.*, 1914, 158, 1760—1763. Compare Cottrell, A., 1901, ii, 12, and Richards and Fraprie, A., 1901, ii, 553).—The author has prepared the heptahydrate, tetrahydrate, and what he considers to be two dihydrates, and two monohydrates of manganous sulphate, as well as two anhydrous salts. One series of hydrates was prepared in the cold, starting with the heptahydrate, and subjecting it to successive dehydration by efflorescence, the final stages being carried out in a vacuum over phosphoric oxide. The starting point of the second series was a cold saturated solution of the tetrahydrate, which was heated to  $98^\circ$  and evaporated by a current of air played on to the surface of the

liquid. No indication of a hexahydrate was obtained, and the formation of a trihydrate was uncertain. W. G.

**Thermochemical Study of Some Hydrates of Manganese Sulphates. Isomerides.** R. DE FORCRAND (*Compt. rend.*, 1914, 159, 12—16).—The author has determined the heats of solution at 15° of the hydrates of manganous sulphate prepared on the one hand in the cold, and on the other at 100° (compare preceding abstract). The results obtained for the series B, prepared at 100°, are in agreement with Thomsen's values for the anhydrous salt and the monohydrate, and for the pentahydrate prepared in series A, in the cold, the heat of solution agrees with that obtained by Thomsen. For the anhydrous salts and the mono-, di-, tri-, and tetra-hydrates of series A, there is a marked difference between their heats of solution and the values given by Thomsen, the difference increasing as dehydration proceeds. The author considers that the anhydrous salt and the hydrates used by Thomsen are polymerides of his salts of series A, the polymerisation being brought about by rise in temperature. This polymerisation is exothermic and irreversible. The difference between the values for the tetrahydrates of the two series is small, and the hypothesis suggested by the author is that on warming the tetrahydrate it loses water and undergoes progressive polymerisation, which reaches its maximum in the neighbourhood of the monohydrate, the final heating from 100° to 300° only serving to complete the dehydration. This polymerisation can be produced in the cold by the action of sulphuric acid as a catalyst on a saturated solution of the monohydrate obtained in series A. W. G.

**The Velocity of Transformation of Steels on Heating, and the Specific Electrical Resistance of Iron.** A. PORTEVIN (*Compt. rend.*, 1914, 159, 51—53).—For a given steel, heated to a given temperature and cooled under identical conditions, the amount of carbon entering into solid solution will depend only on the amount of carbon in solid solution at the commencement of rapid cooling, which is a function of the time of heating at the given temperature. The first value, which can be determined by measuring the electrical resistance of steel, thus affords a measure of the velocity of transformation on heating at a given temperature. The results obtained show that the entry of the carbon into solution is far from being instantaneous. The elevation of the temperature and the increase in the time of heating increase the electrical resistance of the tempered steel. The author finds by extrapolation the value 9.3 microhms at 20° for the resistance of pure iron. W. G.

**The Hardness and Electrical Resistance of Iron-Carbon Alloys.** RUDOLF VONDRÁČEK (*Intern. Zeitsch. Metallographie*, 1914, 6, 172—182).—The hardness of martensite is not to be attributed to the presence of finely divided cementite, which could not give rise to a hardness much greater than that of pearlite. The elec-



trical resistance of martensite is such that the whole of the carbide must be present in solid solution. Cold-working is without any considerable influence on the resistance of steel. The resistance figures indicate that  $\alpha$ -iron is capable of holding as much as 0.14% of carbon in solid solution from 600° downwards when very slowly cooled in presence of a large excess of cementite. The  $\alpha$ -iron present in the eutectoid (pearlite) contains 0.06—0.07% C. at the temperature of formation, increasing to 0.14% with falling temperature. C. H. D.

#### The Influence of Manganese on the Corrosion of Steel.

CECIL H. DESCH and SAMUEL WHYTE (*J. West Scotland Iron Steel Inst.*, 1914, **21**, 176—191).—The corrosion of steels containing manganese in 5% sodium chloride solution has been examined by the method previously described (this vol., ii, 367). A distinct influence of manganese has not been observed. Manganese is preferentially dissolved, the ratio of manganese to iron in the solution increasing to a maximum and then diminishing. The maximum is also marked by a reversal in the etching, ferrite being at first attacked more than pearlite, whilst the etching is normal after the maximum is passed. C. H. D.

#### Magnetic Study of Iron Sesquioxide.

RUBY WALLACH (*Compt. rend.*, 1914, **159**, 49—51).—A study of the variation with temperature of the magnetic susceptibility of the three forms of ferric oxide prepared (1) by precipitation in the cold with ammonia from a freshly prepared, dilute solution of ferric chloride; (2) by boiling the previous form with water; (3) by the action of water on sodium ferrite. For form (1) the magnetic susceptibility at first increases with the temperature, reaching a maximum at 200°, diminishes rapidly to 300°, and then slowly to a minimum at 650°, above which temperature it slowly rises. The magnetic susceptibility of form (2) diminishes continually, there being a rapid fall at 200°, and at 350° its curve joins that of form (1). The curve for form (3) is analogous to that for form (1), its minimum being situated at 750°. To confirm the temperatures of final transformation, the author has made a thermal analysis of the oxides by means of the Le Chatelier-Saladin double galvanometer. W. G.

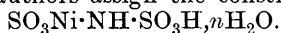
#### Bromination of Cobalt and Nickel in the Presence of Ethyl Ether.

F. DUCELLIEZ and A. RAYNAUD (*Compt. rend.*, 1914, **158**, 2002—2003).—On bromination of cobalt or nickel in dry ether, according to the conditions given for manganese (compare this vol., ii, 273, 470), the bromine readily combines with the metal, giving the respective bromides, containing 1 mol. of ether, namely,  $\text{CoBr}_2 \cdot \text{Et}_2\text{O}$  and  $\text{NiBr}_2 \cdot \text{Et}_2\text{O}$ . The cobalt compound is green, and less stable than the nickel compound, which is yellow. Each of them on heating yields the anhydrous bromide. W. G.

#### Some Compounds of Univalent Nickel.

L. TSCHUGAEV and W. CHLOPIN (*Compt. rend.*, 1914 **159**, 62—64. Compare Bellucci and Corelli, A., 1913, ii, 604; i, 839; this vol., i, 260).—On mixing

concentrated solutions of sodium hyposulphite and nitrite in molecular proportions, the resulting mixture gives with nickel salts of the type  $\text{NiX}_2$  a deep violet or blue coloration, according to the proportion of nickel used. The violet-coloured substance is more soluble than the blue. It has been isolated in a moderately pure state, and to it the authors assign the constitution



With alkali hydroxides it gives a blue precipitate, quite different in character from nickelous hydroxide, and at the same time ammonia is liberated and sodium sulphate formed. Potassium cyanide changes its violet colour to red. Ammonia, pyridine, and ethylenediamine give a deep blue coloration quite different from that obtained under the same conditions with nickelous salts. Ammonium hydrogen sulphide gives an amorphous, black precipitate soluble in potassium cyanide. The blue precipitate obtained with alkali hydroxides is shown to be the hydroxide  $\text{NiOH}$ , and with sodium sulphite it gives the subsulphide  $\text{Ni}_2\text{S}$ . The red coloration obtained with potassium cyanide is due to the formation of the complex cyanide obtained by Bellucci and Corelli (*loc. cit.*).

W. G.

**Colloidal Nickelous Hydroxide.** C. PAAL and GUSTAV BRÜNJES (*Ber.*, 1914, 47, 2200—2202).—Colloidal solutions of nickelous hydroxide are readily obtained from solutions of nickel sulphate by the ordinary methods involving the use of either sodium protalbate or sodium lysalbate, followed by dialysis. The solutions are clear in transmitted light, but in reflected light they are opalescent, with a greenish-yellow colour. Concentration in a vacuum gives brownish-yellow, transparent, brittle lamellæ, which dissolve again to the colloidal solution.

Sodium protalbate or lysalbate has only a slight protective action on colloidal solutions of nickelous hydroxide, so that solutions containing a high percentage of the colloid cannot be obtained.

T. S. P.

**Properties of Recoura's Green Chromium Sulphate.** ANDRÉ KLING, D. FLORENTIN, and P. HUCHET (*Compt. rend.*, 1914, 159, 60—62).—Working with an  $N/2$ -solution of the green chromium sulphate, obtained by Recoura by heating the crystalline, violet sulphate to  $90^\circ$  (compare A., 1896, ii, 27), the authors have determined the variation with time of (a) the amount of sulphuric acid in the solution precipitable by benzidine hydrochloride; (b) the lowering of the freezing point of the solution; (c) the electrical conductivity of the solution. During the first twenty-four hours after the preparation of the solution no sulphate precipitate is obtainable, but after that time the amount increases at first rapidly, and then gradually with passage of time. The molecular lowering of the freezing point and the electrical conductivity at first increase rapidly, even before the presence of the  $\text{SO}_4^{''}$  ion can be detected, and then attain a value which remains almost constant during the rest of the experiment. The green solutions

of chromium sulphate tend towards a state of equilibrium, which is a function of the temperature and concentration, and is the state towards which the violet solutions of the same concentration gradually pass. W. G.

**Transformation Phenomena in Potassium Molybdates and Tungstates.** II. M. AMADORI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 800—805. Compare this vol., ii, 568).—Potassium molybdate is trimorphous, and has a transformation point at about  $460^{\circ}$ . The second transformation point is observed at  $322\text{--}326^{\circ}$  during heating; the thermal effects observed during cooling are of no value, because the substance shows a great tendency to remain in an unstable state in the form stable at higher temperatures. Potassium tungstate is also trimorphous with a transformation point at about  $600^{\circ}$  and a second transformation point (observable only during heating) at  $370\text{--}374^{\circ}$ . To results obtained by cooling the same objections apply as in the case of potassium molybdate. R. V. S.

**Revision of the Atomic Weight of Uranium.** O. HÖNIGSCHMID (*Compt. rend.*, 1914, 158, 2004—2005).—The author has determined the atomic weight of uranium from the ratio  $\text{UBr}_4 : \text{AgBr}$ , and finds the value 238.175. The uranium bromide was prepared by heating a mixture of uranium oxide and carbon in bromine vapour, subliming the product, melting it, and transferring it to a silica weighing tube, the whole process being carried out in a silica apparatus in the absence of air. In one series of determinations the sublimation was performed in bromine vapour, and in the other in nitrogen. The oxide used was prepared from a pure specimen of uranyl nitrate, and carefully purified by repeating the process. W. G.

**Vanadium in Brass.** R. J. DUNN and O. F. HUDSON (*J. Inst. Metals*, 1914, 11, 151—168).—The critical point at about  $460^{\circ}$  in alloys of copper and zinc containing the  $\beta$ -phase is only slightly affected by vanadium, 1% only raising it about  $10^{\circ}$ . Vanadium is practically without influence on the resolution of the  $\beta$ -phase. Alloys containing more than 0.5% V contain hard, blue inclusions, possibly an oxide. C. H. D.

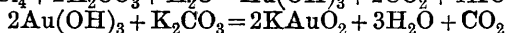
**Preparation of Solutions of Colloidal Vanadic Acid from Orthovanadic Esters.** J. D. RIEDEL, A.-G. (*Chem. Zentr.*, 1914, i, 1738; from *Riedel's Bericht.*, 1914, 13—14. Compare Prandtl and Hess, A., 1913, i, 815).—*iso*Amyl orthovanadate,  $(\text{C}_5\text{H}_{11})_3\text{VO}_4$ , b. p.  $161^{\circ}/19\text{ mm.}$ , forms the most convenient starting point for the preparation of solutions of colloidal vanadic acid, which are free not only from foreign electrolytes, but also from any considerable quantity of alcohols or alcoholic derivatives. The ester (50 grams) is gradually added to boiling water (1 litre), and ebullition is continued until a homogeneous dark red solution is obtained. After cooling, the amylene hydrate is extracted with ether, and the latter removed by passing a current of air through the

boiling solution. In the deep red solution about 7.99% of the vanadic acid is dissolved in the non-colloidal form, which, however, is only dissociated to a slight extent.  
H. W.

**Chemistry of Gold. II. Auto-reduction as a Factor in the Precipitation of Metallic Gold.** VICTOR LENHER (*J. Amer. Chem. Soc.*, 1914, 36, 1423—1426. Compare A., 1913, ii, 514).—Reference is made to the precipitation of metallic gold from aqueous solution by the action of oxidising agents, the action being supposed to consist in auto-reduction. In particular attention is called to the activity of manganese compounds and the geological importance of auto-reduction as a factor in the secondary deposition of gold.  
H. M. D.

**The Reaction in the Preparation of Colloidal Gold Solutions by the Formaldehyde Method, and the Influence of Carbon Dioxide on the Formation of these Solutions.** W. NAUMOV (*Zeitsch. anorg. Chem.*, 1914, 88, 38—48).—The production of a red colloidal solution of gold by Zsigmondy's method (A., 1898, ii, 522) is prevented by the presence of carbonic acid. The colloidal solution may also be prepared by Menz's method if carbon dioxide is removed by boiling (A., 1909, i, 133). A red colloidal solution once prepared, however, is not altered by passing a stream of carbon dioxide through it.

The potassium carbonate in the preparation may be replaced by potassium hydroxide. The first reaction is the formation of gold hydroxide, which is then converted into an aurate. The equations  $\text{HAuCl}_4 + 2\text{K}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Au}(\text{OH})_3 + 2\text{CO}_2 + 4\text{KCl}$  and



are confirmed by determinations of the quantity of carbon dioxide evolved.

Stable, red solutions may also be prepared by reducing potassium aurate with formaldehyde.  
C. H. D.

**Platinum.** A. GUTBIER, F. KRAUSS, and L. VON MÜLLER (*Chem. Zentr.*, 1914, i, 1162; from *Sitzungsber. physikal.-med. Sozi. Erlangen*, 45, 25—30).—In continuation of the previous work on substituted ammonium platinibromides (A., 1911, i, 32), the authors have investigated the corresponding alkali salts. Preparation is effected by addition of a solution of the pure alkali bromide to an aqueous solution of hydrogen platinibromide and crystallisation of the precipitates from dilute hydrobromic acid. The salts are thus readily purified, and crystallise in regular octahedra. The solubility in water and dilute hydrobromic acid decreases with increasing molecular weight. The solutions are red, and become pure yellow on dilution with water. They are readily decomposed by hydrazine hydrate with precipitation of platinum and evolution of nitrogen.

A deep carmine-red solution of pure hydrogen platinibromide is prepared by converting chemically pure platinum into the chloride, repeatedly evaporating this on the water-bath with highly concen-

trated hydrobromic acid, and then treating it similarly three or four times with hydrobromic acid containing bromine. The residue is dissolved in moderately dilute hydrobromic acid and filtered. *Ammonium platinibromide*,  $(\text{NH}_4)_2\text{PtBr}_6$ , is dark brown. The corresponding *potassium* and *rubidium* salts are dark brown and reddish-yellow respectively, and obstinately retain traces of water. The *caesium* salt is reddish-yellow.

H. W.

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### Mineralogical Chemistry.

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**Sulphur-containing Oil extracted from the Schists of Saint Champ.** DEMESSE and RÉAUBOURG (*Bull. Soc. chim.*, 1914, [iv], 15, 625—627).—Analysis of this oil gave the following results: C=77·3, H=9·2, O(by difference)=1·14, N=0·37, S=11·99%. Sulphonation and neutralisation with ammonia convert it into a mixture of sulpho-derivatives similar to those employed therapeutically under various trade names. A. J. W.

**Minerals from the Island of Nisiro (Ægean Sea).** EMANUELE GRILL (*Mem. R. Accad. Lincei*, 1914, [v], 10, 14—23).—The specimens of sulphur, hæmatite, quartz, garnet, pyroxene (diopside), spinel, and calcite here described are, like the Island of Nisiro, of volcanic origin. Octahedral hæmatite was found in homogeneous crystals, which are of uniform specific gravity and consist wholly of ferric oxide; these crystals cannot, therefore, be pseudomorphs, as is probably the case with the martite from Brazil. T. H. P.

**Minerals from the Pegmatites of Ambatofotsikely, Madagascar.** L. DUPARC, R. SABOT, and M. WUNDER (*Bull. Soc. franç. Min.*, 1914, 37, 19—30).—Spessartite (analysis I) is formed as small, brownish-yellow, transparent fragments, and as inclusions in hæmatite. Gahnite (II) as greenish-black fragments with vitreous lustre and hardness 8; regarding some of the iron as ferrous, the formula is calculated as  $90\cdot6(\text{Al}_2\text{O}_3, \text{ZnO}), 8\cdot5(\text{Al}_2\text{O}_3, \text{FeO}), 0\cdot9(\text{Fe}_2\text{O}_3, \text{MnO})$ . Ilmenite (III) as fragments with brownish-black colour and bluish-black streak; it is feebly radioactive. Red-ochre (IV), friable and compact; completely soluble in hydrochloric acid except a small, black residue. Zircon (V), a large, dark brown crystal ( $8 \times 4$  cm.). Hæmatite (VI) occurs as large plates in schists at Betaimby, prov. Mevatanana, and is remarkable in being strongly magnetic. The laterites derived from these schists are washed for gold and platinum metals, and hæmatite, together with magnetite, forms the bulk of the black residual sands. The hæmatite and magnetite were examined for gold and platinum, but with negative results:

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr.
I.	36·31	—	20·39	1·26	15·02	25·24	0·83	0·15	99·20	4·1577
II.*	—	—	54·92	4·80	—	0·33	—	—	99·91	4·6024
III.†	0·16	51·32	—	2·10	42·38	3·37	—	—	100·53	4·7106
IV.§	1·95	0·14	2·66	86·50	1·41	—	—	—	100·46	4·1698
V.‡	28·45	—	—	0·05	—	0·18	—	—	100·48	4·5884
VI.	0·25	0·83	—	99·63	0·63	trace	—	trace	101·34	5·1726

\* Also ZnO, 39·86. † Also U<sub>3</sub>O<sub>8</sub>, 0·20. § Also lost on ignition, 7·80.

‡ Also ZrO<sub>2</sub>, 71·80.

L. J. S.

**Lublinite, the Monoclinic Modification of Calcium Carbonate.** RICHARD LANG (*Jahrb. Min. Beil. Bd.*, 1914, 38, 121—184).—"Rock-milk" of a milk-white colour and with a texture resembling that of mould or cotton-wool occurs as a coating in crevices in the calcareous tufa of the Diessen valley, near Horb, in Württemberg. Under the microscope it is seen to consist of a mass of minute, capillary crystals, which are determined as monoclinic with refractive indices,  $\alpha=1·48$ ,  $\beta=1·54$ , and  $\gamma=1·66$  approximately. It has  $D=2·65$ , and the material acquires a lilac colour after treatment for about twenty minutes with cobalt nitrate solution. The following analysis shows the material to be anhydrous calcium carbonate:

CaO.	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	MgO.	Loss at 100°.	Loss on ignition.	Total.
55·60	0·19	0·19	0·10	0·04	44·02	100·14

A detailed review is given of the literature relating to the different forms of calcium carbonate (compare A., 1909, ii, 492; 1911, ii, 121), and of their different behaviour with colouring reagents. The modifications recognised are: bütschliite (amorphous), calcite (rhombohedral), aragonite (orthorhombic), vaterite (feebly birefringent), and lublinite (monoclinic).

L. J. S.

**Barthite, a Zinc Copper Arsenate from German South-West Africa.** M. HENGLEIN and W. MEIGEN (*Centr. Min.*, 1914, 353—355).—This new mineral occurs as grass-green, crystalline crusts or quartz crystals in cavities in red dolomite from Guchab, in the Otavi valley. The crystals are optically biaxial, and probably monoclinic.  $D^{25}_D=4·19$ ; hardness 3. The following analysis gives the formula:  $3\text{ZnO}·\text{CuO}·3\text{As}_2\text{O}_5·2\text{H}_2\text{O}$ , or, written as a meta-arsenate,  $3\text{Zn}(\text{AsO}_3)_2·\text{Cu}(\text{OH})_2·\text{H}_2\text{O}$ , showing the mineral to be distinct from veselyite:

CuO.	ZnO.	As <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Insol.	Total.
8·5	23·3	64·0	1·0	3·2	1·1	101·1

L. J. S.

**Augite from Bail Hill, Dumfriesshire.** ALEXANDER SCOTT (*Min. Mag.*, 1914, 17, 100—110).—Sharply developed crystals of black augite are found loosely embedded in andesitic tuffs at this locality. The crystals are simple or twinned, and show a peculiar curvature of the faces, and also "hour-glass" and zonal structures. The different sectors of the crystals show differences in optical

characters (refractive indices are given), and no doubt they differ in chemical composition, probably in the relative amounts of titanium dioxide present, since this "hour-glass" structure is typical of titanaugites. It was, however, found impracticable to separate the sectors for analysis; a bulk analysis of the crystals gave:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.
45·66	2·16	3·53	8·78	4·16	0·19	9·34	22·17
Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O > 110°.	H <sub>2</sub> O < 110°.	P <sub>2</sub> O <sub>5</sub> .	Total.	Sp. gr.	
1·50	0·26	1·37	0·61	trace	99·73	3·291	

L. J. S.

**Prehnite from Baffin Land, Arctic Canada.** ROBT. A. A. JOHNSTON (*Victoria Memorial Museum, Geol. Survey, Canada, Bull.* No. 1, 1913, 95—98).—Pale green, translucent prehnite intimately intermixed with calcite and quartz forms small veins in shale near igneous intrusives at Adams Sound on Admiralty Inlet. Analysis of material separated as far as possible from quartz gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Total.	Sp. gr.
44·35	19·44	6·58	25·50	4·00	99·87	2·924

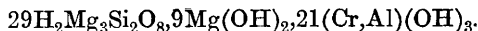
The excess of about 4·38% silica probably represents admixed quartz. On account of the high content of iron, this variety of the mineral is called *ferroprehnite*.

L. J. S.

**A New Alteration Product of Serpentine.** LAURA HEZNER (*Centr. Min.*, 1914, 386—388).—The material is an alteration product of a serpentine rich in chromite, and comes from Macedonia. In its lilac colour it resembles the Tasmanian mineral stichtite (of W. F. Petterd, 1910; compare A., 1912, ii, 1061), but it differs from this in being compact; under the microscope it is, however, seen to be scaly in texture. Analysis gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	H <sub>2</sub> O < 110°.	H <sub>2</sub> O > 110°.	CO <sub>2</sub> .	Total.
31·32	3·87	11·53	1·63	1·15	36·64	0·23	11·09	3·08	100·54

Deducting admixed carbonates and chromite, the formula suggested is:



L. J. S.

**Occurrence of Tourmaline in the Serpentine of the Urals.** L. DUPARC and H. SIGG (*Bull. Soc. franç. Min.*, 1914, 37, 14—19).—Radial aggregates of black needles and prisms of tourmaline occur embedded in serpentine near a limestone contact at Sewersky, in the Sysstert mining district, southern Urals. The antigorite, of which this serpentine is normally composed, is here replaced by chlorite with biotite and in places large plates of muscovite, the



rock being, in fact, altered by the same pneumatolytic agents which gave rise to the tourmaline. Analysis of the tourmaline gave:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
33·72	2·52	29·19	4·99	5·14	0·40	1·70	7·97
Li <sub>2</sub> O.	K <sub>2</sub> O.	Na <sub>2</sub> O.	B <sub>2</sub> O <sub>3</sub> .	F.	H <sub>2</sub> O.	Total.	
traces	0·22	1·04	8·73*	0·50	2·40	98·52	

\* Probably somewhat low.

L. J. S.

**The Mineralogical Constitution of the Shetlands of the South.** E. GURDON (*Compt. rend.*, 1914, 158, 1905—1907. Compare *ibid.*, 1914, 158, 583).—The author has made a mineralogical study of Bridgman Island, Deception Island, and Admiralty Bay in the South American Antarctic. Analyses of the following rocks have been made, and the results are quoted: (a) trachy-andesite from Deception Island; (b) the same; (c) andesite with hypersthene from Admiralty Bay; (d) andesite from Deception Island; (e) labradorite from Deception Island; (f) doleritic basalt from Deception Island; (g) labradorite with olivine from Bridgman Island:

	a.	b.	c.	d.	e.	f.	g.
SiO <sub>2</sub> .....	69·01	67·71	57·30	60·62	53·50	49·84	54·24
Al <sub>2</sub> O <sub>3</sub> .....	14·21	14·65	17·97	16·22	17·62	19·37	17·20
Fe <sub>2</sub> O <sub>3</sub> .....	2·23	1·69	2·17	1·76	2·58	3·42	2·81
FeO .....	2·89	3·29	3·79	5·67	6·07	3·69	4·98
MgO .....	0·62	0·85	2·57	1·62	4·39	4·71	5·84
CaO .....	2·11	2·34	6·72	4·18	9·22	12·35	10·19
Na <sub>2</sub> O .....	6·30	6·09	3·25	6·25	4·15	2·50	2·91
K <sub>2</sub> O .....	2·07	1·99	0·96	1·20	0·75	0·87	0·92
TiO <sub>2</sub> .....	0·58	1·00	0·56	1·54	1·65	1·32	0·91
P <sub>2</sub> O <sub>5</sub> .....	0·12	0·16	0·20	0·24	0·36	0·11	0·09
H <sub>2</sub> O .....	0·09	0·16	4·26	0·56	0·00	1·79	0·09
	100·23	99·83	99·75	99·86	100·29	99·97	100·18

W. G.

**Optically Uniaxial Augite from Mull.** A. F. HALLIMOND with an analysis by E. G. RADLEY (*Min. Mag.*, 1914, 17, 97—99).—The mineral occurs as minute phenocrysts in a dark, glassy, magnetite-bearing rock near Pennygael. It is remarkable in being practically optically uniaxial,  $\omega = 1·714$ ,  $\epsilon = 1·744$  (Na); extinction-angle on the prism cleavages,  $30\frac{1}{2}^\circ$ .  $D^{17} 3·44$ . Analysis gave:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
49·72	0·85	0·90	1·72	27·77	0·98	3·80
MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Li <sub>2</sub> O.	H <sub>2</sub> O at 105°.	H <sub>2</sub> O > 105°.	Total.
12·69	0·12	0·23	trace	0·08	1·27	100·13

L. J. S.

**Ægirite and Babingtonite.** SILVIA HILLEBRAND (*Tsch. Min. Mitt.*, 1913, 32, 247—264).—Analysis of a pure crystal of ægirite (containing not more than about 0·01% impurities) from Brevig, Norway, gave I, corresponding with a mixture of the molecules

$\text{NaFe}^{III}\text{Si}_2\text{O}_6$  (84·0%),  $\text{CaFe}^{II}\text{Si}_2\text{O}_6$  (7·3%),  $\text{CaMnSi}_2\text{O}_6$  (4·0%),  $\text{NaAlSi}_2\text{O}_6$  (3·5%), and  $\text{NaFe}^{III}\text{Ti}_2\text{O}_6$  (1·2%):

	$\text{SiO}_2$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{H}_2\text{O}$	Total	Sp. gr
I.	51·08	0·66	0·80	29·30	2·29	1·11	2·54	trace	11·50	1·04	100·32	3·558
II.*	52·57	—	—	15·03	6·61	6·62	19·85	trace	trace	—	100·68	3·351

\* Also traces of  $\text{K}_2\text{O}$ ,  $\text{Li}_2\text{O}$ .

Pure crystals of babingtonite from Arendal, Norway, gave II, corresponding with a mixture of the molecules  $\text{Ca}_2\text{Si}_3\text{O}_8$  (52·50%),  $\text{Mn}_2\text{Si}_3\text{O}_8$  (15%), and  $\text{Fe}^{II}\text{Fe}_2^{III}\text{Si}_2\text{O}_8$  (32%). The presence of the last of these molecules (analogous to anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) recalls the comparison made by Dauber in 1855 between the crystallographic constants of babingtonite and anorthite.

Both ægirite and babingtonite are only incompletely decomposed by hydrochloric acid acting during three months at 60°; determinations of the composition of the silicic acid so isolated gave no very definite results.

L. J. S.

### Analytical Chemistry.

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**Gas Analysis Apparatus.** G. WEMPE (*Chem. Zeit.*, 1914, 38, 794).—The measuring burette is connected at its upper end through a six-way tap with a series of absorption vessels; rubber connexions are not employed, all the joints being fused. The burette and absorption vessels are provided with jackets and the six-way tap with a mercury-seal; a device is fitted at the top of the gas reservoir for preventing mercury passing into the burette. W. P. S.

**Manostat for Use in Gas Analysis.** HARVEY N. GILBERT (*J. Ind. Eng. Chem.*, 1914, 6, 585—586).—In the combustion of gases confined over mercury in a pipette, the level of the mercury may be kept constant by fixing the mercury reservoir on a support carried on two pivoted parallel arms fixed to a vertical rod; a coiled spring, suspended from the upper part of the rod, is attached to an adjustable point on the lower arm, so that the vertical distance through which the support and reservoir move can be regulated to balance the height of the column of mercury which has left the pipette. W. P. S.

**The Preparation and Properties of "Lacmosol," the Sensitive Constituent of the Indicator, Lacmoid.** R. HORTINGER (*Biochem. Zeitsch.*, 1914, 65, 177—188).—The ordinary commercial preparations of lacmoid contain only about 20% of "lacmosol," which is the constituent to which the indicator owes its distinctive properties. This constituent can be prepared in the following way. Ten grams of resorcinol are heated with 2 c.c. of concentrated sodium nitrite solution for forty minutes at about 105° (but not above 110°). The product is then thrown into at least one litre of concentrated sodium chloride solution acidified with hydrochloric acid. The precipitate, after washing with concen-

trated salt solution, is purified by dissolving in ammonia and reprecipitating with acid (in concentrated salt solution). This precipitate is then dissolved in a small quantity of acetone or alcohol, and the solution thus produced is thrown into about thirty times the volume of ether. The "lacosol" remains in solution, whereas the non-essential substances are precipitated. It is soluble in ether, and can be finally purified by extraction with this solvent in a Soxhlet apparatus. The turning point of the pure indicator is far sharper than that of the ordinary preparation. It possesses a violet colour at the  $[H^+]$  concentration  $1 \times 10^{-5}$ . S. B. S.

**Picric Acid for Standardisation Purposes.** OTTO PFEIFFER (*Zeitsch. angew. Chem.*, 1914, 27, 383).—The use of pure picric acid for the standardisation of iodine and acid and alkali solutions involves in the latter case, according to Sander's method (A., 1914, ii, 482), the comparison of the picric acid solution with the mineral acid by means of a mixture of iodide and iodate, and a thiosulphate solution. Preferable to this indirect method is the standardisation of an alkali solution by direct titration with the picric acid, using dimethylaminoazobenzene as indicator. The alkali must be run into the picric acid solution, and an extremely delicate end-point is obtained by observing, not the colour of the whole solution, but the local brightening in colour which is produced by each drop of alkali solution as it falls, so long as the slightest trace of picric acid remains unneutralised. G. F. M.

**Detection of Halogens in Benzoic Acid.** E. WENDE (*Chem. Zentr.*, 1914, i, 1302; from *Apoth. Zeit.*, 1914, 29, 157).—A quantity of about 0.1 gram of the benzoic acid is heated with 0.5 gram of yellow mercury oxide; the mixture is then boiled with 10 c.c. of dilute nitric acid, filtered, and the filtrate is tested with silver nitrate solution. W. P. S.

**Effect of Ferric Salts and Nitrites on the o-Tolidine and Starch-Iodide Tests for Free Chlorine.** J. W. ELLMS and S. J. HAUSER (*J. Ind. Eng. Chem.*, 1914, 6, 553—554. Compare this vol., ii, 66).—The presence of ferric salts, nitrites, or any oxidising substance, interferes with these tests for free chlorine, the starch-iodide test being affected to the greater extent. In using the test care should be taken to ascertain that the coloration produced is due to chlorine, and not to other substances. W. P. S.

**Methods of Estimating Chlorine in Urine.** H. ROGÉE (*Chem. Zentr.*, 1914, i, 1221; from *Apoth. Zeit.*, 1914, 29, 150—151).—Of various methods examined, those described by Volhard and by Bang (estimation of the chlorine by Mohr's method after the removal of purine bases by blood charcoal) were found to be trustworthy. Mohr's method, however, yielded correct results only in the case of neutral albumin-free urines. Weisz's method, in which an apparatus called a chlorometer is used, gave low results. W. P. S.

**Detection of Iodine in Urine.** ERDMANN (*Chem. Zentr.*, 1914, i, 1221; from *Schweiz. Apoth. Zeit.*, 1914, 52, 93—94).—A method proposed by Losser, depending on the formation of yellow mercurous chloride when a urine containing iodine is treated with mercurous chloride, was found to be capable of detecting the presence of 0.01% of iodine in urine, but not 0.005%; the latter quantity, however, showed a distinct reaction when the urine was treated with chlorine water and chloroform. Barth's test for nitrates in milk (A., 1913, ii, 1069) fails in the case of milks which have been heated for a long time at 60° or higher. W. P. S.

**Physiology of the Thyroid. III. Additions to the Method of Iodine Estimation.** F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1914, 91, 392—399. Compare A., 1913, ii, 722).—Experience in the use of the method of estimating iodine in products of animal origin (*loc. cit.*) leads the authors to recommend certain procedure here described, especially in regard to the incineration of the material. R. V. S.

**Blacher's Method of Estimating the Hardness of Water.** JULIUS ZINK and FRIEDRICH HOLLANDT (*Zeitsch. angew. Chem.*, 1914, 27, 437—440. Compare A., 1908, ii, 897; 1913, ii, 982).—This method was found to be trustworthy for the estimation of hardness, and also of sulphates, in water. W. P. S.

**Disturbing Effect of Colloids in the Determination of Hardness by Clark's Method.** J. D. RUVS (*Chem. Weekblad*, 1914, 11, 599—602).—Determinations of the hardness of water containing gelatin have proved that 5—10 milligrams of this substance per litre lower the apparent hardness by about 2.5°, and 10—25 milligrams by about 7.5°. The author considers that the presence of colloids renders Clark's method wholly untrustworthy. A. J. W.

**Improvement of the Barium Sulphate Estimation of Sulphur in Soluble Sulphates when Sodium Salts are Present.** W. A. TURNER (*Amer. J. Sci.*, 1914, [iv], 38, 41—44).—The effect of sodium salts on the precipitation of barium sulphate may be eliminated by carrying out the estimation as follows: The substance, equivalent to about 1 gram of barium sulphate, is dissolved (after fusion, if necessary, with sodium carbonate and sodium peroxide) in a small quantity of water, and the solution is treated with five times its volume of concentrated hydrochloric acid. The precipitated sodium chloride is collected on an asbestos filter, washed with hydrochloric acid, and the filtrate evaporated to dryness after the addition of water. The residue is dissolved in water, 1 c.c. of 4% hydrochloric acid is added, the solution filtered, diluted to 350 c.c., heated to boiling, and a slight excess of barium chloride is added. The mixture is placed on a water-bath for some hours, and the barium sulphate is then collected and ignited at a low red heat. W. P. S.

**A Volumetric Method for the Estimation of Total Sulphur in Urine.** G. W. RAIZISS and H. DUBIN (*J. Biol. Chem.*, 1914, 18, 297—303).—The method proposed by the authors is a modification of one put forward by Benedict (*A.*, 1909, ii, 827; compare also Rosenheim and Drummond, this vol., ii, 485). After oxidation, the sulphur is precipitated as benzidine sulphate, and the benzidine in this is estimated by titration with potassium permanganate in warm acid solution. The time required for the carrying out of the new method is very much less than what is required by the original Benedict process, and it has the further advantage that much smaller amounts of sulphur may be accurately estimated.

H. W. B.

**Volumetric Estimation of Sulphates.** HORACE NORTH (*Amer. J. Pharm.*, 1914, 86, 249—256).—A modification of Hinman's barium chromate method, which enables the process to be used in the presence of the ions Li, Na, K,  $\text{NH}_4$ , Cu, Mg, Ca, Sr, Zn, Cd, Hg, Al, Ni, Co, Cl,  $\text{PO}_4$  (little),  $\text{B}_4\text{O}_7$ . Iron and chromium should be absent. The solution (about 0.16 gram of  $\text{SO}_4$ ) is placed in a 100 c.c. flask, diluted to 30 c.c., and sufficient hydrochloric acid (D 1.12) is added to have 4 c.c. of free acid present. The liquid is heated to boiling, and 20 c.c. of *N*/3-barium chloride are added; then, after again heating to boiling, 10 c.c. of *N*-potassium dichromate. After rinsing the neck with 10 c.c. of water a mixture of 15 c.c. ammonia (D 0.98) and 2 c.c. of 36% acetic acid is added drop by drop with constant shaking. After cooling, the whole is made up to the mark, and, after filtering through asbestos, 40 c.c. are titrated iodometrically for chromic acid with *N*/10-thiosulphate as usual. The difference in chromic acid found between this result and that of an experiment without addition of sulphate represents the sulphuric acid.

L. DE K.

**New Method of Estimating Thiosulphate and Sulphite in Presence of One Another and also Aluminium and Glucinum.** V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 419—427).—The method recommended by Bodnár (this vol., ii, 67) for estimating thiosulphate and sulphite, when present together, gives good results only with very small proportions of thiosulphate. The method now proposed by the author is based on the varying oxidisability of the two kinds of salts, and exhibits an accuracy of 0.25—1%.

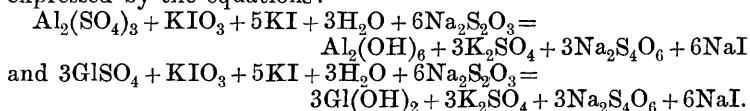
No oxidation of sodium thiosulphate occurs when its solutions are boiled for five minutes, and a current of air passed through for fifteen minutes, whereas sodium sulphite is practically completely oxidised (99%) under these conditions. In the presence of even small proportions of thiosulphate, however, the oxidation of sulphite is very considerably retarded. The author therefore uses potassium iodate as oxidising agent, the procedure being as follows.

An exact weight of 5—10 grams of the mixture is dissolved in water, and the solution carefully neutralised with 1% sodium carbonate solution and made up to 500 c.c. Of this liquid 20 c.c. are measured into each of two Erlenmeyer flasks of 250—300 c.c.

capacity, one portion being mixed with 100 c.c. of water and titrated directly with  $N/10$ -iodine solution in presence of starch. The second portion is mixed with 100 c.c. of water, 10 c.c. of 3% potassium iodate solution, and 10 c.c. of 1% potassium iodide solution, the flask being then covered with a watch-glass and left overnight (seventeen hours), and the liquid titrated with  $N/10$ -iodine solution. The volume of iodine solution employed in the second case corresponds with the amount of thiosulphate present, whilst the difference between the volumes required in the two cases gives the amount of sulphite.

When the proportion of thiosulphate present is small, this method gives accurate results for the sulphite, but low results for the thiosulphate. It is therefore advisable to heat 20 c.c. of the liquid, diluted as described above, on the water-bath for half an hour, and to titrate the cooled liquid with  $N/10$ -iodine solution. If the amount of the latter required does not exceed 0.5 c.c., the author's method for estimating the thiosulphate should be replaced by that of Bodnár (*loc. cit.*).

Experiment shows that the hydrolysis of aluminium and glucinum salts proceeds in presence of thiosulphate, and a method for estimating these salts has been devised in accordance with the reactions expressed by the equations:



A weight of the substance containing not more than 1.5 grams of  $\text{Al}_2\text{O}_3$  is dissolved in water to 500 c.c. To 10 c.c. of this solution, placed in a 250—300 c.c. Erlenmeyer flask, are added 100 c.c. of water, a mixture of 10 c.c. 3% potassium iodate solution, and 10 c.c. 1% potassium iodide solution, and, from a burette, 40 c.c. of  $N/10$ -sodium thiosulphate solution. The flask is covered with a watch-glass, and the liquid boiled for not more than five minutes; the excess of thiosulphate in the cooled liquid is then estimated by titration with  $N/10$ -iodine solution; 1 c.c. of the latter corresponds with 0.001704 gram  $\text{Al}_2\text{O}_3$  or 0.001255 gram  $\text{GlO}$ . Tests made with alum and with glucinum sulphate show that the method gives satisfactory results. When this method is applied to the analysis of clay containing free acid and admixtures, such as compounds of zinc and iron, these should be estimated and the proportion of alumina found suitably corrected: 1 c.c. of  $N/10$ -iodine solution corresponds with 0.002661 gram  $\text{Fe}_2\text{O}_3$ , 0.003592 gram  $\text{FeO}$ , 0.005086 gram  $\text{ZnO}$ , 0.001703 gram  $\text{NH}_3$ , or 0.004905 gram  $\text{H}_2\text{SO}_4$ .

T. H. P.

**Detection of Very Small Quantities of Selenious Acid in Sulphuric Acid.** ERNST SCHMIDT (*Arch. Pharm.*, 1914, 252, 161—165).—Concentrated sulphuric acid containing about 0.25% of selenious acid has long been recommended as an alkaloidal reagent, particularly for morphine and codeine, with each of which it yields a blue and finally an olive-green coloration. Meyer and

Jannek (A., 1913, ii, 788) and Meyer and von Garn (this vol., ii, 67) describe methods whereby the presence of 0.002% of selenium dioxide can be detected, but the following process will detect 0.0005% of selenious acid. One c.c. of 0.1% aqueous selenious acid is mixed with 200 c.c. of pure sulphuric acid; 10 c.c. of the mixture and 0.01 gram of codeine phosphate produce a distinct green coloration after one minute, and a bluish-green coloration after fifteen minutes. Even 1 c.c. of the mixture produces the same colour phenomena. When the dilution of the selenious acid is diminished to 0.0001% the colour reactions can be observed with sufficient sharpness against a white surface, and in comparison with a solution of about 0.01 gram of codeine phosphate in 10 c.c. of pure sulphuric acid. The preceding process is not applicable when the sulphuric acid contains iron (for example, 1 drop of ferric chloride in 10 c.c. of sulphuric acid), but is not influenced by sulphurous acid, and is only retarded, not vitiated, by the presence of tellurous acid.

C. S.

**Estimation of Nitrogen in Guncotton by means of the Nitrometer.** E. G. BECKETT (*J. Soc. Chem. Ind.*, 1914, 33, 628—631).—The ordinary nitrometer method of estimating nitrogen in guncotton (shaking with sulphuric acid and mercury) yields trustworthy results. The 111—115 c.c. of gas evolved from 0.51 gram of guncotton contain about 0.4 c.c. of carbon dioxide plus sulphur dioxide, 0.3 c.c. of carbon monoxide, and 0.6 c.c. of nitrogen; the residual sulphuric acid contains nitrogen equivalent to 0.75 c.c. of nitric oxide. The 15 c.c. of 96.5% sulphuric acid employed were found to contain about 0.4 c.c. of nitrogen gas, of which 0.35 c.c. was evolved during the estimation. The errors introduced by these impurities thus balance one another. A modified method sometimes employed, in which 1 c.c. of water is added to the 15 c.c. of sulphuric acid, gives slightly higher results than the above method, the increase in the volume of gas evolved being caused by the presence of a larger quantity of carbon dioxide plus carbon monoxide plus sulphur dioxide in the nitric oxide, and is due to the heat produced by the addition of the water to the sulphuric acid, and not to the use of more dilute acid. W. P. S.

**Estimation of Nitrogen in Norwegian Saltpetre.** N. BUSVOLD (*Chem. Zeit.*, 1914, 38, 799—800).—The method recommended consists in reducing the nitrate with Devarda's alloy in alkaline solution, and estimating the resulting ammonia by distillation. A current of air is drawn through the apparatus (distillation flask, condenser, and receiver) during the distillation, and towards the end of the operation the flame is removed, the apparatus is closed, and allowed to cool. A low pressure is thus produced, and air is then again admitted and the distillation continued for a short time. Owing to the hygroscopic properties of calcium nitrate, a large quantity of the sample should be weighed out, dissolved in a definite volume of water, and portions of this solution used for the estimation.

W. P. S.



**The Evolution of Nitrogen in the Action of Sodium Hypobromite on Carbamide in a Vacuum.** C. ALBERTO GARCIA (*Bull. Soc. chim.*, 1914, [iv], 15, 574—575).—Working with solutions of carbamide of varying concentrations the author has obtained, in all cases, almost the theoretical quantity of nitrogen evolved by the action of sodium hypobromite, provided that the reaction took place in a vacuum. He explains the low results usually obtained by this method as due to solution of a portion of the nitrogen in the water used as solvent. W. G.

**Estimation of Amino-Acid- and Polypeptide-Nitrogen in Barley, Malt, and Beer.** LUDWIG ADLER [with RUCKDESCHEL] (*Chem. Zentr.*, 1914, i, 1529; from *Zeitsch. ges. Brauwesen*, 1914, 37, 105—108, 117—121, 129—133).—Sørensen's formaldehyde method (A., 1908, 1, 115) was found to be trustworthy for the estimation of amino-acids and polypeptides in materials used in brewing; it affords a means of ascertaining the protein decomposition reactions taking place during germination and mashing of the malt. The amount of pre-formed amino-substances in malt is about 38.5% of the quantity of total soluble nitrogen; this amount increases when the malt is steeped in water. W. P. S.

**Estimation of Protein-ammonia in Water.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1914, 27, 440).—One hundred c.c. of the water are acidified with 1 drop of concentrated sulphuric acid, about 0.06 gram of potassium persulphate is added, the solution is heated on a water-bath for fifteen minutes, cooled, and treated with 5 c.c. of a mixture consisting of equal volumes of Nessler's reagent and sodium potassium tartrate solution. The coloration obtained is compared with that produced by adding a definite quantity of ammonium chloride to 100 c.c. of the water previously treated with 1 drop of sulphuric acid, 0.05 gram of potassium persulphate, and 5 c.c. of the mixed reagent. W. P. S.

**Availability of Nitrogen in Kelp.** JOHN A. CULLEN (*J. Ind. Eng. Chem.*, 1914, 6, 581—582).—In the estimation of available nitrogen in kelp trustworthy results are obtained by the alkaline permanganate method only when a quantity of the latter is employed sufficient to oxidise the whole of the organic matter present. W. P. S.

**Reactions of Nitrates with Formic Acid and the Analysis of Nitrates.** UGO MOLINARI (*Chem. Zentr.*, 1914, i, 1221—1222; from *Staz. sperim. agrar. ital.*, 1913, 47, 24—32).—The method proposed by Quartaroli (A., 1911, ii, 1085) yields the best results when 95% formic acid is used for the decomposition of nitrates and when the reaction takes place in a Schiff's nitrometer, but in no case are the results trustworthy; the results obtained with potassium nitrate are from 91.33 to 94.55% of the quantity present, and with barium nitrate from 89.97 to 92.72%. The reaction does not proceed strictly according to the equation given by Quartaroli

(*loc. cit.*); a quantity of nitric oxide is always formed, and the yield of this gas, and of the nitrous oxide and carbon dioxide, varies with the conditions of the experiment. W. P. S.

**The Factor for Calculation of the Phosphorus Content when Estimated by Neumann's Method.** WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1914, 64, 393—400).—In calculating the phosphorus content in analyses carried out by Neumann's method (A., 1903, ii, 243; 1905, ii, 68) it was found that the better results were obtained when 1 c.c. of  $N/2$ -sodium hydroxide was regarded as the equivalent of 0.565 mg. of phosphorus instead of the theoretically calculated quantity 0.553. S. B. S.

**Estimation of Phosphorus in Biological Material.** A. E. TAYLOR and C. W. MILLER (*J. Biol. Chem.*, 1914, 18, 215—224).—For the estimation of comparatively large quantities of phosphorus, such as occur in urine, a modification of Neumann's method is described, in which the ammonium phosphomolybdate precipitate is washed with alcohol by centrifugalisation before being dissolved in  $N/2$ -alkali.

Minute amounts of phosphorus of the order of 0.0002 to 0.0010 gram are best estimated by a new colorimetric method depending on the colour produced on reducing the phosphomolybdate first formed with phenylhydrazine. For details, the original paper must be consulted. With this method the authors have found that blood serum contains from 0.004 to 0.006 gram of phosphorus in lipoidal combination per 100 c.c. of serum. H. W. B.

**Detection of Phosphorus in Bones.** K. WÖRNER (*Chem. Zentr.*, 1914, i, 1605; from *Zeitsch. physikal. chem. Unterr.*, 1914, 27, 106).—The powdered bone is heated in a porcelain crucible with one-third of its weight of magnesium powder, and the resulting phosphide is detected by the liberation of phosphine when the mixture is treated with water. W. P. S.

**Estimation of Inorganic Phosphoric Acid in the Presence of the Esters of Phosphoric Acid.** WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1914, 64, 401—408).—Inorganic phosphoric acid can be precipitated as ammonium phosphomolybdate of normal composition in the presence of 4% by volume of sulphuric acid and 15% ammonium nitrate within six hours at 37°. Small concentrations of phytin do not interfere with the precipitation, whereas large quantities do. Up to a six-fold excess of phytin phosphorus and a concentration of this of about 0.05%, it is possible to obtain not less than three-quarters of the total inorganic phosphorus by Neumann's method after a single precipitation. Glycerophosphoric acid influences the precipitation to a smaller degree than does phytin. S. B. S.

**Preparation of Neutral Ammonium Citrate.** ERMON D. EASTMAN and JOEL H. HILDEBRAND (*J. Ind. Eng. Chem.*, 1914, 6, 577—580).—With the aid of the hydrogen electrode, the authors have developed an indicator method for the preparation of tri-

ammonium citrate solution. The hydrion-concentration given by solutions of this salt, D 1.09, is shown to be  $10^{-7.4}$ . Rosolic acid is used as the indicator, and this concentration is obtained by the use of an easily prepared colour standard, made by mixing hydrochloric acid and disodium hydrogen phosphate solution. W. P. S.

**Estimation of the Phosphoric Acid of Basic Slag Soluble in Citric Acid.** F. HAUSSDING (*Landw. Jahrb.*, 1913, 45, 119—126).—Whilst the direct precipitation method and Lorenz' method gave the same results with pure solutions of ammonium phosphate, the latter method gave somewhat lower results when employed with basic slags; in the case of an abnormal slag the difference was as much as 0.58%. Popp's iron citrate method might take the place of the more elaborate method of the "Verband." It is considered, however, that Lorenz' method furnishes more correct results.

N. H. J. M.

**Estimation of Carbon in Soils and Soil Extracts.** J. W. AMES and E. W. GAITHER (*J. Ind. Eng. Chem.*, 1914, 6, 561—564. Compare T., 1906, 89, 595).—The carbon present in soils is oxidised completely, and carbonates are decomposed when from 1 to 3 grams of the soil are boiled for thirty minutes with a mixture consisting of 3.3 grams of chromic acid, 10 c.c. of water, and 50 c.c. of sulphuric acid (D 1.84), provided that the soil has been ground to pass through a 60-mesh sieve. If more water is added, the results obtained are too low. Carbon may also be estimated in 1% hydrochloric acid extracts of soils and in 4% ammonia solutions of humus by means of the chromic acid and sulphuric acid mixture. The alkaline permanganate method of oxidising the carbon was found to give low results.

W. P. S.

**Analysis of Illuminating Gas by the Bunte Burette, especially the Estimation of Carbon Monoxide.** E. CZAKÓ (*Chem. Zentr.*, 1914, i, 1218; from *J. Gasbeleucht.*, 1914, 57, 169—172).—Carbon monoxide may be estimated accurately in gas by means of the Bunte burette provided that the gas is allowed to be in contact for two minutes with three successive quantities of 5 c.c. of colourless cuprous chloride solution; the gas should not be shaken with the solution. When it is desired to estimate hydrogen, methane, and nitrogen, in addition to carbon monoxide, the slow combustion method is to be preferred to the absorption process.

W. P. S.

**Condition of Carbonic Acid in the Blood. I. Method for the Estimation of Small Quantities of Carbonic Acid.** G. QUAGLIARIELLO and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 844—850).—The authors' experiments show that the sources of error in Winkler's method pointed out by Sørensen and Andersen (A., 1908, ii, 534) are negligible. They employ this method for the titration of carbonic acid, the carbon dioxide being extracted by a modification of Vesterberg's method (A., 1910, ii, 345), which

is described with a figure of the apparatus necessary, and by means of which the whole process can be carried out in the absence of air. The quantity of carbonic acid present in 1—10 c.c. of a 0.115*N*-sodium carbonate solution can be estimated with an error of 0.2—0.7%.  
R. V. S.

**The Destruction of Organic Material by the Fresenius-Babo Method, after Preliminary Treatment with Antiformin, and the Estimation of Traces of Lead in Tissues Treated by this Method.** ALEXANDER FRIEDMANN (*Zeitsch. physiol. Chem.*, 1914, 92, 46—52).—The antiformin is prepared by treating bleaching powder with sodium carbonate, filtering off the precipitated chalk, and adding sodium hydroxide. The dried, powdered tissue is covered with a 50% antiformin solution, and allowed to remain for twenty-four hours. The particles become swollen, and are then readily attacked by the chlorate and hydrochloric acid employed in the Fresenius-Babo method.

The lead in the completely oxidised liquid is precipitated as sulphide, and subsequently estimated volumetrically by Kühn's method (A., 1906, ii, 493).  
H. W. B.

**Analysis of Bronze and Brass.** RICHARD EDWIN LEE, JOHN P. TRICKEY, and WALTER H. FEGELEY (*J. Ind. Eng. Chem.*, 1914, 6, 556—560).—The following is an outline of the procedure recommended, the metals being estimated in separate portions of the alloy, with the exception of zinc, which is estimated in the filtrate from the iron if the latter is present. Lead is estimated as sulphate after the alloy has been dissolved in nitric acid in the presence of tartaric acid, whilst copper is estimated iodometrically by dissolving the alloy in nitric acid, adding potassium hydroxide solution, dissolving the cupric hydroxide in acetic acid, and adding potassium iodide. Tin and antimony are separated by treating the alloy with nitric acid, and weighed together, whilst another portion of the sample is dissolved in sulphuric acid and the solution titrated with permanganate solution in order to estimate the antimony. After heavy metals have been precipitated as sulphides, the zinc is titrated in the filtrate with ferrocyanide solution, iron, if present, having been removed previously by treating the oxidised filtrate with ammonia.  
W. P. S.

**Investigation of Pyrophoric Cerium-Iron Alloys.** HANS ARNOLD (*Zeitsch. anal. Chem.*, 1914, 53, 496—503).—The method is as follows: 0.5—1 gram of the alloy is dissolved in hydrochloric acid containing bromine, about 0.5 gram of potassium chloride is added, and the silica rendered insoluble by evaporation. After collecting the silica, 3—5 grams of tartaric acid are added to the filtrate, and the solution is then poured into 50 c.c. of concentrated ammonia. After heating to 60° 15—30 c.c. of ammonium sulphide are added drop by drop while stirring. The precipitate, which besides the iron may contain also copper and zinc, is collected and washed with warm water containing ammonium sulphide and a

little ammonia, also some ammonium tartrate; it is then burnt to oxide and weighed, and then submitted to further analysis for copper and zinc, etc.

The filtrate from the iron is evaporated in a Kjeldahl flask, and the residue evaporated with 10 c.c. of concentrated nitric acid and 2 grams of potassium chlorate, which operation is then repeated with another 10 c.c. of acid and 1 gram of potassium chlorate; this completely destroys the tartaric acid. The residue is then dissolved in acid water, and the cerium precipitated as usual with oxalic acid. After destroying the excess of oxalic acid with nitric acid, etc., and removing traces of antimony with hydrogen sulphide any alumina is recovered by precipitation with ammonia.

L. DE K.

**Microchemical Detection of Aluminium and its Distribution in the Vegetable Kingdom.** ERNST KRATZMANN (*Chem. Zentr.*, 1914, i, 1459; from *Pharm. Post*, 1914, 47, 101—102, 109—113).—Characteristic crystals of caesium alum are obtained when a drop of a solution containing an aluminium salt is mixed on a microscope slide with a drop of a reagent consisting of equal volumes of a 2 mol. caesium chloride solution and an 8 mol. sulphuric acid solution. As little as 0.001 mg. of aluminium nitrate may be detected by the test. Plant ashes may be tested directly, but the addition of sulphuric acid is recommended when much calcium carbonate is present. The crystals are also obtained when sections of plants are treated with the reagent. Aluminium is of very frequent occurrence in plants, but the "alumina grains" mentioned by Radlkofer and Wehnert as being present in the leaves of *Symplocarpeae* could be identified as aluminium compounds only in the case of *S. lanceolata* and *S. polystachya*.

W. P. S.

**Colorimetric Estimation of Small Quantities of Manganese in Water.** H. LÜHRIG (*Chem. Zeit.*, 1914, 38, 781—783. Compare (this vol., ii, 492).—Quantities of manganese amounting to less than 1 mg. per litre may be estimated accurately by treating 100 c.c. of the water with 3 c.c. of nitric acid (D 1.40) and an amount of silver nitrate more than sufficient to precipitate the chlorides present, then adding 3 grams of ammonium persulphate, and boiling the mixture for five minutes. The permanganate coloration obtained is compared with that shown by a known quantity of permanganate.

W. P. S.

**New Method of Separating Iron from Manganese.** O. HACKL (*Chem. Zentr.*, 1914, i, 1375; from *Jahrb. K. K. Geol. Reichsanstalt*, 1914, 63, 151—170).—When a neutral solution containing ferrous sulphate and manganese sulphate is boiled with the addition of potassium chlorate and zinc oxide, the iron is precipitated as basic ferric sulphate whilst the manganese remains in solution. At least 2.5 grams of potassium chlorate and 1.3 grams of zinc oxide are required for the precipitation of 0.2 gram of iron, and the volume of the solution should be 500 c.c. The basic ferric sulphate is collected on a filter, washed with cold water, and the quantity of iron then estimated volumetrically. The composition of the pre-

precipitate varies slightly according to the conditions of the precipitation.  
W. P. S.

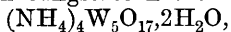
**The Analytical Examination of Tungsten.** HANS ARNOLD (*Zeitsch. anorg. Chem.*, 1914, 88, 74—87).—The methods adopted for the estimation of tungsten in ores are not suitable for the analysis of metallic tungsten. The finely powdered metal may be dissolved by a mixture of ammonia and hydrogen peroxide, or by ammonium persulphate. Coarser powders must be oxidised by alternately roasting and moistening with nitric acid. The massive metal is best dissolved electrolytically, using ammonia with a little ammonium persulphate in a platinum basin as cathode. Fragments of the metal also dissolve readily in fused potassium or sodium nitrite.

Strongly ignited tungsten trioxide is not attacked by ammonia, but if finely ground and mixed with a dilute solution of sodium carbonate, it is easily dissolved by ammonia. The ignited oxide is also dissolved if added in small quantities to hot ammonia solution.

In the analysis of tungsten an alkaline solution is mixed with tartaric acid (1 mol. to 1 mol.  $\text{WO}_3$ ), acidified with hydrochloric acid, and saturated with hydrogen sulphide whilst hot. The sulphide precipitate thus obtained is free from tungsten, but may contain some silica. Molybdenum and arsenic require special treatment in this group.

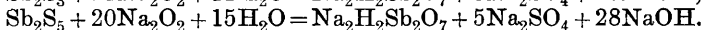
The separation of tungsten from the metals precipitated by ammonium sulphide is difficult. The benzidine precipitation (Knorre, A., 1905, ii, 286) is not quantitative. It is therefore necessary to precipitate tungstic acid by pouring the alkaline solution into boiling concentrated hydrochloric acid. The precipitate is washed with dilute acid. The filtrate contains the remaining metals, together with large quantities of alkali or ammonium salts, chiefly tartrate. It is evaporated to dryness and ignited in small quantities in a covered platinum basin. The carbon must not be completely removed, in order to prevent the oxidation of manganese.

Commercial ammonium tungstate has the formula



differing from the formula usually given, but corresponding with Werner's sodium paratungstate,  $\text{Na}_4\text{W}_5\text{O}_{17} \cdot 11\text{H}_2\text{O}$ . The minute quantities of impurities in several commercial varieties are tabulated.  
C. H. D.

**Detection of Antimony in Qualitative Inorganic Analysis.** JULIUS PETERSEN (*Zeitsch. anorg. Chem.*, 1914, 88, 108).—When antimony sulphide is warmed with water and sodium peroxide, the following reactions take place:



Sodium antimonate crystallises on cooling.

This reaction may be applied to the mixed precipitate containing sulphides of arsenic, antimony, and tin. When much tin is present, stannic oxide is precipitated, but may be removed by

filtering the boiling solution. Arsenic may be tested for after removal of antimony.

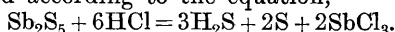
C. H. D.

**Estimation of Antimony in Minerals.** A. CAFFIN (*Mon. Sci.*, 1914, [v], 4, i, 148—149).—Two methods are commonly used. The antimony sulphide isolated in the usual manner is weighed, and the sulphur contained therein estimated by conversion into sulphate in alkaline solution by means of a current of chlorine. After acidifying with hydrochloric acid and adding also some tartaric acid, the sulphate is decomposed with barium chloride, etc. This method, although tedious, is accurate, but, according to the author, it is necessary to free the ignited barium sulphate from any carbonate (due to co-precipitated barium tartrate) by treating with weak hydrochloric acid.

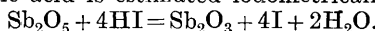
On the other hand, the process based on the electrolytic deposition of the antimony from its solution in sodium monosulphide (with addition of a little potassium cyanide or sodium sulphite) does not give, to judge from its appearance, a pure metallic deposit; in fact, the results are always too high, and the author suspects the presence of antimony hydride.

L. DE K.

**Analysis of Stibium Sulphuratum Aurantiacum.** F. LEHMANN and M. BERDAU (*Chem. Zentr.*, 1914, i, 1699—1700; from *Apoth. Zeit.*, 1914, 29, 186—187).—The principle of the proposed method is as follows: Antimony pentasulphide is decomposed by concentrated hydrochloric acid according to the equation,



The antimony trichloride is then oxidised by hydrogen peroxide, and the antimonous acid is estimated iodometrically,



A quantity of about 0.2 gram of the substance is boiled with 25 c.c. of 25% hydrochloric acid until decomposed, 10 c.c. of hydrogen peroxide solution are added, the mixture is again boiled, and filtered through glass-wool. The cold filtrate is treated with 2 grams of potassium iodide, and the liberated iodine is titrated with thio-sulphate solution. Each c.c. of *N*/10-thiosulphate solution corresponds with 0.006 gram of antimony or 0.01 gram of antimony trioxide.

W. P. S.

**Detection of Platinum with Stannous Chloride.** EGON LANGSTEIN and PAUL H. PRAUSNITZ (*Chem. Zeit.*, 1914, 38, 802).—In using the colour reaction described by Wöhler (*A.*, 1909, ii, 245) care should be taken that the solution to be tested for platinum does not contain organic substances, since these, when treated with *aqua regia* and hydrochloric acid, yield solutions giving a similar coloration to that yielded by platinum; for instance, filter-paper or the humus substances present in ores gives a coloration, under the conditions of the test, which may be mistaken for the platinum reaction. The test is trustworthy when organic substances present have been destroyed previously.

W. P. S.

**Estimation of Small Quantities of Methane in Mine Gases.** ERNST MURMANN (*Chem. Zentr.*, 1914, i, 1776; from *Österr. Chem. Zeit.*, 1914, 17, 69).—When the quantity of methane in a mine gas is less than 0.05% by vol., errors in its estimation may arise owing to the incomplete absorption of the carbon dioxide. This may be remedied by causing the inlet tubes to the absorption vessels to dip into the barium hydroxide solution; the end of the inlet tubes should also be drawn out into fine jets. With these alterations no trace of carbon dioxide will be found in the third absorption vessel.

W. P. S.

**Separation of Hydrocarbons by Liquid Sulphur Dioxide.** L. EDELEANU (*Chem. Zentr.*, 1914, i, 1785; from *Petroleum*, 1914, 9, 862—864).—Aromatic and cyclic unsaturated hydrocarbons may be estimated in petroleum distillates by shaking the latter with liquid sulphur dioxide; these hydrocarbons are soluble in the sulphur dioxide, whilst the paraffin and naphthene hydrocarbons are practically insoluble. The estimation is carried out at a temperature of  $-12^{\circ}$ , and a thick-walled graduated burette is employed.

W. P. S.

**Spindle Pycnometer, a New Instrument for the Estimation of Alcohol.** H. WÜSTENFELD and CH. FOEHR (*Chem. Zentr.*, 1914, i, 1537; from *Deut. Essigind.*, 18, 114—116, 125—127).—The use of the ordinary form of pycnometer in the estimation of alcohol is hampered by imperfect meniscus formation. To overcome this defect, Klemann has devised an apparatus which, when filled with the distillate, floats in toluene. The construction is obvious from the figure. The liquid to be investigated is poured into *a* and the height read off on the scale *b*. *c* is a glass bulb which increases the buoyancy of the apparatus. The level of filling and the floating equilibrium are determined from the graduated scale. The volume of the liquid in the spindle is determined by weighing with distilled water, the weight by immersion in toluene. The apparatus has the advantage over the weight pycnometer that determinations can be made without using the balance. Only 50 c.c. of distillate are required. The contents need not be brought to a definite mark or to normal temperature if temperature-correction tables are used. One instrument suffices for solutions containing 0—12% of alcohol. The density of toluene at different temperatures (compared with water at  $15^{\circ}$ ) has been determined:  $12.5^{\circ}$ , 0.87228;  $15^{\circ}$ , 0.87005;  $17.5^{\circ}$ , 0.86774 (0.86773);  $20.0^{\circ}$ , 0.86550 (0.86549);  $22.5^{\circ}$ , 0.86314;  $25.0^{\circ}$ , 0.86089.



H. W.

**A Colour Reaction given by Quinol in the Solid State.** MALDINEY (*Compt. rend.*, 1914, 158, 1782—1783).—On mixing together a little solid potassium carbonate and quinol a pale blue



coloration is obtained, which gradually deepens in intensity to that of Prussian blue. This colour is destroyed by water, alcohol, or ammonia, slowly by ether, and immediately by heat. Chloroform and benzene are without effect on it. The solution in water is yellow, gradually turning brown, the liquid on evaporation yielding brown crystals. The blue substance becomes brownish-black in a few hours on exposure to air. With sodium carbonate quinol gives a mauve-grey coloration, and with ammonium or lithium carbonates no coloration.

W. G.

**Influence of Atmospheric Conditions in the Testing of Sugars.** F. J. BATES and F. P. PHELPS (*J. Washington Acad. Sci.*, 1914, 4, 317—318\*).—Experiments have been made to determine the correction for the loss of water by evaporation during the filtration of raw sugar solutions under varying atmospheric conditions. The observations are satisfactorily represented by the equation  $Q = CT(P_s - P_a)$ , where  $Q$  is the change due to evaporation in time  $T$ ,  $P_s$  the vapour pressure of the sugar solution, and  $P_a$  the pressure of the water vapour in the atmosphere. If the solution is not poured back upon the filter, the change is so small as to be negligible in ordinary sugar testing. In this case the experiments gave  $C = 0.00017$ , whereas experiments in which the solution was returned to the filter gave  $C = 0.0006$ .

H. M. D.

**Estimation of Saccharine Substances in the Liver.** H. BIERRY and (Mme.) Z. GRUZEWSKA (*Compt. rend.*, 1914, 158, 1828—1830).—The total carbohydrate content of the liver is estimated as follows: Immediately after death the liver is removed, weighed, ground to pulp, and a portion (10—25 grams) weighed out and frozen with liquid air. The solid mass is ground up in a mortar, inserted in a freezing mixture, transferred to a flask with 100 c.c. of 5% hydrochloric acid, and heated in an autoclave at 120° for thirty minutes. The cold liquid is neutralised with sodium hydroxide, the protein substances precipitated with mercuric nitrate and filtered off, and the filtrate neutralised and made up to 300 c.c. In this solution the excess of mercury is eliminated by addition of zinc dust, and the sugar then estimated by the Mohr-Bertrand method. By this method and their method for estimating glycogen (compare A., 1913, ii, 160, 635) the authors have determined the amount of glycogen and total carbohydrate, both expressed as dextrose, in the livers of marmots at the end of winter, and in livers of dogs, rabbits, and chicken. In the case of the cold-blooded animal, the marmot, the glycogen and total carbohydrate content are practically equal, whereas in the case of the normal homothermic animals, the dog, rabbit, and chicken, there is always a small amount of carbohydrate in addition to the glycogen, which is present either as free sugar or as reserves other than glycogen.

W. G.

**Estimation of Sugars in Beet Molasses by Clerget's Method.** E. SAILLARD, WEHRUNG, and RUBY (*Chem. Zentr.*, 1914, i, 1781—1782; from *Mon. Sci.*, 1914, [v], 4, 232—245).—Since the ordinary Clerget

\* and *Zeitsch. Ver. Deut. Zuckerind.*, 1914, 579—596.

method yields low results, owing to the fact that the proteins in molasses exhibit a different rotation in alkaline and acid solutions, the following method is recommended for the estimation of sugars in beet molasses. Fifty-two grams of the molasses are treated with 20 c.c. of basic lead acetate solution, diluted to 200 c.c., and filtered; 100 c.c. of the filtrate are then treated with sulphur dioxide or oxalic acid to remove lead, the acid is neutralised with calcium carbonate or barium carbonate, a small quantity of animal charcoal is added, and the mixture is filtered. Fifty c.c. of the filtrate are then mixed with a quantity of sodium chloride equivalent to the amount of hydrochloric acid used for the subsequent inversion, the solution is diluted to 100 c.c., and polarised at  $20^{\circ}$  (reading =  $A$ ). Another quantity of 50 c.c. of this filtrate is then mixed with 25 c.c. of water and 6.5 c.c. of hydrochloric acid ( $D$  1.18), inverted, neutralised with sodium hydroxide, cooled to  $20^{\circ}$ , diluted to 100 c.c., and polarised (reading =  $B$ ). The percentage of sugar,  $S$ , is calculated from the formula:

$$S = \frac{200(A + B)}{\text{Coeff. of inversion} - t/2}$$

(compare A., 1912, ii, 698).

W. P. S.

**Estimation of Mannitol.** JAN SMIT (*Zeitsch. anal. Chem.*, 1914, 53, 473—490).—The processes based on the crystallisation of the mannitol, its polarimetric determination in presence of borax, and on its power of forming additive products with aldehydes are unsuitable in practice.

The process employed by Wagenaar for the estimation of glycerol (A., 1911, ii, 663) (which depends on the titration of copper hydroxide held in solution in presence of free alkali) has, however, been found useful for the estimation of mannitol. Of course, a special table had to be constructed, and interfering substances should be absent. Ammonia and also dextrose may be eliminated by heating with sodium or calcium hydroxides; sugar may also be got rid of by fermentation. Colouring matters formed may be removed by basic lead acetate, the excess of which is then in turn removed by sulphuric acid, and any lactic acid present is extracted with ether. Glycerol may be removed previously from the dry residue by extracting with a mixture of two volumes of absolute alcohol, and three volumes of ether. Amino-acids may be removed with phosphotungstic acid. Sorbitol and dulcitol, which, however, occur but rarely, interfere with the direct application of the process.

L. DE K.

**Estimation of Rhamnose in the Presence of Other Methylpentoses.** EMIL VOTOČEK and R. POTMĚŠIL (*Bull. Soc. chim.*, 1914, [iv], 15, 634—639).—Rhamnose can be estimated in presence of other methylpentoses by conversion into the corresponding nitrile, hydrolysis to  $\alpha$ -rhamnohexonic acid, and oxidation of this substance to mucic acid by the action of nitric acid. When other methylpentoses, such as rhodose, are present, the total amount of these sugars can be determined by the methylfurfuraldehyde

method, the percentage amount of those other than rhamnose being estimated by difference. A. J. W.

**Estimation of Glycogen in Yeast.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1914, 92, 75—88).—A critical examination of Euler's method (this vol., i, 635) for the estimation of glycogen in yeast. Experiments by the present author show that yeast "gum" is not destroyed by the boiling alkali employed in Euler's process, and, therefore, as it also furnishes dextrose on hydrolysis, a portion of what is assumed by Euler to be glycogen is, in reality, yeast "gum." Further experiments lead the author to conclude that, owing to the presence of other substances of a cellulose-carbohydrate nature, it is impossible separately to estimate the glycogen in yeast. H. W. B.

**Estimation of Hydrocyanic Acid and Alkali Cyanides.** G. E. F. LUNDELL and J. A. BRIDGMAN (*J. Ind. Eng. Chem.*, 1914, 6, 554—556).—The method described consists in rendering the cyanide solution slightly ammoniacal, adding a small quantity of dimethylglyoxime solution, and titrating the mixture with a standardised nickel ammonium sulphate solution; the dimethylglyoxime serves as the indicator, since no permanent red precipitate of nickel dimethylglyoxime is obtained until all the cyanide has been combined, according to the equation  $\text{NiSO}_4 + 4\text{KCN} = \text{K}_2\text{Ni}(\text{CN})_4 + \text{K}_2\text{SO}_4$ . W. P. S.

**The Insoluble Bromide Number of Oils and its Estimation.** ALEX. GEMMELL (*Analyst*, 1914, 39, 297—308).—Since the results obtained in the estimation of the insoluble bromide number of oils are influenced by various conditions of experiment, and particularly by the solubility factor, the following method of procedure is recommended as being capable of yielding trustworthy and concordant results. Five grams of the oil are saponified with alcoholic potassium hydroxide solution, the soap is dried, dissolved in 100 c.c. of water, and the fatty acids are liberated. After cooling, 30 c.c. of ether are added, the ethereal layer is separated, the aqueous portion is shaken with 20 c.c. of ether, and the whole ethereal extract is diluted with ether to 100 c.c. Twenty c.c. of this solution are then treated with 2 c.c. of glacial acetic acid, cooled in ice-water, and bromine is added. The precipitate is washed five times with cold ether, using 5 c.c. each time, then dried and weighed. It is better to work with the fatty acids, as secondary reactions take place when the glycerides are brominated directly. The precipitates obtained from the fatty acids approximate more closely in composition to the pure hexabromide (vegetable oils) or octabromide (marine animal oils) than is the case when the glycerides themselves are employed for the estimation. W. P. S.

**A New Reaction of Fats (Chromium-chrysoidine Reaction).** Fatty Substances of the Epidermal Tissue in General. LEONARDO MARTINOTTI (*Zeitsch. physiol. Chem.*, 1914, 91, 425—439).—A group of dyes belonging to the class of aminoazo-compounds

have the property of fixing fats, and, in the presence of an oxidising reagent, of making them insoluble. Chrysoidine lends itself well to this purpose, and the best oxidisers are chromic acid and the dichromates. All these substances stimulate the formation of epithelium in skin wounds. The reaction demonstrates the presence of fatty substances in the human epidermis, especially in the membranes, in keratohyalin, eleidin, and the eleidin derivatives of nail and hair.

In staining by this method, the material is fixed in 10% formaldehyde, cut by the freezing microtome, and immersed for five to ten minutes or longer in a 1% aqueous chrysoidine solution. After washing for a short time, the sections are placed in the oxidising agent (10% chromic acid or potassium dichromate) for one minute, then washed and mounted in the usual way. Detailed recommendations are made as to the choice of particular dyes and oxidising agents in the groups mentioned in order to obtain the best results with different tissues.

R. V. S.

**The Melting and Solidifying Points of Mixtures of Fatty Acids and the Use of these Points to Estimate the Composition of such Mixtures.** E. TWITCHELL (*J. Ind. Eng. Chem.*, 1914, 6, 564—569).—Whilst the lowering of the solidifying point of a pure, fatty acid caused by the addition of other fatty acids varies too much to permit the use of this method in calculating the composition of a mixture of fatty acids, the lowering of the melting point is more constant. The author has applied the melting-point method to the solid fatty acids obtained from various oils and hydrogenated oils, and gives the results of the investigation in detail. The fatty acids of cottonseed oil were found to consist of palmitic acid, 25·9%, and unsaturated acids with eighteen carbon atoms, 72·8%. The fatty acids of menhaden oil contained palmitic acid, 22·7; other solid, saturated acids, 11·8; unsaturated acids with eighteen carbon atoms, 26·7; and unsaturated acids with twenty-two carbon atoms, 20·2%.

W. P. S.

**The Estimation of  $\beta$ -Hydroxybutyric Acid.** ERNEST LAURENCE KENNAWAY (*Biochem. J.*, 1914, 8, 230—245).—A full description of work of which a preliminary account has already been given (this vol., ii, 304).

H. W. B.

**Estimation of Lactic Acid.** CHARLES G. L. WOLF (*J. Physiol.*, 1914, 48, 341—347).—It is found that the estimation of lactic acid by means of the zinc salt gives more satisfactory results than by the oxidation methods. In concentrating the fluids containing the acids, the evaporation should take place in a vacuum at as low a temperature as possible, to avoid loss of the acid. The extraction from the concentrated solution by ether is best accomplished by absorbing the solution on blotting paper (Adams' paper), and extracting in a Soxhlet apparatus for three to four hours. The proteins may be removed in a quite satisfactory manner by Schenk's reagent.

S. B. S.

**Detection of Malonic Acid.** H. J. H. FENTON (*Proc. Camb. Phil. Soc.*, 1914, 17, 477).—The substance under examination is mixed with anhydrous methyl or ethyl alcohol containing hydrochloric acid, the mixture is heated for a few minutes, then neutralised, and an alcoholic solution of bromomethylfurfuraldehyde is added. On rendering the mixture slightly alkaline with alcoholic potassium hydroxide solution, an intense blue fluorescence is obtained if malonic acid or its esters are present. The reaction appears to be characteristic of these substances, and is not given by acetoacetic and dicarboxyglutaconic esters. W. P. S.

**Examination of Iron Gallate Inks. Apparatus for the Extraction of these Inks with Ethyl Acetate.** RICHARD KEMPF (*Chem. Zentr.*, 1914, i, 1531; from *Mitt. K. Materialprüfys.-Amt. Gross Lichterfelde*, 1914, 31, 451—455).—The apparatus consists of a tall glass vessel provided with a cooling jacket; the spiral stem of a funnel extends to the bottom of the vessel, and the lower end of the stem ends in a bulb having fine perforations. The condensed solvent (ethyl acetate) from the reflux apparatus falls into the funnel, passes down the stem, and rises in the form of small drops through the acidified ink contained in the vessel; the solvent collects on the surface of the ink, and flows thence back into the extraction flask. W. P. S.

**Estimation of the Oxyproteic Acid Fraction in Normal and Pathological Urines.** REMPEI SASSA (*Biochem. Zeitsch.*, 1914, 64, 195—221).—The author has subjected to a critical experimental examination the various methods for estimating the "oxyproteic" fraction of urines (that is, the acids yielding barium salts soluble in water, but insoluble in mixtures of ether and alcohol, and giving a precipitate with mercuric acetate). He has devised a modified method, the essential point of which is that the liquid containing the soluble barium salts is evaporated to a syrup and then mixed with kieselguhr before extraction with the mixture of alcohol and ether. The "oxyproteic" nitrogen was found to vary very little in normal individuals (4.3—4.7% of the total nitrogen), whereas in cases of cachexia, including carcinomatous and phthisical patients, it was markedly increased (5—9.6%). This increase is not, however, distinctive of carcinoma, as other authors have stated. S. B. S.

**The Analysis of Essential Oils.** A. BEHAL (*Bull. Soc. chim.*, 1914, [iv], 15, 565—568).—An examination of the cause of error in the estimation of esters in essential oils by the usual method. The author finds that it is due to the formation of small amounts of ethyl esters on heating the oils with *N*/2-alcoholic potassium hydroxide. These ethyl esters, being volatile, are not condensed in the apparatus usually employed. The author has determined the loss in the case of a number of pure acetic and formic esters commonly occurring in essential oils. The loss is greater the longer is the time of contact and the smaller is the amount of

alkali used. The error can be largely eliminated by using a water reflux condenser, or, better, by working in a sealed tube at 100°.

W. G.

**Detection of Acetone in Urine.** FLEISCHMANN (*Chem. Zentr.*, 1914, i, 1784; from *Schweiz. Apoth. Zeit.*, 1914, 52, 222).—Ten c.c. of the urine are mixed in a test-tube with 1 c.c. of acetic acid and four drops of a 5% sodium nitroprusside solution; 10 c.c. of ammonia are then poured on the surface of the mixture. When acetone is present, a violet-coloured ring appears at the junction of the two liquids. Alcohol and aldehyde do not give the reaction.

W. P. S.

**Turbidity Methods for the Determination of Acetone, Acetoacetic Acid, and  $\beta$ -Hydroxybutyric Acid in Urine.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1914, 18, 263—271).—The relative turbidities of the unknown and standard solutions, after treatment with certain reagents, are measured by means of an ordinary Duboscq colorimeter, in the same way as are ordinary colour intensities.

The acetone in from 0.5 to 5 c.c. of urine is first transferred by a rapid air current into 10 c.c. of a 2% solution of sodium hydrogen sulphite, then diluted and mixed with 15 c.c. of Scott-Wilson's mercury cyanide reagent. After bringing to 100 c.c., the turbidity is compared with a similar solution prepared from a known quantity of acetone. The acetoacetic acid + acetone is similarly estimated by heating the urine during the aspiration, which converts the whole of the acid into acetone.

For the determination of  $\beta$ -hydroxybutyric acid, the urine is first boiled to expel acetone and acetoacetic acid, and then distilled with potassium dichromate and sulphuric acid, as in Shaffer's method. The acetone thus formed is then estimated by the turbidity produced by the Scott-Wilson reagent, as already indicated above. The accuracy is such that when various quantities of  $\beta$ -hydroxybutyric acid were added to urine, the quantities actually found by this method in seventeen instances were within 97 to 101% of the theory.

H. W. B.

**A Manometric Method for the Estimation of Urea (Carbamide).** WALTHER LÖB and ARTUR PROROK (*Biochem. Zeitsch.*, 1914, 65, 273—282).—The substance containing carbamide is allowed to flow into the hypobromite solution from a graduated cylinder. Both the cylinder and vessel containing the hypobromite reagent are connected with a manometer, and the whole apparatus (which consists of glass and is figured in the text) can be immersed in a thermostat. The manometer, when small quantities of carbamide only are to be estimated, can be filled with water instead of mercury. The apparatus can be calibrated with solutions of pure carbamide before use. To estimate carbamide in serum, 5—10 c.c. of this fluid will suffice when a water manometer is employed.

S. B. S.

**Creatine and Creatinine Metabolism. II. The Estimation of Creatine.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1914, 18, 191—194).—The procedure consists in evaporating the creatine solution, to which has been added about an equal bulk of normal hydrochloric acid, to dryness. This quantitatively converts amounts of creatine up to 100 milligrams into creatinine, which is then estimated colorimetrically by Folin's method. When applied to urine, a pinch or two of powdered or granulated lead must also be added to prevent the formation of pigment. The production of any turbidity in the subsequent process of estimation due to the presence of traces of dissolved lead is prevented by the addition of 5% Rochelle salt to the alkali solution employed. This process is claimed to be accurate and very rapid. H. W. B.

**Berberine and its Estimation.** ERW. RICHTER (*Arch. Pharm.*, 1914, 252, 192—205).—Picrolonic acid is a very suitable reagent for the gravimetric estimation of berberine in its salts and drugs (compare Matthes and Rammstedt, A., 1907, ii, 592). Its suitability was first tested by means of berberine chloride, the purity of which was indicated by an estimation of the water (by drying in a vacuum; compare Frerichs and Stoepel, A., 1913, i, 1094) and chlorine (found, 12.65 and 8.22% respectively). A solution of the chloride (about 0.1 gram) in 20 c.c. of water is treated in a separating funnel with 10 c.c. of 15% sodium hydroxide, and then with 60 grams of ether. After the base has dissolved completely in the ether, 40 grams of the ethereal solution are treated with 5 c.c. of approximately *N*/10-picrolonic acid, the mixture is shaken for a short time, and after about an hour the precipitated picrolonate is collected in a Gooch crucible, washed with 10 c.c. of a mixture of alcohol and ether (3:1), and dried at 110°. The percentage of berberine found is 79.32 ( $C_{20}H_{18}O_4NCl \cdot 3H_2O$  requires berberine 78.97, water 12.69, and Cl 8.34%).

Berberine in a drug or tincture is estimated as follows. The coarsely powdered drug, 2.5 grams, is completely extracted by alcohol in a Soxhlet apparatus. The alcoholic extract is freed from alcohol on the water-bath, the residue is dissolved in 15 c.c. of water, 10 c.c. of 15% sodium hydroxide and, after shaking, 60 grams of ether are added; the mixture is shaken for fifteen minutes, 1 gram of tragacanth powder is added, and the mixture is shaken until the liquid is quite clear. Twenty-four grams of the yellow ethereal solution (equivalent to 1 gram of the drug) are treated with 5 c.c. of approximately *N*/10-picrolonic acid, and the resulting precipitate is collected and treated as above. The weight multiplied by 56.1 gives the percentage of berberine in the drug.

The estimation of the berberine in a tincture is very similar to the preceding. C. S.

**Microchemical Detection of Strychnine and Brucine in the Seeds of *Strychnos Nux Vomica*.** R. WASICKY (*Chem. Zentr.*, 1914, i, 1464; from *Zeitsch. Allg. Öesterr. Apoth. Ver.*, 1914, 52, 35, 41—42, 53—55, 67—69).—Investigation of many proposed

tests showed that inorganic reagents are usually of little use in the detection of brucine and strychnine in vegetable preparations. Mayer's and Marne's reagents react only with strychnine, whilst iodine-potassium iodide gives mixed crystals of both alkaloids. Gold chloride gives a reaction which to some extent distinguishes the alkaloids from one another, and potassium ferrocyanide serves for the detection of strychnine. Picrolonic acid is the best reagent for the detection of brucine in the presence of strychnine; with strychnine it yields small, needle-shaped yellow crystals, which do not change when heated, whilst with brucine it gives a flocculent precipitate, which on warming forms clusters of rhombic, optically active crystals.

W. P. S.

**Estimation of Albumin in Urine.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1914, 18, 273—276).—Two methods are described. The "turbidity" method consists in comparing the turbidities produced by sulphosalicylic acid in the unknown and standard protein solutions, and the gravimetric method in coagulating the protein in 10 c.c. of the urine contained in a weighed centrifuge tube, washing with water and alcohol, and drying at 100° to constant weight. Both methods give approximately the same results.

H. W. B.

**Detection of Albumin and Other Proteins in Urine. Reactions of an Acetic Acid Soluble Albumin.** A. LESPINASSE (*Chem. Zentr.*, 1914, i, 1710; from *Bull. Sci. Pharmacol.*, 1914, 21, 150—156).—The presence of albumin in the urine of persons who daily take doses of quinine can only be detected by the coagulation test after the urine has been rendered slightly acid with acetic acid and treated with a small quantity of sodium chloride; the usual precipitating reagents cannot be used with such urines. Protein decomposition products may be detected in the filtrate from the albumin precipitate by means of the biuret reaction. In certain urines the author noted the presence of an albumin which was soluble in acetic acid; this albumin was precipitated by dilute acetic acid, but dissolved readily in an excess of the acid, and was not reprecipitated by nitric acid. Hot hydrochloric acid precipitated the albumin, but the precipitate dissolved in an excess of the acid, yielding a violet-coloured solution. Millon's, Tanret's, and Esbach's reagents yielded precipitates with the urine. The precipitate obtained by heating the urine with a small quantity of acetic acid did not dissolve when the mixture was boiled for twenty minutes, but when an excess of the acid was added before boiling, no precipitate was obtained. All the proteins present were precipitated on heating the urine with trichloroacetic acid, and the filtrate gave no reaction with the biuret test.

W. P. S.

**Precipitation of Lactalbumin in Cows' Milk.** W. O. WALKER and A. F. GRANT CADENHEAD (*J. Ind. Eng. Chem.*, 1914, 6, 573—574).—The following method yields more trustworthy results than does that in which the albumin is separated by heating the filtrate from the casein precipitate with acetic acid. After the casein has been



precipitated with dilute acetic acid and removed by filtration, the filtrate is neutralised with sodium hydroxide solution, one drop of 10% acetic acid is added, the solution heated to 45° and treated with a reagent consisting of 8 grams of tannin, 190 c.c. of 50% alcohol, and 8 c.c. of 25% acetic acid. The precipitate is collected after thirty minutes, and the nitrogen estimated in it by Kjeldahl's method, the factor 6.34 being used to calculate the nitrogen into albumin.

W. P. S.

**Estimation of Casein in Milk by means of the Tetraserum.** B. PFYL and R. TURNAU (*Arb. K. Gesundheitsamte.*, 1914, 47, 347—361).—The following volumetric method is proposed: 50 c.c. of the milk are treated with six drops of 1% phenolphthalein solution and titrated with  $N/10$ -alkali solution. A second quantity of 50 c.c. of the milk is then mixed in a stoppered flask with 5 c.c. of carbon tetrachloride and 1 c.c. of 20% acetic acid (the acidity of this acid must be estimated accurately), the mixture is shaken thoroughly, and filtered; 25 c.c. of the filtrate (tetraserum) are now titrated with  $N/10$ -alkali solution. From the first titration and the acidity of the acetic acid is calculated the quantity of alkali used for 25 c.c. of milk plus 0.5 c.c. of acetic acid ( $a$  c.c. of  $N/10$ -alkali solution); then, knowing the quantity of alkali solution used for the titration of the serum ( $b$  c.c. of  $N/10$ -alkali solution) and the amount of fat in the milk ( $f$  grams per 100 c.c.), the quantity of casein (grams per 100 c.c.) is calculated from the formula  $x = 0.457(a - b \cdot 99.3 - f/100)$ . By taking into account the specific gravities of the milk and the serum, slightly more accurate results may be obtained. The authors find that casein obtained from milk contains 15.5% of nitrogen, and that each gram of the protein requires 8.75 c.c. of  $N/10$ -alkali solution for neutralisation towards phenolphthalein.

W. P. S.

**A Titration Method for the Estimation of Phytin.** WOLFGANG HEUBNER and HERMANN STADLER (*Biochem. Zeitsch.*, 1914, 64, 422—437).—Phytic acid in presence of 0.6% hydrochloric acid can be estimated by titration with ferric chloride solution containing 0.05 to 0.2% of the iron salt and 0.6% hydrochloric acid, ammonium thiocyanate in 0.03% concentration (of initial volume) being employed as indicator. One mg. of iron corresponds with 1.19 mg. of phytin. The titration can be carried out in the presence of inorganic phosphates or esters of phosphoric acid, which are not precipitated in the presence of acid, provided that they are not present in too large excess over the phytin.

S. B. S.

**Method of Increasing the Sensitiveness of Telmon's Reaction for the Detection of Blood in Organic Liquids.** GEORGES RODILLON (*Chem. Zentr.*, 1914, i, 1706; from *Bull. Sci. Pharmacol.*, 1914, 21, 156—157).—This test may be rendered about one hundred times more sensitive by mixing 10 c.c. of the liquid under examination with 2 c.c. of Meyer's reagent (this must be quite colourless) and a few drops of hydrogen peroxide; from 2 to 3 c.c.

of 90% alcohol are then poured on the surface of the mixture. A red coloration appears at the junction of the two liquids if blood is present. Urine containing pus, but free from blood, gives a positive reaction with the original test; if, however, such urine be diluted until it no longer gives a reaction, and then further diluted with ten times its volume of water, the presence or absence of blood may be ascertained by means of the modified test.

W. P. S.

**Sensitiveness of the Peroxydase Reaction.** A. BACH (*Ber.*, 1914, **47**, 2122—2124).—The author has subjected the solution of peroxydase obtained from horse-radish to purification by means of ultra-filtration, for which process a simple but convenient apparatus is described. The product was much more active than that obtained by Bach and Tscherniak (*A.*, 1908, i, 746), and still more so than that described by Bach and Chodat (*A.*, 1903, i, 377).

For testing the sensitiveness of the peroxydase reaction, guaiacol is found to be the most suitable substance, on account of its relative resistance to hydrogen peroxide in the absence of a catalyst. When a mixture of 8 c.c. of a 0.1% solution of guaiacol with 1 c.c. of a 0.1% solution of hydrogen peroxide was treated with 1 c.c. of a solution containing one part by weight of dry peroxydase per 10<sup>9</sup> parts of water, a brownish-red coloration is distinctly visible after twenty minutes, and gradually deepens. D. F. T.

**Nephelometry in the Study of Nucleases.** PHILIP ADOLPH KOBER and SARA S. GRAVES (*J. Amer. Chem. Soc.*, 1914, **36**, 1304—1310).—A method is described for estimating undigested nucleic acids which consists in adding a 0.2% solution of egg-albumin, faintly acidified with acetic acid, to a dilute solution of the nucleic acid, and estimating the resulting suspensions by means of the nephelometer. The reagent is not appreciably affected by most substances met with in physiological work, and will readily detect 1 part of yeast nucleic acid in 1,000,000 parts of water.

E. G.

**The Cammidge Pancreas Reaction.** C. A. PERKELHARING and C. J. C. VAN HOOGENHUYZE (*Zeitsch. physiol. Chem.*, 1914, **91**, 151—164).—The authors' experiments indicate that this reaction (Cammidge, *British Med. Journal*, 1906, 1130) is due to animal gum or urinary dextrin present in small quantity in normal urine and in increased quantity in pathological cases, in which it is sufficient to give rise to Cammidge's reaction. This "dextrinuria" can be produced in normal persons by the administration of large quantities of sugar.

R. V. S.

**Applicability of the Dialysis Process to the Investigation of Clinical and Biological Questions.** EMIL ABDERHALDEN (*Chem. Zentr.*, 1914, i, 920; from *Münch. med. Woch.*, 1914, **61**, 233—238).—Attention is called to the various sources of error, especially as regards the dialysing membranes, as there is no material known

which is permeable to peptones but not to proteins. The proteins can also be separated by coagulation, and experiments are being made to apply the method of ultra-filtration. Another source of error is that the substrate may yield non-specific reactions. The author describes a dialysis apparatus which he uses in his experiments.

S. B. S.

**Adsorption Phenomena in Abderhalden's Dialysis Process.** F. PLAUT (*Chem. Zentr.*, 1914, i, 920; from *Münch. med. Woch.*, 1914, **61**, 238—241).—An increase of substances which can yield a positive ninhydrin reaction in the dialysate can be caused by the presence of inorganic substances like kaolin, barium sulphate, talc, and kieselguhr. It is possible that organic substances such as are used in Abderhalden's reaction have a similar effect. Such phenomena as these described may lead to erroneous results in the applications of the reactions.

S. B. S.

**The Abderhalden Reaction.** HELMUTH THAR and NINA KOTSCHEV (*Biochem. Zeitsch.*, 1914, **63**, 483—496).—The authors have directed their experiments to ascertain whether the serum of pregnant individuals really produces a degradation of the placenta proteins in accordance with Abderhalden's theory of protective ferments. They carried out a large number of experiments by means of the dialysis method, and collected together a portion of the dialysates of both sera alone (of pregnant and normal individuals) and of sera with placenta. In the collected dialysates from a large number of tests, the total and amino-nitrogen (by van Slyke's method) were estimated. In the non-pregnant cases the dialysates from the serum alone did not contain more total nitrogen and amino-nitrogen than the dialysates of sera + placenta. On the other hand, in the pregnant cases (of which the dialysates yielded a positive ninhydrin reaction, but negative reactions with the biuret and sulphosalicylic acid tests), the dialysates from the serum + placenta dialysates contained more total and amino-nitrogen than the dialysates from serum alone. This increase was not observed when the dialysis was carried out at 0°. On the other hand, experiments by the optical method, and by the estimation of amino-nitrogen when sera were allowed to act on placenta peptone, failed to reveal any difference between the actions of sera from pregnant and normal cases. The evidence that the pregnant sera contain a ferment which breaks down placenta proteins is insufficient.

S. B. S.

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## General and Physical Chemistry.

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**The Emissivity of Metals and Oxides. I. Nickel Oxide (NiO) in the Range 600° to 1300°.** G. K. BURGESS and P. D. FOOTER (*Physikal. Zeitsch.*, 1914, 15, 721—723).—The emissive capacity of nickel oxide for monochromatic red light of wave-length  $\lambda = 0.65 \mu$  has been found to decrease with rise of temperature between 700° and 1300°. From data obtained at 938°, 1058°, 1159°, and 1255°, it increases with increasing wave-length between  $\lambda = 0.5$  and  $\lambda = 0.7 \mu$ . The curves showing the relationship between the emissive capacity and the wave-length indicate the existence of a broad absorption band in the ultra-red region.

The total emission of the oxide was also measured by means of a radiation pyrometer. Between 700° and 1200° the total emission increases approximately as a linear function of the temperature, but between 1200° and 1300° the rate of increase is appreciably smaller.

H. M. D.

**Optical Properties of Yttrium Platinocyanide.** S. BOGUSLAWSKI (*Ann. Physik*, 1914, [iv], 44, 1077—1105).—The interference phenomena exhibited by sections of crystals of yttrium platinocyanide are described and explained. Measurements have also been made of the optical constants.

H. M. D.

**The Spectrum of Elementary Silicon.** SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1914, [A], 90, 512—520).—Measurements have been made of the wave-lengths of lines in the spark spectrum of silicon between  $\lambda 2124$  and  $\lambda 6371$ . In the final observations, silicon electrodes were available which contained as much as 99.56, 99.86, and 99.98% of silicon, the impurities present being titanium, iron, and aluminium. These electrodes were used in correcting the lines given by less pure samples of silicon which were employed in the earlier experiments. It is pointed out that the use of silicon electrodes is rendered difficult by the rapid formation of a coating of oxide, which causes the spark to become much less luminous. This difficulty was overcome by frequently removing the electrodes and grinding the surfaces with an emery wheel.

The wave-length numbers are compared with and discussed in reference to the data obtained by previous observers.

H. M. D.

**Ultra-red Spectra. II. A Direct Measurement of the Magnitude of Energy Quanta.** NIELS BJERRUM (*Ber. Dcut. physikal. Ges.*, 1914, 16, 640—642. Compare A., 1912, ii, 1114).—By application of the theory of quanta, it is shown that the frequency of molecular rotation can be obtained from the formula  $\nu = n \cdot h / 2\pi^2 J$ , in which  $J$  is the moment of inertia,  $n$  an integer, and  $h$  is the fundamental quantum of energy. The rotation frequencies calculated from this formula are in satisfactory agree-

ment with the values found by von Bahr (A., 1913, ii, 810) in experiments on the ultra-red absorption of hydrogen chloride. From this it follows that the energy of rotation of the hydrogen chloride molecules is represented by  $nh\nu$ , and that the same unit is involved in the changes of both rotational and vibrational energy.

H. M. D.

**Spectrum Analysis by the Secondary Rays from Rontgen Rays and its Application to the Case of Rare Substances.** MAURICE DE BROGLIE (*Compt. rend.*, 1914, 159, 304—305).—Using the method already described (compare this vol., ii, 598), the author has determined the number  $N$ , as calculated by Moseley's formula, indicating the position of the element in the periodic table, in the case of gallium and germanium, tin and antimony, and lanthanum, using rays belonging to series  $K$ . The values obtained correspond well with the positions generally assigned to these elements.

W. G.

**The Ultraviolet Spectrum of Aqueous Solutions of Nitric Acid, Metallic Nitrates, and in Particular of Copper Nitrate.** G. MASSOL and A. FAUCON (*Compt. rend.*, 1914, 159, 174—175. Compare Hartley, T., 1902, 81, 556; 1903, 83, 221).—Contrary to the results obtained by Hartley (*loc. cit.*), the authors find that copper nitrate falls into line with other metallic nitrates in giving the absorption band of nitric acid, provided that a sufficient thickness of solution is used. The band is, however, less sharply defined, an aqueous solution of copper nitrate being more transparent to the rays between  $\lambda$  3150 and 2800 than solutions of the other nitrates.

W. G.

**The Constant Presence of Rare Earths in the Scheelites, Revealed by Cathodic Phosphorescence.** CH. DE ROHLEN (*Compt. rend.*, 1914, 159, 318—320).—The author has examined a number of specimens of scheelite (calcium tungstate) under the conditions given by Urbain and Scal for fluorides (compare A., 1907, ii, 30), and has found bright and dark rays in the spectra of cathodic phosphorescence similar to those attributed by them to the rare earths. All the specimens of scheelite examined contained the rare earths, the relative proportions of these elements varying considerably from one specimen to another. All the rare elements to which this method is applicable were found in one specimen or another, and all the spectral phenomena observed could be explained by the known rare elements.

W. G.

**Ultraviolet Spectrum of Neoytterbium.** J. BLUMENFELD and G. URBAIN (*Compt. rend.*, 1914, 159, 401—405).—The authors have mapped the arc spectra of the two extreme fractions of the series of eight giving neoytterbium by the method previously described (compare this vol., ii, 731). These two spectra are identical save for a few rays in the one fraction, due to thulium, and a few in the other due to lutecium. There are five hundred rays between

the limits  $\lambda$  2300 and 3500, and these are given in a list, with their intensity appended to them. W. G.

**The Absorption of Ultraviolet Rays by the Chloro-derivatives of Methane.** G. MASSOL and A. FAUCON (*Compt. rend.*, 1914, **159**, 314—316. Compare Hartley, T., 1881, **39**, 153; Liveing and Dewar, A., 1883, 837; Martens, A., 1902, ii, 117).—The authors have examined three specimens of carbon tetrachloride having respectively b. p.  $76.2^\circ/762.4$  mm.,  $76^\circ/758$  mm.,  $76.7^\circ/760$  mm. Of these, the first two specimens gave broad absorption bands in the ultraviolet, whilst the third showed no absorption band. Specimen 2 was then submitted to fractional distillation, and a number of fractions were obtained boiling from  $61.4^\circ$  to  $76.3^\circ$ , all of which showed an absorption band. A final fraction was obtained, b. p.  $76.4^\circ/758$  mm., which gave no absorption band, and was shown to be pure carbon tetrachloride. The others contained carbon disulphide as an impurity, and this produced the absorption band.

Neither chloroform nor dichloromethane gave absorption bands in the ultra-violet. All three chloro-derivatives are colourless, and transparent to the visible and ultraviolet rays, only absorbing the rays of very short wave-length. The transparency for the latter rays diminishes as the number of chlorine atoms in the molecule increases. W. G.

**The Fluorescence Excited in Gases by Ultra-Schumann Waves.** W. STEUBING (*Physikal. Zeitsch.*, 1914, **15**, 742—744).—In a previous paper (this vol., ii, 401), Wood and Hemsalech have put forward the view that ultra-Schumann waves are emitted by the spark discharge, and that these give rise to the fluorescence of the gases in the surrounding atmosphere. The author criticises this view, and maintains that no satisfactory proof has yet been given (1) that the fluorescence spectrum is different from that of the exciting spark discharge; (2) that scattering of the light emitted by the spark discharge is eliminated by the experimental arrangement adopted by Wood and Hemsalech; and (3) that ultra-Schumann waves are actually emitted by the spark. H. M. D.

**Theories of Rotational Optical Activity.** G. BRUHAT (*Phil. Mag.*, 1914, [vi], **28**, 302—304).—A theoretical note in which the theories put forward by Drude and Lorentz on the optical rotatory power are discussed (compare also Livens, A., 1913, ii, 543). It is shown that the two theories hold equally from the point of view of the observable phenomena of anomalous rotatory dispersion and circular dichroism, and their comparison can only be made on the results expected for the dependence of the rotation on the concentration and on the nature of the solvent. Drude's theory points out that the rotatory power is independent of these two factors, whilst Lorentz's theory makes it depend on the mean index of refraction of the active medium according to the relationship  $[\omega] = k(\epsilon^2 - 1)[\alpha(\epsilon^2 - 1) + 1]$ . This theory does not therefore provide for cases like that of sucrose, in which  $[\omega]$  remains constant

at  $1/200$ , whilst the factor  $(\epsilon^2 - 1)(\epsilon^2 + 2)$  varies about  $1/3$ . The author also cites other reasons why the Drude theory is to be preferred before that of Lorentz.

J. F. S.

**Thermodynamics of Photochemical Equilibrium.** A. SCHIDLÖF (*Arch. Sci. phys. nat.*, 1914, [iv], 38, 31—35. Compare this vol., ii, 601).—A continuation of the theoretical paper previously published (*loc. cit.*). It is shown that a photochemical equilibrium is only dependent on the factor  $\nu/T$ , in which  $\nu$  is the frequency of the light and  $T$  the temperature of the reaction. A number of corrections in the equations previously published are given.

J. F. S.

**The Photochemical Properties of Coloured Resinates.** J. LARGUIER DES BANCELS (*Compt. rend.*, 1914, 159, 316—317. Compare A., 1912, ii, 882).—Coloured resinates when exposed to light slowly lose their solubility in benzene. This process is accelerated by the presence of small quantities of mineral salts. Of the chlorides and nitrates of a large number of metals tried, only those of uranium, zinc, and cadmium exert any marked influence, the effect produced being, within certain limits, proportional to the amount of active salt present. The action of uranium is much more powerful than that of zinc or cadmium, which are of the same order. To produce the same effect in the same time, the concentration of zinc or cadmium nitrates requires to be twenty times that of uranium nitrate. The results obtained with uranium and zinc salts are not due to their hydrolysis in aqueous or alcoholic solution giving an acid solution. Certain salts, such as those of copper, iron, chromium, and thorium entirely modify the properties of the resinates, rendering them insoluble, or producing a precipitation which interferes with the experiment.

W. G.

**The Magnetic Spectrum of the  $\beta$ -Rays Excited in Metals by Soft X-Rays.** H. ROBINSON and W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], 28, 277—281).—A preliminary account is given of experiments designed to throw light on the connexion between the energy of the  $\beta$ -ray and the frequency of the X-ray exciting it, which may be expected to be connected with it by the relation  $E = h\nu$ , where  $E$  is the energy,  $\nu$  the frequency, and  $h$  is Planck's constant. A nickel anticathode was employed, on account of the relative simplicity of the X-rays from this element. The elements iron and lead have so far been employed as generators of  $\beta$ -rays. The magnetic spectra of the  $\beta$ -rays consisted of bands, not lines; this is ascribed to the production of  $\beta$ -rays at different depths below the surface of the generating metal. The evidence so far obtained points to  $\beta$ -rays being generated which are characteristic both of the element forming the anticathode and of that forming the generator, but it cannot be decided yet whether the simple quantum theory will serve to explain the connexion between the complete  $\beta$ -ray spectrum and that of the X-rays.

F. S.

**Spectrum of  $\beta$ -Rays Excited by  $\gamma$ -Rays.** SIR ERNEST RUTHERFORD, H. ROBINSON, and W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], **28**, 281—286).—The investigation deals with the velocities of  $\beta$ -rays excited by penetrating  $\gamma$ -rays in various metals, principally lead, and the connexion, if any, between these velocities and those of the primary  $\beta$ -rays accompanying the  $\gamma$ -rays. A fairly thick glass tube containing radium emanation was used as the source of  $\gamma$ -rays, surrounded by a cylinder of the generating metal. A thickness of 0.14 mm. of lead or gold sufficed to obliterate the lines in the magnetic spectrum of the primary  $\beta$ -rays. The bands observed in the spectrum are due under these conditions to  $\beta$ -rays generated in the metal cylinder. They are sharply defined at the edge corresponding with the greater velocity and due to  $\beta$ -rays escaping from the outer surface, and gradually fade in intensity towards the other edge, owing to the loss of velocity of the  $\beta$ -rays which come from the interior.

The most prominent groups of  $\beta$ -rays excited in lead were compared with the strongest groups of primary rays from radium-*B*, having velocities between 0.6 and 0.8 that of light, for which an identity is to be expected on the view that radium-*B* is isotopic with lead. It was found that, within the limits of experimental error, the velocities of the  $\beta$ -rays were the same in each case.

Comparative measurements were made with cylinders of aluminium, silver, gold, and lead around the source. With the first, no groups of  $\beta$ -rays could be detected amidst the general fog; with silver, the lines were faint and difficult to measure; with lead and gold, well-marked lines of similar intensity were obtained. These lines are certainly due to the conversion into  $\beta$ -rays of some of the more penetrating  $\gamma$ -rays of radium-*B*, and their greater intensity with heavy metals is due to the much greater absorption of the  $\gamma$ -rays in these metals than in those of smaller atomic weight. With the silver, comparison with lead revealed no certain difference in the velocity of the three strong groups of rays, but the velocities of a number of the  $\beta$ -rays excited in gold were of the order of 2% higher than those given by lead. F. S.

**Excitation of  $\gamma$ -Rays by  $\beta$ -Rays.** H. RICHARDSON (*Proc. Roy. Soc.*, 1914, [A], **90**, 521—531. Compare Chadwick, A., 1912, ii, 1025).—The nature of the radiations excited when the  $\beta$ - and  $\gamma$ -rays of radium-*B* and radium-*C* impinge on different substances has been investigated with special reference to the bearing of the results on the type of radiation emitted by different metals on which radium-*C* is deposited. The experiments show that the excitation of characteristic radiations is mainly, if not entirely, due to the  $\beta$ -rays and not to the  $\gamma$ -rays. The amount of  $\gamma$ -radiation excited by the  $\alpha$ -rays of radium-*C* is negligible in comparison with that exerted by the  $\beta$ -rays.

From an examination of the radiations emitted by about twenty different elements, it is found that the only radiations excited are those which fall into the *K* and *L* groups found by Barkla. The mass-absorption coefficients for these radiations agree very well with



the numbers obtained previously by Barkla and Chapman (*Proc. Roy. Soc.*, 1912, [A], **86**, 439) for the absorption of the characteristic radiations excited by *X*-rays.

In addition to the penetrating type of radiation for which the absorption coefficient  $\mu=0.115$ , radium-*C* has been found to emit a small amount of soft radiation similar in type to that emitted by radium-*B*, and for which  $\mu=40$  (in aluminium). When radium-*C* is deposited on different metals, a soft radiation is given out which consists of the characteristic radiation of the metal excited by the  $\beta$ -rays of radium-*C*, together with the soft radiation emitted by radium-*C* itself.

H. M. D.

**The Spectrum of the Penetrating  $\gamma$ -Radiation from Radium-*B* and Radium-*C*.** SIR ERNEST RUTHERFORD and E. N. DA C. ANDRADE (*Phil. Mag.*, 1914, [vi], **28**, 263—273).—Previous results for the wave-lengths of the soft  $\gamma$ -rays ( $\mu=40(\text{cm.})^{-1}$  Al) from radium-*B* between the angles of reflection from rock-salt of  $8^\circ$  to  $16^\circ$  showed two lines at  $10^\circ$  and  $12^\circ$  corresponding with the "*L*" series for lead. By the same method the more penetrating rays,  $\mu=0.5$  of radium-*B*, and  $\mu=0.115$  of radium-*C*, have been examined, and lines found with angles of reflection from rock-salt between  $0^\circ 44'$  and  $4^\circ 22'$ , those greater than  $1^\circ 24'$  belonging mainly to radium-*B* and the others to radium-*C*. The chief lines are at  $1^\circ 0'$  and  $1^\circ 40'$ , the latter probably a close doublet,  $1^\circ 37'$  and  $1^\circ 43'$ .

A new transmission method was devised to determine these very high-frequency rays with greater accuracy, in which the cone of rays, passing normally through a rock-salt crystal on to a photographic plate beyond, was deprived by reflection of those rays striking the crystal at the reflection angle, leaving blank absorption lines on the corresponding part of the plate, whilst the reflected rays formed dark, reflected lines on another part of the plate. From the position of either the absorption or reflection line and the geometry of the arrangement, the reflection angle could be determined with considerable accuracy. The results are expressed in the following table:

Old reflection method.	New transmission method.		Mean wave-length. ( $\times 10^{-9}$ cm.).
	Absorption lines.	Reflection lines.	
$0^\circ 44'$	$0^\circ 42'$	$0^\circ 43'$	0.71
$1^\circ 0'$	$1^\circ 0'$	$1^\circ 0'$	0.99
$1^\circ 11'$	$1^\circ 10'$	$1^\circ 10'$	1.15
$1^\circ 24'$	$1^\circ 24'$	$1^\circ 25'$	1.37
{ $1^\circ 37'$	$1^\circ 37'$	$1^\circ 36'$	1.59
{ $1^\circ 44'$	$1^\circ 44'$	$1^\circ 44'$	1.69
$2^\circ 0'$	—	$2^\circ 0'$	1.96
—	$2^\circ 20'$	$2^\circ 20'$	2.29
$2^\circ 28'$	—	—	2.42
$2^\circ 40'$	—	—	2.62
$3^\circ 0'$	—	$3^\circ 0'$	2.96
$3^\circ 18'$ *	$3^\circ 18'$ *	—	3.24
$4^\circ 0'$ *	—	—	3.93
$4^\circ 22'$	—	—	4.28

\* Possibly second order.

The wave-length of the most penetrating ray,  $0.71 \times 10^{-9}$  cm., is seven times shorter than any previously measured, the "K" line of silver being  $0.56 \times 10^{-8}$  cm., and it is very surprising that the architecture of the crystal is sufficiently definite to resolve such short waves, especially when the thermal agitation of the atoms is remembered. Putting the rock-salt crystal in liquid air did not improve the definition of the lines.

The penetrating  $\gamma$ -rays from radium-B of wave-lengths 1.59 and 1.69 ( $\times 10^{-9}$  cm.) probably belong to the "K" series for lead, and their wave-lengths agree fairly with that obtained by extrapolation of Moseley's "K" series from aluminium to silver, but the strong line of radium-C, of wave-length 0.99, cannot be the "K" series line for bismuth, the wave-length of which would be only a few per cent. higher than that of lead, and probably belongs to a new series not yet observed, which may be called the "H" series.

A method is given for calculating approximate wave-lengths of  $\gamma$ -rays from the values of the absorption-coefficients,  $\mu$ , in aluminium. The "hardening" of the  $\gamma$ -rays of radium-C by passage through lead is ascribed to the weeding out of the rays of wave-lengths 0.99 and 1.15, leaving only that of wave-length 0.71.

F. S.

**X-Radiation Similar to that from Radium.** F. DESSAUER (*Physikal. Zeitsch.*, 1914, 15, 739—741).—In general the hardness of X-rays is very much less than that of  $\gamma$ -rays, the absorption-coefficients for the former being approximately from ten to eighty times as large as for the latter. An examination of the composition of X-rays has shown, however, that these contain a small proportion of extremely hard rays which resemble closely, and in fact are probably identical with, the  $\gamma$ -rays emitted by radioactive substances. The curve obtained by plotting the intensity of the X-rays as a function of the absorption-coefficient shows that the intensity falls at first very quickly, with diminution in the absorption-coefficient, but at about  $\mu = 0.4$  (in aluminium) the rate of decrease in the intensity with diminution of the absorption-coefficient becomes very much smaller. For values of  $\mu$  less than about 0.35, the curve is but very slightly inclined to the abscissa as compared with its inclination at values of  $\mu$  from 0.40 to 0.55.

This relationship indicates that X-ray tubes may possibly be utilised as a powerful source of highly penetrating  $\gamma$ -radiation, and may find application for this purpose in medicine.

The factors which exert an influence on the composition of X-rays have been systematically investigated. The proportion of highly penetrating rays is found to increase with decreasing frequency of the discharge, with increase of the potential, and with increasing current density at the cathode. The hardness also appears to increase when the temperature of the cathode rises (within certain limits) and when that of the anti-cathode falls.

H. M. D.

**The X-Ray Spectrum of Nickel.** W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], 28, 274—277).—A detailed investigation of the X-ray

spectrum of nickel, which had previously been investigated by Bragg (*Proc. Roy. Soc.*, 1913, [A], **89**, 246). The angles of reflection from crystals of rock salt, heavy-spar, and potassium ferrocyanide of the radiations from a nickel anti-cathode were measured. It is shown that the strong  $\alpha$ - and  $\beta$ -lines are close doublets, and have angles of reflection as follows:  $\alpha=17^{\circ}6'$ ,  $17^{\circ}9'6''$ ;  $\beta=15^{\circ}22'$ ,  $15^{\circ}25'$ . These lines were not completely resolved in the first-order spectrum. In addition to the strong  $\alpha$ - and  $\beta$ -lines, evidence was obtained of the existence of a series of faint lines between the  $\alpha$ - and  $\beta$ -lines. It is shown that in the case of elements belonging to the *K* series of Barkla, a very large proportion of the radiation appears to be concentrated in the  $\alpha$ - and  $\beta$ -lines. The absorption of the radiation was measured by means of two electroscopes, and it is shown that with a tube of 30,000 volts 79% of the radiation was absorbed exponentially with a value  $\mu/\rho=55.5$  in aluminium. The remaining 21% was absorbed approximately exponentially with a value of  $\mu/\rho=10.36$ . The radiation became increasingly penetrating as the voltage was raised, and on the assumption that absorption occurred exponentially, it was found that  $\mu/\rho=3.25$  at 42,000 volts and 2.54 at 51,000 volts. J. F. S.

**Velocity of Sound in Argon and the Influence of Röntgen Rays.** FRANZ STRIEDER (*Ber. Deut. physikal. Ges.*, 1914, **16**, 615–616).—The results of measurements of the velocity of sound in argon by Kundt's method indicate that this is not influenced to a measurable extent by the action of Röntgen rays on the gas. This is contrary to the results obtained by Küpper (*Ann. Physik*, 1914, [iv], **43**, 905) in experiments with polyatomic gases. H. M. D.

**The Amount of Radium and Radium Emanation Present in the Waters of Several Western Springs.** R. W. BOYLE and D. MCINTOSH (*Trans. Roy. Soc. Canada*, 1913, **7**, iii, 163).—A determination of the radioactivity of the water of the undermentioned Canadian springs by the usual methods has given the following results, expressed in millionths of a milligram of radium per litre: Sinclair, 4.0; Fairmount, 3.5; and Banff, uncertain. In all three cases traces of radium itself were also indicated. G. F. M.

**Thermionic Currents in a High Vacuum.** J. E. LILIENTHAL (*Physikal. Zeitsch.*, 1914, **15**, 744–746).—A reply to a paper with the same title by Langmuir (this vol., ii, 412), in which the author claims priority in respect of certain observations connected with thermionic currents in high vacua. H. M. D.

**Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles.** W. I. PAVLOV (*Proc. Roy. Soc.*, 1914, [A], **90**, 398–411).—The ionising properties of positive ions have been examined by a direct method. The results indicate that the positive ions emitted by heated sodium phosphate give rise to negative ions by collision with gas mole-

cules. The curves obtained by plotting the ionisation of the gas against the velocity of the positive ions are of the same form for hydrogen, oxygen, and nitrogen, and appear to approach the velocity axis asymptotically.

With a modified form of apparatus, it was found that the ionising potential for positive ions in hydrogen is about 10 volts, which is of the same order of magnitude as the ionising potential for negative corpuscles. Whereas, however, the ionisation velocity curves are straight lines when the ionisation is due to negative corpuscles, the curves are markedly convex to the velocity axis when the ionisation is brought about by positive ions.

The values obtained for the ionising potential of negative corpuscles in hydrogen and helium by Franck and Hertz (A., 1913, ii, 174) have been confirmed by a different method of measurement.

H. M. D.

**Action of a Wehnelt Cathode.** FRANK HORTON (*Phil. Mag.*, 1914, [vi], 28, 244—252).—Experiments have been carried out to determine whether the emission of electrons from lime in a Wehnelt cathode depends on the nature of the substance on which it is heated, and further experiments have been made to test the separation of calcium and oxygen by the passage of a thermionic discharge from lime, and to determine the connexion between the recombination of these elements and the electron emission. As a result of the experiments, the author comes to the conclusions: (1) That the electron emission from a Wehnelt cathode has its origin in the lime itself, and the lime does not merely serve to help the electrons to escape from the metal. (2) When an electric current passes through lime at a high temperature, the amount of oxygen liberated is only a very small fraction of what would be expected if the conductivity of the lime were entirely electrolytic. It is suggested that the conductivity is entirely electrolytic, and that the products of electrolysis diffuse through the lime and recombine. It appears unlikely, however, that such recombination should occur so rapidly and completely, through a layer of solid lime, especially as the charged oxygen atoms would be liberated on the vacuum side of the oxide layer, and with a strong electric field tending to drag them away from the cathode. (3) The chemical combination of calcium and oxygen does not by itself give rise to any detectable electron emission. From these results it appears improbable that either the theory of Fredenhagen (A., 1913, ii, 903) or that of Gehrts (A., 1913, ii, 1005) can furnish an explanation of the activity of the Wehnelt cathode.

J. F. S.

**The Ionisation of Platinum by Cathode-Rays.** NORMAN CAMPBELL (*Phil. Mag.*, 1914, [vi], 28, 286—302).—It was found that the ionisation produced by cathode-rays in falling on platinum can be very greatly reduced by prolonged heating of the metal in a vacuum or in oxygen. The heating first produces no effect, then there is a sudden large change, followed by a slow change, of

which the end is never reached. It is probable that ultimately the platinum would not be ionised at all by cathode-rays of less than 40 volts' speed. The metal can be put back into its initial state by bombardment with cathode-rays of 100 volts' speed in a pressure of gas below 0.01 mm., but mere contact of the gas or vapours does not restore it appreciably. This restored condition, however, is much less permanent than initially, and a few minutes heating, instead of a few hours, brings the sudden change.

Thus the same treatment which reduces greatly thermionic and photoelectric effects reduces also the ionisation produced at a metal surface by cathode-rays. An explanation of the effects is offered on the view that hydrogen is present in the metal in two forms, first, condensed on the surface, and, secondly, dissolved in the interior, the sudden diminution of the ionisation by heating corresponding with the abolition of the surface layer and the further gradual diminution to the progressive removal of the dissolved gas. To explain the temporary restoration of the surface by the electric discharge, recourse is had to a surface "double layer." F. S.

**The Positive Ionisation from Heated Platinum.** CHARLES SHEARD (*Phil. Mag.*, 1914, [vi], 28, 170—187).—The increase of positive thermionic currents from platinum wires in high vacua, produced either by heating the wire, earthed, to a higher temperature than that at which the ionisation is subsequently measured, or by heating it, charged to a negative potential, to a temperature sufficient to cause it to discharge negative electricity, has been re-examined in dry air at atmospheric pressure. Testing the ionisation always at 628°, and heating the wire, earthed, to various temperatures, revealed two maxima, one after previous heating at 654° and the other at 756°. Experiment showed that the negative emission from the wire when heated and charged negatively became appreciable at 760°. The results are interpreted on the theory that, on heating the wire, decomposition of a molecule *AB* occurs with production of two ions, *A* positively and *B* negatively charged, *A* being expelled or stored up, later to be expelled when an electric force is applied. At higher temperature *B* loses its electron. Various effects result in accordance with a number of possibilities, which are too numerous to be considered in an abstract. It is necessary to assume the presence of at least two substances capable of so producing ions on heating.

By heating the wire in the flame of a Bunsen burner, an increased positive emission was also obtained, probably in part due to the removal of a surface material incapable of producing ions and in part due to the hydrogen absorbed, owing to its affinity for electrons. Heating in carbon dioxide decreased, if anything, the positive emission. The decay with time of the positive currents at different temperatures showed the existence of two sources of ions, the first source decaying according to an exponential law and the second increasing to a maximum before decaying. This results in the ionisation-time curves showing a formal resemblance to the decay curves of the radium active deposit. F. S.

**Emission of Electricity from Various Substances at High Temperatures.** G. W. C. KAYE and W. F. HIGGINS (*Proc. Roy. Soc.*, 1914, [A], **90**, 430—437. Compare A., 1912, ii, 525; 1913, ii, 661).—The emission of electricity by various substances has been investigated at temperatures of 2000—2500° by experiments in a carbon-tube furnace. The effect due to the carbon was eliminated by difference measurements. The substances examined included the oxides of calcium, strontium, barium, magnesium, silicon, aluminium, and iron, and the metals tin, aluminium, iron, copper, and brass. With the exception of brass, all these substances were found to give off large quantities of negative electricity during the volatilisation which occurred at the temperature of the experiments. Without the application of any extraneous potential difference, currents of the order of 4 amperes per cm.<sup>2</sup> were obtained with barium oxide and alumina. The corresponding value for tin was 2 amperes, and for iron 1, whilst brass gave a current of 0.5 ampere in the opposite direction, indicating the emission of large quantities of positive electricity. H. M. D.

**Absorption of Gases in the Discharge Tube.** F. H. NEWMAN (*Proc. Roy. Soc.*, 1914, [A], **90**, 499—506).—Experiments have been made on the absorption of gases by the electrodes in discharge tubes, the main object being to ascertain whether there is any connexion between the amount of gas absorbed and the quantity of electricity passing during the discharge.

The liquid alloy of sodium and potassium absorbs nitrogen and hydrogen, whether used as cathode or anode, but the quantity of gas absorbed, relatively to the quantity of electricity passing, is greater when the alloy is made the cathode. Mercury behaves similarly towards oxygen. In all cases the ratio of the absorption to the quantity of electricity passing increases as the pressure of the gas in the discharge tube is reduced.

It is suggested that the gases are transformed into active modifications under the influence of the electric discharge. The active forms then enter into combination with the electrode substances. This hypothesis is supported by the fact that the known active modification of nitrogen is absorbed when passed over sodium-potassium alloy. The greater absorption which is observed when the metals are used as the cathode is probably due to the combination of the positive rays with the metal.

Experiments in which molten cadmium, zinc, bismuth, and lead were tested for absorption of nitrogen gave negative results with the ordinary discharge. H. M. D.

**Conductivity. II. Conductivity of Some Formates and of Hydrogen Chloride in (Anhydrous) Formic Acid. Cases of Apparent Agreement of Strong Electrolytes with the Mass Law.** H. I. SCHLESINGER and A. W. MARTIN (*J. Amer. Chem. Soc.*, 1914, **36**, 1589—1620).—Schlesinger and Calvert (A., 1912, ii, 26) have shown that solutions of ammonia in anhydrous formic acid are excellent conductors, and that ammonium formate,

although highly ionised, obeys the law of mass action. A study has now been made of the behaviour of sodium, potassium, and phenylammonium formates in anhydrous formic acid. Determinations of the conductivities and freezing points of hydrogen chloride in the same solvent have also been carried out.

The formates in anhydrous formic acid obey the law of mass action up to concentrations of 0.3—0.6 molar if the degree of ionisation is calculated from the conductivity values which have not been corrected for viscosity. The ionisation constants are as follows: sodium formate, 0.816; aniline formate, 0.814; potassium formate, 1.02; and ammonium formate, 1.23. The same is true of solutions of hydrogen chloride, the ionisation constant of which is only 0.04. At higher concentrations than 0.3—0.6 molar the formates show deviation from the mass law, the degree of ionisation being less than it should be. The results also indicate that the greater the value of the ionisation constant, the higher is the concentration at which the deviation begins; thus, ammonium formate begins to deviate above 0.55 molar, potassium formate at above 0.45 molar, and sodium and aniline formates at about 0.3 molar. This suggests that a relationship exists between the degree of ionisation and the volume of the non-ionised molecule.

When the conductivities are corrected for the viscosity of the solutions and the ionisation constants calculated from these corrected values, the agreement with the mass law disappears. Evidence is adduced to show that the uncorrected conductivities of these solutions should be used for the calculation of the degree of ionisation.

The results obtained by Zanninovich-Tassarini (A., 1896, ii, 352) on the conductivities and freezing-point depressions of solutions of hydrogen chloride in formic acid have been found to be incorrect.

E. G.

**The Acid Dissociation Constants of the Carbohydrates.** L. MICHAELIS (*Biochem. Zeitsch.*, 1914, 65, 360—362).—In the former series of measurements of the acid dissociation constants (Michaelis and Rona, A., 1913, ii, 379) it was found that maltose had a higher value than might have been expected. It is now shown that the preparation used was not pure. A preparation was obtained, therefore, by the slow precipitation of a saturated solution of the sugar in 70% alcohol by ether vapour. For this, the value of  $k$  found was  $9.0 \times 10^{-13}$ . This is only slightly greater than that found for the reducing mono- and di-saccharides.

S. B. S.

**Potential of Silver in Non-aqueous Solutions of Silver Nitrate.** VERNETTE L. GIBBONS and F. H. GETMAN (*J. Amer. Chem. Soc.*, 1914, 36, 1630—1655).—A résumé is given of previous work on the potentials of metals in aqueous and non-aqueous solutions of their salts, and an account is furnished of an investigation of the behaviour of silver in non-aqueous solutions of silver nitrate.

The conductivities of solutions of silver nitrate in ethyl alcohol, methyl alcohol, acetone, aniline, and pyridine have been deter-

mined for concentrations between  $0.1N$  and  $0.0001N$ . It has been found that the conductivity curve for solutions in aniline approaches a second maximum as the solutions become more dilute. The results also indicate a relationship between the dielectric constant and the normalities of all the conductivity curves. Measurements have been made of the transport numbers of silver nitrate in ethyl alcohol, methyl alcohol, and pyridine. The *E.M.F.* has been determined for a large number of concentration cells in the different solvents, and for these experiments a special form of apparatus was employed, which was free from defects due to capillarity and constant communication of the two liquids. Calculations of the electrode potential of silver gave the following values: in ethyl alcohol,  $0.8314$ ; in methyl alcohol,  $0.8298$ ; in acetone,  $0.9022$ ; and in pyridine,  $0.3711$ . The data obtained in these experiments indicate that the abnormalities observed in non-aqueous solutions of silver nitrate are due to the combination of the solvent and solute to form complex compounds which undergo gradual dissociation. E. G.

**Volta Effect and Unimolecular Layers.** J. GUYOT (*Compt. rend.*, 1914, **159**, 307—311).—The apparent potential difference at the contact of a metal and pure water diminishes notably, and may become inverted by depositing on the surface of the water very thin layers of certain insoluble organic compounds. As each drop of the latter is placed on the water the diminution effect increases, until the surface of the water is entirely covered. At this stage the surface tension is equal to that of pure water, but, on the addition of more drops, the surface tension falls rapidly, whilst the diminution in the Volta effect becomes less and less, and finally disappears. The author has measured this Volta effect in the case of a number of glycerides and their corresponding acids, esters of dibasic acids, dibasic acids, esters of monobasic acids and their corresponding alcohols, metallic salts, an aldehyde, a benzene hydrocarbon, and some aromatic hydroxy- and alkoxy-compounds. The results obtained are practically the same, whether the pure substance is used or its solution in benzene or toluene. W. G.

**Variation of Electrical Potential Across a Semi-permeable Membrane.** F. G. DONNAN and G. M. GREEN (*Proc. Roy. Soc.*, 1914, [A], **90**, 450—455).—In a previous paper (A., 1911, ii, 848) it was shown that the potential difference between two differently concentrated solutions of an electrolyte, separated by a membrane which is impermeable to the electrolyte, but permeable to the solvent, can be represented by the formula  $\pi = RT/nF \cdot \log c_1/c_2$ , in which  $c_1$  and  $c_2$  are the molar concentrations of the  $K^+$  ions of the electrolyte  $kA$ . In the derivation of this formula, it was assumed that the membrane is permeable to other salts with the same cation  $K^+$ , although impermeable to the salt  $kA$ .

Measurements have now been made of the potential difference between two differently concentrated solutions of potassium ferrocyanide, separated by a membrane of colloidal copper ferrocyanide.



In these experiments,  $1N$ -solution was combined with solutions varying from  $0.1N$  to  $0.01N$ , and in a second series a  $0.1N$ -solution was combined with solutions varying from  $0.05N$  to  $0.005N$ .

On comparing the observed potential differences with those calculated from the above formula, it is found that there is a fairly constant deviation of the order of 25% in all the measurements which involve the  $1N$ -solution. A much closer agreement is exhibited by the results for pairs of solutions in which the  $0.1N$ -solution is the stronger, although the percentage deviation increases as the ratio of the concentrations increases. When the assumptions involved in the calculation of the potential difference are taken into account, it would seem that the experimental data afford evidence of the correctness of the above formula in its application to the case investigated.

H. M. D.

**Thermodynamics of Normal Cells.** ERNST COHEN and W. D. HELDERMAN (*Chem. Weekblad*, 1914, **11**, 740—746).—A comparison of the results given by von Steinwehr in his paper on the Weston cell (this vol., ii, 622) with those previously obtained by Cohen (A., 1900, ii, 703).

A. J. W.

**Electrolytic Deposition of Metals in Valve Cells.** GÜNTHER SCHULZE (*Ann. Physik*, 1914, [iv], **44**, 1106—1120).—The action of an alternating current on the deposition of copper from a copper sulphate solution, in which a tantalum electrode is immersed, has been examined with special reference to the valve effect. When the tantalum forms the cathode, about 35% of the total copper is deposited in such a condition that it is redissolved in the succeeding phase of the current discharge when the tantalum forms the anode. The remainder separates as a fine powder, and settles at the bottom of the containing vessel. In the initial period of this phase, the soluble copper is redissolved, and the cell then ceases to transmit the current in this direction.

The proportion of soluble copper which is deposited during the passage of the current through the solution to the tantalum is practically independent of the applied potential difference, the current density (at higher densities), the concentration of the electrolyte, and the thickness of the active tantalum layer. It increases with the temperature and with diminution in the current density (at low densities), and also increases as the strength of the acid in combination with the copper decreases.

The proportion of soluble copper is influenced to a large extent by the addition of other electrolytes to the solution, this influence being determined by the valve potential of the added electrolyte. The lower this valve potential, the greater is the diminution in the quantity of deposited copper.

From experiments with solutions of the nitrates, sulphates, and acetates of the heavy metals, it has been found that the proportion of the heavy metal, which is deposited in a soluble form by the same alternating current, varies with the nature of the acid radicle, but in all three cases the numbers obtained afford a series in which the metals are arranged in the same order.

Similar phenomena are exhibited with an aluminium electrode, but the valve-action effects are not so clearly developed in this case.

H. M. D.

**Concentration Cells Built up from Ammoniacal Solutions of Silver Salts.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, **28**, 222—227).—It is shown that the *E.M.F.* of concentration cells of the type  $\text{Ag} \mid \text{ammoniacal silver chloride (1)} \mid \text{ammoniacal silver chloride (2)} \mid \text{Ag}$ , in which the two solutions have the same ammonia and different silver chloride concentrations, can be calculated from the formula  $96540E = 2v/u + v \cdot RT \cdot \log C/c$ , in which  $C$  is the silver chloride concentration in the stronger,  $c$  that in the more dilute, solution.

The *E.M.F.* of cells in which the two solutions have the same silver chloride concentration and contain different quantities of ammonia is similarly given by  $96540E = nRT \cdot \log A/a$ , in which  $A$  and  $a$  are the free ammonia concentrations of the concentrated and dilute solutions respectively, and  $n$  is the ratio of ammonia to silver in the complex silver salt in the solutions. The calculated *E.M.F.*'s are in satisfactory agreement with the experimental data recorded in the literature if it is assumed that  $n = 2$ . H. M. D.

**Indices of Migration of the Ions and the Transport of Ammonia in Ammoniacal Solutions of Silver Nitrate.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, **28**, 215—222).—Measurements of the relative mobilities of the positive and negative ions show that the proportion of the current carried by the negative ion increases somewhat when ammonia is added to an aqueous solution of silver nitrate. From experiments with solutions obtained by the addition of ammonia to silver nitrate in the molar ratios 2:1 and 1:1, it has been found that the change in the ammonia concentration at the electrodes indicates respectively the transport of somewhat less than 2 and 1 mols. of ammonia for each silver ion. It is suggested that the complex ions involved in the transport of the electric charge are those represented by the formulæ  $\text{Ag}^+, 2\text{NH}_3$  and  $\text{Ag}^+, \text{NH}_3, \text{H}_2\text{O}$ , and that the corresponding ion in pure aqueous solution is  $\text{Ag}^+, 2\text{H}_2\text{O}$ . H. M. D.

**Indices of Migration of the Ions and the Transport of Ammonia in Ammoniacal Solutions of Copper Sulphate.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, **28**, 227—229).—The relative mobilities of the ions in aqueous solutions of copper sulphate are practically unaltered on the addition of ammonia. The change in the ammonia concentration resulting from the passage of the current indicates that at least four, and possibly five, molecules of ammonia are associated with the copper ion in the ammoniacal solutions. H. M. D.

**Preparation of Alloys for Magnetic Researches.** J. DE FREUDENREICH (*Arch. Sci. phys. nat.*, 1914, [iv], **38**, 36—45).—Alloys of iron with nickel and cobalt, corresponding approximately with

the formulæ  $\text{Fe}_2\text{Ni}$  and  $\text{Fe}_2\text{Co}$ , have been prepared by melting the two metals together in a magnesite crucible in an electric resistance furnace. Attempts to prepare these alloys by the thermite process from iron oxide and the second metal gave products which contained about 2% of aluminium and 2% of silicon. Such alloys had a magnetic saturation which was considerably smaller than the correct value for the pure alloys, and since no relationships could be deduced between the magnetic saturation and the impurities, the alloys were valueless for the purpose of the author. The magnetic saturation of the ferrocobalt alloy is 10% larger than that of pure iron, whereas the alloys prepared by the thermite process were only 6.5% larger.

J. F. S.

**Magnetic Susceptibility and Electrolytic Dissociation.** A. QUARTAROLI (*Gazzetta*, 1914, **44**, ii, 43—63).—The method previously described (this vol., ii, 619) has been applied to the study of the magnetic susceptibility of a number of solutions of iron, manganese, nickel, and cobalt salts, either alone or in the presence of mannitol or ammonium chloride, citrate, or tartrate.

The results show that, although an undeniable relation exists between electrolytic dissociation and magnetic susceptibility, the latter does not depend merely on the free ions of the magnetic elements. Where complex ions are present, the susceptibility may be even greater than with the simple salts. Additional support is thus afforded by the general rule that the contribution of atoms to the physical constants of compounds is a variable dependent on the other atoms present, and probably also on the order of arrangement.

T. H. P.

**Photographic Analysis of Explosions in the Magnetic Field.** HAROLD B. DIXON, C. CAMPBELL, and W. E. SLATER (*Proc. Roy. Soc.*, 1914, [A], **90**, 506—511).—The explosion-waves in a series of gas mixtures have been photographed as the waves entered, traversed, and emerged from a magnetic field, and also when they travelled through the same tube in the absence of the magnetic field. The mixtures examined were: (1) cyanogen and oxygen with varying proportions of nitrogen; (2) hydrogen and oxygen in different proportions; (3) acetylene and oxygen; (4) carbon disulphide and oxygen; (5) carbon monoxide and oxygen. In no case do the photographs show any influence of the field on the explosion-wave phenomenon, and since the mechanism of a compression-wave affords a satisfactory explanation of the observed effects, the authors draw the conclusion that the velocity of the explosion-wave is not connected with the ionising action of electrons.

H. M. D.

**The Dilatation of Ferro-nickels over a Wide Temperature Interval.** P. CHEVENARD (*Compt. rend.*, 1914, **159**, 175—178).—A study of the dilatation and contraction of alloys of iron and nickel, varying from pure iron to pure nickel, over a temperature

range from  $-195^{\circ}$  to  $750^{\circ}$ . The difference between the linear dimensions of bars of the alloys before and after heating are a measure of the amplitude of the irreversible transformation. These differences gradually tend towards zero on passing from iron to the alloy  $\text{Fe}_3\text{Ni}$ , which is apparently the limit of irreversible alloys. The alloys between  $\text{Fe}_2\text{Ni}$  and  $\text{FeNi}_2$  have abnormal, quasi-reversible properties. For the alloy  $\text{FeNi}_2$ , the dilatation takes place according to a parabolic law between  $0^{\circ}$  and  $800^{\circ}$ .

W. G.

**Determination of the Specific Heat of Chlorine.** HERMANN SCHMIDT (*Physikal. Zeitsch.*, 1914, 15, 720).—The author refers to his previous measurements of the velocity of sound in gases, in which the position of the stationary waves in a Kundt tube was made evident by the ionisation of the gas.

H. M. D.

**Molecular Complexity at the Melting Point.** D. E. TSAKALOTOS (*J. Chim. phys.*, 1914, 12, 461—463).—A theoretical paper in which it is shown that the fatty acids mixed with water constitute binary systems which do not follow the general law put forward by Thole, Mussell and Dunstan (T., 1913, 103, 1108) that binary systems which have positive viscosity curves have also fusion curves which exhibit one or more maxima. The viscosity curves of the lower fatty acids and water are entirely positive, but the fusion curves show no maxima. The author explains the anomaly by the assumption that the molecular compounds formed between the acid and water exist only in the liquid state, and are dissociated as the mixture approaches its freezing point. An associated liquid is also considered as a binary system the constituents of which are alike, and that in certain cases the complex molecules dissociate as the freezing point is reached, in the same way as in the above-mentioned cases.

J. F. S.

**Unimolecular Layers and Superfusion.** HENRI LABROUSTE (*Compt. rend.*, 1914, 159, 306—307).—In the case of substances such as trilaurein and tribenzoin, which exhibit marked superfusion, the matter obtained by joining together unimolecular layers appears in the liquid state if the substance can exist superfused at the experimental temperature. Fused or superfused substances can be spread out on water having a temperature considerably lower than the melting point of these substances provided that the temperature of the water is higher than the lowest temperature at which it is possible to obtain the substance in the superfused state. These rules do not apply to those substances, such as camphor, which spread out spontaneously on water, even in the solid state, owing to their volatile or soluble nature.

W. G.

**An Exact Vapour Pressure Formula.** IVAR W. CEDERBERG (*Physikal. Zeitsch.*, 1914, 15, 697—705).—According to van der Waals, the relation between the vapour pressure  $p$  of a liquid and

the temperature  $T$  may be approximately represented by the formula  $\log \pi_0/p = a(\theta_0/T - 1)$ , in which  $\pi_0$  is the critical pressure,  $\theta_0$  the critical temperature, and  $a$  a constant. It has already been pointed out that  $a$  is not constant, but is a function of the temperature. For a number of substances, the curves which are obtained by plotting  $a$  as a function of  $T$  are found to be convex to the temperature axis, and approximately symmetrical with reference to a line drawn through the minimum point on the curve at right angles to the temperature axis. Where this is not the case, the curve may be made symmetrical by an alteration of the critical pressure to an extent which falls within the limits of experimental error. On the assumption that this curve is symmetrical in all cases, it is suggested that the dependence of  $a$  on the temperature is represented by  $a = \alpha \cdot \beta^{(T/\theta_0 - v)^2}$ , in which  $\alpha$  is the minimum value of  $a$ ,  $\beta$  is a constant, and  $v$  is the reduced temperature corresponding with the minimum value of  $a$ . The resulting formula,  $\log \pi_0/p = \alpha \cdot \beta^{(T/\theta_0 - v)^2} \cdot (\theta_0/T - 1)$ , is found to afford an exact representation of the vapour pressures of water and benzene from the lowest temperatures up to the respective critical temperatures.

Since the van der Waals' equation may be regarded as a special form of the reduced vapour-pressure equation  $p/\pi_0 = F(T/\theta_0)$ , it was to be expected that the constants in the above equation would, at least in part, be found to have the same value for different substances. In point of fact, the value of  $\beta$  is approximately equal to 2 and  $v$  to  $\frac{3}{4}$  for non-associated substances, and for this group of liquids the vapour-pressure formula may be simplified by the introduction of these values. The constant  $\alpha$  varies, however, from one substance to another. It is shown that  $\alpha$  is connected with the latent heat of vaporisation by means of the formula  $\alpha = \frac{3}{4} M \lambda / p(V - v)$ , in which  $M$  is the modulus of Briggs' logarithms,  $\lambda$  the molecular heat of vaporisation,  $V$  the molecular volume of the saturated vapour, and  $v$  that of the liquid at the temperature ( $v = \frac{3}{4}$ ) corresponding with the minimum value of  $a$ .

H. M. D.

**An Apparatus for Boiling-point Determination without Thermometer Correction.** THEODOR PAUL and KARL SCHANTZ (*Ber.*, 1914, **47**, 2285—2288).—An apparatus is described embodying the principles of Beckmann's boiling-point apparatus and Kahlbaum's still-head; the condenser can, by rotating, be moved from a reflux position to one for direct distillation. Without disconnecting the apparatus in any way, it is therefore possible to determine the boiling point of a mixture first at constant composition and then during distillation. For details the original paper should be consulted.

D. F. T.

**Advantageous Form of Still for the Exact Measurement of Boiling Point during Fractional Distillation.** THEODORE W. RICHARDS and FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1914, **36**, 1787—1791).—Apparatus is described which has been devised for

the exact determination of boiling points. Its essential feature is that the whole stem of the thermometer is maintained at the temperature of the vapour, and the boiling point of the actual distillate can thus be accurately ascertained.

It consists of a flask and a wide tube held parallel to the neck, and connected with the latter by two side-tubes at the top and bottom. The upper side-tube, which forms the exit tube for the vapour, is joined to the upper end of the neck of the flask. The lower side-tube, which serves to return the prematurely condensed liquid to the flask, is a constricted continuation of the end of the wide tube; it is bent into the form of a shallow U, and fused into the neck of the flask at a point a few cm. above the bulb. The wide tube is open at the top, where it is so constricted as to receive and hold closely a Beckmann thermometer at a point near the zero mark. The thermometer can be made to fit without grinding, as a liquid seal will collect at this point and prevent the escape of vapour, but for use with hygroscopic liquids a ground joint must be employed. The wide tube and upper connecting tube are encased in a thick shell of asbestos.

In a second form of the apparatus, suitable for use with small Anschütz thermometers, the upper end of the wide tube is fitted with a glass stopper provided with a hook, from which the thermometer can be suspended.

The apparatus is of simple construction, efficient, and convenient in use, and can be easily cleaned. E. G.

**Theory of the Fractional Distillation of Mixtures of Water and Alcohol.** E. CHENARD (*Bull. Soc. chim.*, 1914, [iv], 15, 646—649).—A study of the conditions governing fractionation by condensation, which requires, as essential, the continuous removal of the condensed liquid from contact with the vapours producing it. The apparatus consisted of an unpolished copper tube 35 cm. long and 1 cm. internal diameter, bent slightly downwards and fitted midway with a tube for collecting the condensed liquid and exhausting the apparatus. A thermometer at each end of the tube gave the temperatures between which condensation occurred. The ratio of condensed liquid ( $p$ ) to the total weight of vapour ( $P$ ) passing through the tube varied with the velocity of flow of the vapour through the tube. This ratio,  $p/P$ , was higher with a low velocity, as was also the ratio of condensed alcohol to total alcohol. W. G.

**Laboratory Fractionating Apparatus.** HENRI VIGREUX (*Bull. Soc. chim.*, 1914, [iv], 15, 682—685. Compare Hildt, this vol., ii, 103).—A comparison of the effectiveness of the Chenard and Vigreux fractionating columns for separating such mixtures as water and alcohol or benzene and toluene by fractional distillation. Length for length, the Vigreux column is far more efficient than the Chenard. W. G.

**Heat of Formation of Solid Solutions.** H. W. FOOTE and BLAIR SAXTON (*J. Amer. Chem. Soc.*, 1914, **36**, 1704—1708).—An account is given of determinations of the heats of solid solution of sodium chlorate in silver chlorate, and of silver chlorate in sodium chlorate. The method employed consisted in determining the heats of solution in water of the mixed crystals and of mechanical mixtures of the same empirical composition. The difference between these two values gives the heat of formation of the mixed crystals from the single salts. Four samples of mixed crystals were prepared by means of Foote's data (A., 1892, ii, 453). Two of the samples were on the sodium chlorate side, and crystallised as cubes, whilst the other two contained an excess of silver chlorate and were tetragonal.

The results show that both the molecular heats of formation of the solid solutions are small and of opposite sign. The values for the isometric crystals are almost constant, showing that there is little or no heat of dilution, but those for the tetragonal crystals show a small variation, indicating that in this case there is a small heat of dilution. The amount of silver chlorate which can be taken up by sodium chlorate to form mixed crystals increases with the temperature, and the process is accompanied by absorption of heat, whereas in the case of the tetragonal crystals the reverse is true. In the relation of the heat of solution to the temperature-coefficient of solubility, Le Chatelier's law is therefore applicable to solid solutions as well as to solutions of other types. E. G.

**A Regularity between Molecular Heat of Combustion and its Bearing on the Constitution of the Hydrocarbons.** GERVAISE LE BAS (*Chem. News*, 1914, **110**, 26—27, 37—38).—The molecular heat of combustion of gaseous, liquid, and solid paraffins is proportional to the number of valency units in the hydrocarbon molecule. From the data for the gaseous paraffins this ratio is equal to 26·5, which is regarded as the effective combustion value of the hydrogen atom. The effective combustion value for combined carbon is therefore  $4 \times 26\cdot5 = 106\cdot0$ . In the case of the olefines and acetylenes, the observed heats of combustion are greater than those calculated from the effective heat values of carbon and hydrogen, the differences corresponding with the double and triple bonds being +15·8 and +44·3 cal. respectively.

The heats of combustion of *cyclopropane* and *cyclobutane* are also greater than the calculated values to the extent of 15·3 and 18·0 cal., whilst for *cyclopentane* and *cyclohexane* the observed and calculated values are in satisfactory agreement. It is supposed that this corresponds with the stability of the various ring systems.

The data for benzene and its derivatives indicate that these are saturated compounds, whilst *cyclohexadiene* and *cyclohexene* behave like unsaturated hydrocarbons. The fact that benzene behaves like a saturated hydrocarbon on combustion is discussed

with reference to the question of its constitution. Since no double bonds are present, it is suggested that the unsaturation is distributed uniformly between all the carbon atoms in the molecule as represented by the formula



H. M. D.

**Calculation of Constants for the Heats of Combustion of Hydrocarbons.** H. STANLEY REDGROVE (*Chem. News*, 1914, 110, 73—74).—Polemical. The method of procedure, adopted by Le Bas (preceding abstract) in deducing constants from the heats of combustion of the hydrocarbons, is subjected to criticism. The relation between the heat of combustion of the saturated hydrocarbons and the valency number, according to which the constant for carbon is exactly four times the constant for hydrogen, is, in the author's opinion, accidental in character. If a general relationship were involved, it would hold for compounds containing other elements, which is not the case.

H. M. D.

**Heat of Vaporisation of Normal Liquids.** JAMES KENDALL (*J. Amer. Chem. Soc.*, 1914, 36, 1620—1630).—The accuracy of the various equations which have been proposed for representing the variation of heat of vaporisation with temperature has been tested by comparison with the experimental results obtained for octane, methyl butyrate, carbon tetrachloride, and fluorobenzene by Young. For the first three compounds, the author's equation (this vol., ii, 101) and that of Mills (*A.*, 1907, ii, 226) show the best agreement with Young's figures, whilst in the case of fluorobenzene the experimental results are shown to be inaccurate.

It is pointed out that no conclusions can be drawn as to the relative theoretical merits of the different formulæ, and that at present they are merely of service as checks on the experimental data.

E. G.

**Influence of Temperature on the Density and Electrical Conductivity of Aqueous Salt Solutions.** II. HEINRICH CLAUSEN (*Ann. Physik*, 1914, [iv], 44, 1067—1076. Compare *A.*, 1912, ii, 119).—The density and electrical conductivity of aqueous solutions of rubidium chloride, bromide, iodide, nitrate, and sulphate, and also of caesium chloride, have been measured at 6°, 18°, and 30°. The experimental data are interpreted in accordance with the views put forward by Heydweiller (*A.*, 1910, ii, 106; 1912, ii, 433), and afford further support for the theory that the difference in the density of solution and solvent is determined by coefficients characteristic of the ionised and non-ionised molecules.

H. M. D.



**Electrical Conductivity and Viscosity of Solutions of Sodium Iodide and Potassium Iodide in Mixtures of Ethyl Alcohol and Water.** E. P. WIGHTMAN, P. B. DAVIS, A. HOLMES, and HARRY C. JONES (*J. Chim. phys.*, 1914, 12, 385—427).—The viscosity and fluidity of  $N/8$ -solutions of sodium iodide and potassium iodide in ethyl alcohol, and in mixtures of ethyl alcohol and water from 100—0%, have been determined at temperatures 15°, 25°, and 35°. Conductivity determinations have been made of  $N/8$ - and  $N/128$ -solutions of potassium iodide in alcohol-water mixtures from 0·0—96·09% alcohol at 20°, and a further series of  $N/8$ ,  $N/32$ ,  $N/128$ , and  $N/1024$  in similar alcohol-water mixtures at the same temperature. There is a slight increase in the viscosity of alcohol-water mixtures when sodium iodide or potassium iodide is dissolved in them to form a  $N/8$ -solution in all cases from 100% alcohol to 60% alcohol; below this concentration there is a slight diminution in the viscosity. On elevation of temperature, the point where the fluidity curve of the solution cuts that of the solvent is displaced, and the displacement is to be attributed to a change in the association of the solvent. The change in the association is greater for water than for alcohol. The viscosity changes are to be explained by the theory previously put forward by Jones and his collaborators (A., 1906, ii, 737). A continuous diminution in the electrical conductivity of solutions of potassium iodide and sodium iodide occurs on passing from pure water to pure alcohol, the diminution being most noticeable in those solutions containing a high percentage of water, and least noticeable in those containing a small percentage of water. This is probably to be explained by the fact that the association of alcohol is changed only very slightly by the addition of small quantities of water, whilst the association of water is strongly affected by the addition of small quantities of alcohol. Since viscosity and association are closely connected, it is to be taken that the same explanation will apply to the viscosity changes, or, to express it differently, in mixtures of alcohol and water there is a far larger change in the viscosity of the water than in that of the alcohol. The decrease in the conductivity of potassium iodide with increase in the percentage of alcohol is more rapid than the corresponding decrease for sodium iodide in the same solvents, due, no doubt, to the greater atomic volume of the potassium iodide (compare Jones and Veazey, A., 1907, ii, 438; 1908, ii, 259, 260). Hydration has practically no influence on the conductivity at any temperature, however; with the elevation of temperature the dissociation of feebly hydrated ions produces a slight increase in the temperature-coefficient of most solutions containing water. Alcohol solutions have temperature-coefficients which are linear functions, and consequently indicate that no "alcoholation" has occurred. The conductivity curves, which appear to be non-symmetrical, become symmetrical if they are prolonged up to 100%, and then they form symmetrical curves with the point of symmetry at 80% alcohol instead of 50%. On raising the temperature, the curves tend to become linear functions, which is to be attributed to the fact that

under similar conditions the fluidity curves also tend to become linear. J. F. S.

**Stalagmometric Estimations of Small Hydroxyl Ion Concentrations.** JULIUS GRÖH and IRENE D. GÖTZ (*Biochem. Zeitsch.*, 1914, **66**, 165—172).—By means of a Donnan stalagmometer, the surface tension at the interface of a solution of 0.25% stearic acid and aqueous solutions of alkalis was measured. It was found that a calibration curve could be obtained for concentrations of pure sodium hydroxide solutions between the concentrations  $2 \cdot 10^{-4}$  and  $25 \cdot 10^{-4}$  *N*. The method is more sensitive when the alkaline solution contains neutral salts (for example, potassium chloride in about 0.3*N* concentration). In this case measurements could be made over the range of  $5 \cdot 10^{-5}$  to  $6 \cdot 10^{-4}$  *N*. The method is still more sensitive when the hydroxyl ions arise from the hydrolytic dissociation of weak salts, when concentrations of OH ions to  $2 \cdot 10^{-7}$  *N* affect the tension at the interface. It was found, however, that it was not possible to employ the changes in the tensions at the interfaces to determine the hydrolysis constant, owing to disturbing influences (possibly adsorption phenomena).

S. B. S.

**Stalagmometric Studies of Solutions of Colloids and Crystalloids. V. The Relationship between Physiological and Physico-chemical Action of Neutral Salts.** L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 173—190).—Capillary-active substances, such as ethyl alcohol, phenol, thymol, menthol, camphor, quinol,  $\alpha$ -naphthol, sodium glycocholate, albumose, and caseinogen, lower the surface tension of water more in the presence than in the absence of salts when the solutions are not saturated with the substances. These phenomena run parallel with the physiological activities of the substances. The surface tensions of the salt solutions saturated with these substances are, however, not smaller than those of the salt-free solutions. The surface tension of saturated ammonium sulphate solution is not lowered by thymol, camphor, menthol, or glycocholic acid. The various phenomena are best explained on the assumption of hydrate formation by salts.

S. B. S.

**Stalagmometric Studies of Solutions of Colloids and Crystalloids. VI. The Action of Phenol on the Surface Tension of Protein Solutions.** L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 191—201).—The surface tension of solutions of serum, various proteins, peptones, and ereptone are lowered more by phenol than is that of pure water. The same phenomenon is shown by *p*-cresol and chloral hydrate, but not by ethyl alcohol, propyl alcohol, triacetin, and camphor. This lowering is not caused by the concentration at the surface of the phenol, but by that of the protein. The diminution of the bactericidal activity of phenol by serum, as observed by Ehrlich and Bechhold, can be explained by means of the surface-tension theory. S. B. S.

**Stalagmometric Studies of Solutions of Colloids and Crystalloids. VII. Pharmacological Activity and the Lowering of Surface Tensions.** L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 202—206).—The measurements of the surface tensions of a number of phenol solutions show the general relationship between the capacity of substances to lower the surface tension of water and their pharmacological action as indicated by Traube and others. S. B. S.

**Stalagmometric Studies of Solutions of Colloids and Crystalloids. VIII. Some Complexes of Protein and Starch with other Colloids.** L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 207—217).—Soaps diminish the surface tension of water less in the presence of proteins than in their absence. The effect of the proteins is increased if the mixtures are kept some time before the stalagmometric measurements are made. Similar phenomena were observed with starch solutions, and with mixtures of albumoses and peptones with proteins. The results are explained on the assumption of the formation of colloidal complexes. Bile salts are bound by proteins, but not by starch. S. B. S.

**Stalagmometric Studies of Solutions of Colloids and Crystalloids. IX. Colloidal Complexes of Cholesterol.** L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 218—224).—The stalagmometric measurements indicate the formation of colloidal complexes in soap-cholesterol and soap-protein mixtures, which change with changing hydroxyl ion concentration. A complex, but not quite similar to these, is formed with lecithin and cholesterol. No evidence of a complex between saponin and cholesterol could be obtained. S. B. S.

**Stalagmometric Studies of Solutions of Colloids and Crystalloids. X. The Action of Certain Narcotics on Lecithin Solutions.** L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 225—230).—Narcotics increase the surface tension of lecithin solutions. After narcosis, the surface tension of the urine is often lowered by non-volatile products. S. B. S.

**The Adsorption Isotherm in the Region of very Small Concentrations.** G. TRÜMLER (*Kolloid. Zeitsch.*, 1914, **15**, 10—18).—The question of the validity of the exponential adsorption formula at very small concentrations has been examined by experiments on the adsorption of fluorescein from aqueous solution by animal charcoal. The concentration of the fluorescein was determined spectrophotometrically in the case of the more concentrated solutions (0.05—0.0005 gram per litre), and by measurement of the intensity of the fluorescence in the case of the more dilute solutions (0.0005—0.000005 gram per litre).

From observations on the rate of adsorption, it was found that the initial stage in which the fluorescein is rapidly absorbed is succeeded by a period of relatively slow fall in the concentration

of the fluorescein solution. No definite condition of equilibrium was attainable, and on this account the experiments were arranged so as to afford a measure of the initial rapid absorption. This method of procedure is justified by the probability that the slow absorption is due to a secondary change not directly connected with the true adsorption.

The experimental results are in satisfactory agreement with the requirements of the formula  $x = a \cdot c^n$  if  $a = 0.25$  and  $n = 0.18$ . It would thus appear that there is no measurable lower limit of concentration at which the exponential formula loses its validity as a means of expressing the adsorption from solution. H. M. D.

**Dissociation of Hydrogen into Atoms. I.** IRVING LANGMUIR and G. M. J. MACKAY (*J. Amer. Chem. Soc.*, 1914, **36**, 1708—1722).—In earlier papers (A., 1912, ii, 231, 826, 1162) it has been shown that hydrogen, particularly at low pressures, is readily dissociated into atoms by metallic wires at very high temperatures. It has now been found, however, that there is good reason for suspecting that the actual values recorded for the degree of dissociation are much too high, and this was thought to be due to an incorrect assumption as to the diffusion-coefficient of hydrogen atoms through molecular hydrogen.

Experiments have therefore been carried out by methods which do not necessitate any assumption as to the magnitude of the diffusion-coefficient. Single-loop filaments of pure tungsten wire were mounted in large, cylindrical lamp-bulbs. The temperatures were determined by means of the relation  $T = 11230/7.029 - \log H$ , where  $H$  is the intrinsic brilliancy of the filament in international candle-power per sq. cm. of projected area. On this scale, the m. p. of tungsten is  $3540^\circ$  (abs. temp.), which is regarded as more probable than the lower values usually assigned to it. The temperatures were also determined by measuring the resistance, and also by matching the colour of the emitted light against that of a standard provided with a blue screen. The three methods nearly always gave concordant results.

Measurements have been made of the total losses of heat from tungsten wires in hydrogen at pressures ranging from 10 mm. up to ordinary atmospheric pressure, and also at very low pressures from 0.01 to 0.2 mm. Experiments have also been made with nitrogen in order to compare the loss of heat in this gas with that in hydrogen.

The results obtained show a striking difference in the effects in the two gases. In the case of nitrogen, the values for the power consumption decrease steadily at all temperatures as the pressure is reduced, and in hydrogen at temperatures up to  $1500$ — $1700^\circ$  a similar decrease occurs. At higher temperatures in hydrogen, however, the power consumption is much greater at low pressures than at atmospheric pressure. At very high temperatures, that part of the loss of heat which depends on the dissociation of the hydrogen increases very rapidly, and becomes 50 or 100 times as large as the possible experimental error. E. G.

**Osmotic Data in Relation to Progressive Hydration.** W. R. BOUSFIELD (*Proc. Roy. Soc.*, 1914, [A], **90**, 544—548).—A theoretical paper in which it is shown that the formula connecting the osmotic pressure with the vapour-pressure lowering of a solution may be deduced on the basis of a definition of osmotic pressure which does not permit of the assumption that this varies with hydrostatic pressure. The expressions given previously for the osmotic data in terms of progressive hydration (T., 1914, **105**, 609) can now be written in the simpler and more accurate form

$$P/R'T = \Delta/F' = \delta p/p = i/h - n,$$

in which  $P$  is the osmotic pressure in atmospheres,  $\Delta$  the freezing-point lowering,  $\delta p/p$  the relative lowering of the vapour pressure,  $h$  the total number of molecules of water per molecule of solute,  $n$  the number of molecules of water combined with one molecule of solute, and  $i$  is the ionisation factor. The values of the constants are  $R' = 4.557$  and  $F' = 103.6$ .  
H. M. D.

**Attempt at a Physical Explanation of the Semipermeability of Living Cells to Ions.** PIERRE GIRARD (*Compt. rend.*, 1914, **159**, 376—379).—If between an acid solution of barium chloride and pure water, each containing an electrode, a goldbeater skin 0.1 mm. in thickness intervenes, chlorine diffuses through into the water five times faster than the barium. If, on the other hand, an alkaline solution of barium chloride is used, it is the barium which diffuses the faster. If the thickness of the membrane is increased to 0.5 mm., the passage of the two ions equalise one another. In the system electrode-acid solution of barium chloride-water-electrode, the algebraic sum of the differences of potential is equal to +0.075 volt. The interposition of the thin membrane between the water and the barium chloride inverts the sign of the sum of the potential differences, and it becomes equal to -0.025 volt, this inversion favouring the passage of the chlorine ions. The author considers that it is this state of polarisation of the membrane which gives it its relative semipermeability, this being relative only on account of the progressive lowering of the state of polarisation. He is of the opinion that the above process is analogous to that which takes place in living cells. W. G.

**The Most Simple Method of Crystallographic Description.** E. VON FEDEROV (*Zeitsch. Kryst. Min.*, 1914, **54**, 17—45).—For many years the author has been endeavouring to perfect a system whereby the crystalline form of a substance may be made to serve for its identification. In the course of this work, the difficulties incidental to the measurement of crystals, and the recording of the data necessary for their complete description, have been reduced to a minimum. The usual method of describing crystals is held to be very inconvenient, and such descriptions often contain numerous errors.

A special universal goniometer, designed for rapid rather than specially accurate work, is described. The necessary angles are measured with this instrument, and from them a gnomostereo-

graphic projection is made upon a specially prepared diagram. By the method of zonal calculation, involving the employment of bipolar spherical co-ordinates, all other angles on the crystal can be calculated by simple addition or subtraction of natural co-tangents. The author appeals to crystallographers to employ his method of description in order to facilitate the tabulation of data for his tables for crystallochemical analysis. E. H. R.

**The Theoretical and Experimental Investigation of Crystal Structure.** P. GROTH (*Zeitsch. Kryst. Min.*, 1914, **54**, 65—73).—A historical sketch of the development of the modern theory of crystal structure is given, followed by a description of the recent work of W. H. Bragg and W. L. Bragg, and a discussion of their results. It must now be concluded that molecules as such do not exist in crystals, but only in amorphous substances. Barlow and Pope came to the same conclusion in an entirely different manner. Polymorphism can no longer be explained by the difference in size between the molecules of the two modifications. Among other important questions which now arise is that of the difference between chemical and physical isomerides. In future, the "topic parameters" will be replaced by the actual dimensions of the space-unit of the crystal. E. H. R.

**Chemical Significance of Crystalline Form.** WILLIAM BARLOW and WILLIAM JACKSON POPE (*J. Amer. Chem. Soc.*, 1914, **36**, 1675—1686, 1694—1695).—The authors reply to the objections raised by Richards (A., 1913, ii, 483) to their views on the relationship between crystal structure and chemical constitution, and point out that their method of quantitative treatment for the elucidation of this relationship has proved so fertile in co-ordinating chemistry and crystallography as to be incapable of being affected by such adverse criticism. E. G.

**Further Remarks Concerning the Chemical Significance of Crystalline Form.** THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1914, **36**, 1686—1694).—A reply to Barlow and Pope (preceding abstract). E. G.

**An Association of Crystals of Unlike Symmetry.** A. DUFFOUR (*Compt. rend.*, 1914, **159**, 260—263).—A study of mixed crystals of the isodimorphous dichromates of potassium and ammonium. From solutions containing less than 65% of ammonium salt, triclinic crystals, similar to those of the potassium salt, separate; when this proportion is exceeded, monoclinic crystals are formed, isomorphous with the ammonium salt, together with an unstable form of the potassium salt. From a solution containing 60% of ammonium dichromate, monoclinic crystals are first deposited. Subsequently, triclinic crystals grow upon the former, which themselves gradually disappear. From the regular manner in which the triclinic crystals become orientated upon the monoclinic variety, the author is led to modify the axial ratios of the

triclinic potassium salt. There is now seen to be a close morphotropic resemblance between the two kinds of crystal, which would account for the regular manner of growth of the one upon the other.

E. H. R.

**Mixed Crystals of Ammonium Chloride with Manganese Chloride.** H. W. FOOTE and BLAIR SAXTON (*J. Amer. Chem. Soc.*, 1914, **36**, 1695—1704).—Although several investigators have studied the products which are formed when mixed solutions of ammonium and manganese chlorides are allowed to crystallise, the extent of mixed crystal formation and the conditions under which mixed crystals are produced instead of double salts have not hitherto been determined.

A study of this subject has now been carried out by the solubility method employed by Foote (A., 1912, ii, 847) in investigating the mixed crystals of ammonium chloride with nickel and cobalt chlorides. Determinations have been made of the solubility of various mixtures of ammonium and manganese chlorides at 25°, and both the residues and solutions have been analysed.

The results show that ammonium chloride and the double salt  $2\text{NH}_4\text{Cl} \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$  (Saunders, A., 1892, 781) form two series of mixed crystals,  $\alpha$  and  $\beta$ , there being a gap between the limiting composition of each type. An investigation of the heats of formation of the mixed crystals has shown that that of the  $\beta$ -crystals is positive, whilst that of the  $\alpha$ -crystals is negative. The  $\beta$ -crystals are to be regarded as a solid solution of ammonium chloride in the double salt, and the  $\alpha$ -crystals as a solid solution of the double salt in ammonium chloride.

E. G.

**Reversible Transformation of Emulsoid Solutions of Gum Arabic and Gelatin into the Suspensoid Condition and the Properties of these Systems.** O. SCARPA (*Kolloid. Zeitsch.*, 1914, **15**, 8—10).—When ethyl alcohol is added gradually to an aqueous solution containing about 2% of gum arabic or gelatin, the liquid becomes opalescent, and ultramicroscopic observation indicates that the emulsoid has been transformed into a suspensoid. The change in question is reversible.

The colloidal particles of the suspensoid system move towards the positive pole in an electrical field, indicating that both gum arabic and gelatin are electro-negative colloids. The suspensoid solution of gum arabic is coagulated on the addition of most salts, acids, and bases, but a perfectly clear, non-opalescent solution is obtained by the addition of mercuric chloride. The opalescent solutions of gelatin are precipitated by mercuric chloride, copper sulphate, and ferric chloride, but most other electrolytes convert the suspensoid into an optically clear solution. The coagulation is in most cases reversible, and this holds also for the product which separates at the positive pole when an electric field is applied.

H. M. D.

**Adsorption, Imbibition, and Osmotic Pressure of Colloids.** M. POLÁNYI (*Biochem. Zeitsch.*, 1914, **66**, 258—268).—By means of a

thermodynamic cycle, the following relationships were deduced. When a gel is in equilibrium with a solution,  $u = c/RT \cdot d\pi/dc$ , where  $u$  is the amount of the dissolved substance concentrated in the gel,  $c$  the concentration of the solution,  $\pi$  the imbibition pressure of the gel, and  $R$  and  $T$  have the ordinary significance. The statement that has often been made, but not verified, that substances which favour imbibition are positively adsorbed, whereas those which inhibit imbibition are negatively adsorbed, is a strict law if certain premises are made. Such premises are fulfilled when the separation of the adsorbed substance can take place continuously, and the adsorption process is a reversible one. Accepting the same premises, substances which increase the osmotic pressure of colloids are positively adsorbed by the colloids, whereas those which diminish the osmotic pressure are negatively adsorbed. The following equation expresses the relation of a colloid to the solution,  $v' = c/RT \cdot dp/dc$ , where  $v'$  is the concentration of the substance in the colloid and  $p$  the osmotic pressure of the colloidal solution.

S. B. S.

**Contraction Phenomena.** RAPHAEL ED. LIESEGANG (*Kolloid. Zeitsch.*, 1914, **15**, 18—23).—An account is given of a number of peculiar structures, the development of which is attributed to the contraction in gels and other systems in which chemical interaction is accompanied by the formation of precipitation membranes. The formation of completely enclosed cavities and of cavities communicating with the exterior may result in this way, and the importance of these effects in the interpretation of certain geological configurations is emphasised.

H. M. D.

**Reversible Reactions of Water on Iron and Ferrous Oxide.** G. CHAUDRON (*Compt. rend.*, 1914, **159**, 237—239. Compare Sainte-Claire Deville, *ibid.*, 1870, **70**, 105; Preuner, A., 1904, ii, 317).—A study of the equilibrium between iron and water at temperatures between 300° and 1000°. An apparatus similar in principle to that of Sainte-Claire Deville's (*loc. cit.*) was used, the source of heat being an electric furnace. The equilibrium was determined for the system iron, water, hydrogen, ferrous oxide, and for the system ferrous oxide, water, hydrogen, magnetic oxide of iron. There are two series of equilibria: (1) iron and ferrous oxide; (2) ferrous oxide and magnetic oxide of iron.

W. G.

**Mechanism of Irreversible Phenomena Deduced from the Boltzmann-Gibbs Law of Distribution.** R. MARCELLIN (*J. Chim. phys.*, 1914, **12**, 451—460).—A theoretical paper in which results deduced by another method (A., 1911, ii, 27) are now obtained from the law of distribution of Boltzmann-Gibbs. It is shown (1) that a physico-chemical complex in process of transformation is made up of two systems which are changing in opposite directions, and consist of a system I, the mass of which is constantly increasing, and a system II, the mass of which is constantly decreasing. The velocity of change which is observed experiment-



ally is the resultant of these two changes, and is given by the formula  $V = M[\exp(-A_1/RT) - \exp(-A_2/RT)]$ , in which  $M$  is a constant depending on the temperature and the nature of the substance of the reacting system,  $A_1$  and  $A_2$  are respectively the affinities of the systems I and II, and  $V$  is the velocity at the time  $t$ . The velocity with which the opposing systems are destroyed is given as a function of the temperature by the expression  $d \log_e v / dT = A / RT^2 + \alpha / RT + \beta / R$ , in which the constants  $\alpha$  and  $\beta$  are small in comparison with  $A$ . From the fact that a reaction does not take place instantaneously, the conclusion is to be drawn that the molecules capable of transformation are in an exceptional condition (critical condition), which is different from the mean condition. The energy necessary for converting a molecule in the mean condition into one in the critical condition is given by the expression  $E = RT^2 \cdot d \log_e v / dT$ . J. F. S.

### Velocity of Catalysis of Butyric Acid by means of Thoria.

A. KOEHLER (*Bull. Soc. chim.*, 1914. [iv]. 15, 649—657).—A study of the conditions governing the catalytic influence of thorium oxide on the conversion of butyric acid into butyrene by heat, the catalyst being distributed on the surface of glass balls in a copper tube. The results show that the amount of acid converted into ketone in a given time by a given weight of thorium oxide is constant and independent of the velocity of flow of the acid vapour. The velocity of decomposition is also independent of the weight of the catalyst used, the surface being constant, but it is apparently a function of the surface offered by the catalyst, and is probably proportional to this surface. The velocity of decomposition diminishes on diluting the acid with an inert vapour, when this dilution passes a certain limit. W. G.

**The Question of Associate Atoms.** F. H. LORING (*Chem. News*, 1914, 110, 25—26).—It is supposed that the atoms of certain elements, the atomic weights of which seem to be invariable, are in reality composite, and contain two or more associate atoms in perfectly definite proportions. H. M. D.

**Theory of Valency and Molecular Structure.** WILLIAM C. ARSEM (*J. Amer. Chem. Soc.*, 1914, 36, 1655—1675).—The theory put forward in this paper is based on the conception of molecules and atoms as systems of moving electrons, and of valency as a consequence of the relative stability of these systems. For example, a binary molecule composed of two univalent atoms is regarded as a stable system formed of two systems of moving electrons, the dynamic equilibrium being such that one electron oscillates periodically from one system to the other, and is common to both systems, neither of which is complete in itself. The oscillating electron is termed the "valence electron." Valency is thus the property or power which an atom possesses of sharing a certain number of electrons with one or more other atoms in such a way that the atoms so united form a complete or perfect electron system

which is electrically neutral. This theory is developed and applied to the explanation of the mechanism of chemical reactions, tautomerism, conductivity of metals, association, and dissociation and conductivity in electrolytes and gases. E. G.

**An Efficient Stirring Apparatus.** WILHELM GLUUD and RICHARD KEMPF (*J. Soc. Chem. Ind.*, 1914, **33**, 680).—The aim of the construction is to meet as many needs as possible with one apparatus. It consists of a flask of 1500 c.c. capacity, constricted somewhat at the base so as to be equally efficient for small quantities of liquid. It is fitted with a hollow, ground-glass stopper, through which the stirring rod passes, with a condenser, and with a dropping funnel. The absence of rubber stoppers makes it suitable for nitrations, etc., and the whole apparatus may be heated in an oil bath without risk of fracture. A pear-shaped trap, which is filled with paraffin oil or other suitable liquid, is fused on to the stirring rod in the flask, and an extension of the stopper dips into it, so as to seal off the interior of the flask from the metal fittings of the stopper and upper portion of the stirring rod. The apparatus is easily detachable for cleaning purposes. G. F. M.

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## Inorganic Chemistry.

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**Bromine Hydrate.** H. GIRAN (*Compt. rend.*, 1914, **159**, 246—248. Compare Löwig, *Ann. Phys. Chem.*, 1829, **16**, 376; Roozeboom, A., 1886, 177).—A thermal analysis of mixtures of bromine and water containing more or less bromine than suffices to saturate the water, points to the composition of the hydrate of bromine being  $\text{Br}_2 \cdot 8\text{H}_2\text{O}$ , and this formula is confirmed by chemical analysis of a specimen of the hydrate carefully freed from any occluded bromine or water, by centrifuging it on kaolin at a temperature just above  $0^\circ$ . W. G.

**A New Method of Determining the Atomic Weight of Iodine.** MARCEL GUICHARD (*Compt. rend.*, 1914, **159**, 185—188).—The author has determined the atomic weight of iodine by weighing the iodine and oxygen liberated from a given weight of iodic anhydride on decomposition by heat. The iodic anhydride was prepared by the action of carefully purified, fuming nitric acid on iodine, and the product freed from occluded gases by heating at  $330^\circ$ , repeatedly crystallised, and finally dehydrated by heating in a vacuum at  $240^\circ$  for fifteen hours in the final decomposition tube. The iodine liberated in the estimation was condensed in a spiral tube 1 metre long, and the oxygen absorbed by carefully purified heated copper, the decomposition being regulated so that not more

than 6 grams of iodic anhydride were decomposed in five hours. All starting materials and end products were weighed in sealed, evacuated tubes. The mean of five determinations gave 126.915 as the atomic weight of iodine. W. G.

**Nitrogen Generator.** CHAS VAN BRUNT (*J. Amer. Chem. Soc.*, 1914, **36**, 1448—1450).—The apparatus consists of a bulb provided with a long stem and a side-tube, and partly filled with an ammoniacal solution of ammonium carbonate or chloride; a tube filled with copper shavings is fitted into the top of the bulb. The stem of the latter is connected with a tube rising to the height of the bulb, and on this tube is a side-tube which extends upwards and enters the tube containing the copper shavings. A current of air is forced into the tube connected with the stem of the bulb, and rises upwards through the side-tube, carrying with it bubbles of the ammoniacal solution; the latter is thus circulated continuously and allowed to pass through the copper shavings, whilst the air, deprived of oxygen, collects in the upper part of the bulb and escapes through the side-tube of the latter. W. P. S.

**Active Nitrogen.** H. B. BAKER, ERICH TIEDE, R. J. STRUTT, and EMIL DOMCKE (*Ber.*, 1914, **47**, 2283—2284).—The contradictory results of Tiede and Domcke (*A.*, 1913, ii, 210; this vol., ii, 196) and Baker and Strutt (this vol., ii, 357) are due to differences in the apparatus employed. With the apparatus of the former investigators it was possible to increase the brightness of the after-glow of the electric discharge in nitrogen by the introduction of a little oxygen, a slightly larger quantity of oxygen, however, causing an entire disappearance of the effect. On the other hand, with the apparatus employed by the latter investigators, no appreciable diminution in the after-glow was observed even with pure nitrogen which gave the desired effect in the other apparatus.

It is therefore probable that a trace of oxygen favours those conditions in the discharge which give rise to active nitrogen, but in a suitable apparatus the result can be obtained even with the purest nitrogen. D. F. T.

**The Nitrogen After-glow. Nitrogen Glow and Metallic Vapour.** ERICH TIEDE and EMIL DOMCKE (*Ber.*, 1914, **47**, 2284—2285).—A final reply to König and Elöd (this vol., ii, 266), rejecting the suggestion that to metallic vapours are to be attributed the effects in the after-glow of nitrogen, which the authors have ascribed to oxygen (compare Baker, Tiede, Strutt and Domcke, preceding abstract). D. F. T.

**Preparation of Ammonia from Nitrogen and Hydrogen at High Pressure and Temperature in Presence of a Catalyst.** NICOTEM CARO (D.R.-P. 272638).—In the preparation of ammonia by passing a mixture of hydrogen and nitrogen at high pressure and temperature over soda-lime, potash-lime, etc., containing metals of the iron group, the latter are conveniently replaced by

either titanium or vanadium, or both, these giving an equally high yield of ammonia and showing less sensitiveness towards impurities acting as contact-poisons. T. H. P.

**Manufacture of Readily Soluble, Stable Perborate Preparations.** VEREINIGTE FABRIKEN FÜR LABORATORIUMSBEDARF (D.R.-P. 271194).—The normal salts used in the original process (A., 1913, i, 1052) are replaced by the corresponding acid salts, these being mixed, in the dry or dissolved state, with perborate in such proportion that their acidity is not more than sufficient to neutralise one-half of either the alkali or base present in the perborate. The preparation of the complex perborates is facilitated and their consistency improved if the constituents are either mixed with water or aqueous alcohol and dried at a gentle heat, or fused on a water-bath, and thus partly or completely dehydrated. T. H. P.

**Carbon: its Molecular Structure and Mode of Oxidation.** MAURICE COPISAROW (*Mem. Manchester Phil. Soc.*, 1914, 58, No. x, 1—11).—Basing his arguments on the three assumptions that a carbon molecule contains a large number of atoms, that a carbon atom is always quadrivalent, and that carbon exists in three allotropic modifications, the author advances reasons for his opinions that polyatomic molecules of elements may be represented by constitutional formulæ in a similar manner to the molecules of compounds, and that polyatomic molecules, combining with one another and yielding, finally, single molecules, must either disintegrate before the reaction, or more probably form a complex or complexes which are stable or unstable, according to the conditions (compare Dixon, T., 1896, 69, 774; 1899, 75, 630; Rhead and Wheeler, T., 1910, 97, 2181; 1911, 99, 1140; 1913, 103, 461).

The arrangement of the atoms in a carbon molecule must be such that the atoms can rotate freely or form a partly rigid structure, or a completely rigid structure; these three cases are considered to correspond with amorphous carbon, graphite, and diamond respectively. C. S.

**The Formation of Carbon Monoxide During the Rapid Combustion of Carbon.** F. M. G. JOHNSON and D. MCINTOSH (*Trans. Roy. Soc. Canada*, 1913, 7, iii, 161—162).—Percentages of carbon monoxide varying from 6.2 to 8.9 have been found in the gases produced by the combustion of a mixture of carbon with excess of potassium chlorate, either in a vacuum or in air. Since the temperature of the combustion was only about 1000°, the presence of carbon monoxide is not due to thermal decomposition of the dioxide, and it is therefore held to confirm the view that the formation of the monoxide is the first stage in the combustion of carbon. G. F. M.

**Colloidal Silicon.** R. ASTFALK and A. GUTBIER (*Kolloid. Zeitsch.*, 1914, 15, 23—27).—The authors have prepared colloidal silicon by reduction of silica by the action of magnesium, potassium, and

sodium. Magnesium and potassium give rise to products which yield colloidal solutions of different degrees of stability. According to the results of numerous experiments, these solutions may be divided into two groups, but it has not been found possible to determine the conditions which yield solutions belonging to the respective groups. Both series of solutions are readily coagulated by rise of temperature and by the addition of electrolytes. By dialysing the more stable solutions prepared by reduction with potassium, it was found possible to concentrate the colloidal solutions to some extent by evaporation over concentrated sulphuric acid. In this way, solutions containing approximately 0.05% of the disperse phase could be obtained.

The yellow solutions obtained from the product of the reaction with sodium are in some respects much more stable. They are readily dialysed, and can be concentrated over concentrated sulphuric acid without much coagulation; the solutions are, however, sensitive towards electrolytes.

H. M. D.

#### Attempts to Produce the Rare Gases by Electric Discharge.

THOMAS R. MERTON (*Proc. Roy. Soc.*, 1914, [A], 90, 549—553).—The question of the production of neon and helium by electric discharge in vacuum tubes has been further examined with an arrangement of apparatus which differs considerably from that employed either by Collie and Patterson (*T.*, 1913, 103, 419) or by Strutt (this vol., ii, 201). In the design of this apparatus, the most rigorous precautions were taken to ensure the exclusion of air. Hydrogen was admitted into the completely exhausted apparatus by heating a small, enclosed palladium tube, and after the passage of an induction-coil discharge, the residual gas was examined spectroscopically in a fine capillary tube attached to the apparatus. In some of the earlier experiments the residual gas showed the spectrum of argon, but this was found to be due to an exceedingly small, but continuous, leakage of air into the apparatus. When this was eliminated, no trace of argon, neon, or helium was observed after the passage of the discharge through hydrogen. Experiments with electrodes of aluminium, copper, nickel, silver, platinum, and palladium all gave negative results.

It is pointed out that in the previous experiments (*loc. cit.*) the diatomic impurities in the residual gas were removed by means of cooled charcoal, a process which would also have removed any argon present. It is probable that in those experiments in which the author found considerable quantities of argon, neon and helium would have been detected if the argon had been removed in this way.

The spectroscopic test for argon appears to be more delicate than that for neon, and since there is about a thousand times as much argon as neon in the atmosphere, it follows, therefore, from Strutt's estimate of the sensitiveness of the test for neon that a millionth of a c.c. of air might be sufficient for the detection of argon.

It is considered doubtful whether stopcocks can be relied on in dealing with quantities of gas of this order of magnitude.

H. M. D.

**Attempts to Produce the Rare Gases by Electric Discharge.**

J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1914, [A], 90, 554—556).—A series of experiments is described in which finely powdered metallic uranium, previously heated to redness in a vacuum, was subjected to cathode-ray bombardment in a bulb tube, which was sealed on to the apparatus used by Merton (see preceding abstract). A small charcoal bulb, a hard glass tube containing copper and copper oxide, and a small bulb filled with phosphoric oxide, were also sealed on to this apparatus. In nearly all the experiments described, neon and helium could be readily detected in the residual gas after passing the discharge for ninety minutes. In one experiment, in which the coil, giving a 10-inch spark with a platinum break, was replaced by a larger coil with a mercury break, neither neon nor helium could, however, be detected in the residual gas.

Since in no case was argon found to be present except in very small amounts, the author considers that the neon and helium cannot possibly be attributed to air leakage.

H. M. D.

**Crystallised Sodium Silicate.** EDUARD JORDIS (*Chem. Zeit.*, 1914, 38, 922).—Crystallised sodium silicates with 6, 9, and about 10  $\text{H}_2\text{O}$  had m. p.  $62.3^\circ$ ,  $47.2^\circ$ , and  $37.2^\circ$ , respectively. A compound with  $10\text{H}_2\text{O}$  is, however, difficult to obtain pure, as it gradually changes into the salt with  $9\text{H}_2\text{O}$ . When sodium silicate is heated for some time at  $100^\circ$ , a salt with  $1.5\text{H}_2\text{O}$  is obtained. The salt with  $9\text{H}_2\text{O}$  forms rhombic crystals, that with  $6\text{H}_2\text{O}$  monoclinic crystals. When the hydrated salts are heated or dried in a desiccator, there is difficulty in determining whether the resulting salts are definite compounds or mixtures.

W. P. S.

**The Gases Retained by Iodine and Silver.** PH. A. GUYE and F. E. E. GERMANN (*Compt. rend.*, 1914, 159, 225—227).—Using their special apparatus for the estimation and analysis of small volumes of gases (compare this vol., ii, 740), the authors have determined the amount of gas evolved on heating 1 gram of silver with one and a-half times its weight of iodine, carefully purified and previously heated in a vacuum. Two samples of silver were used: (1) ordinary pure silver (99.8%); (2) extra pure silver (100.0%), prepared by melting silver in a quartz vessel, bubbling hydrogen through it, and leaving it to solidify in an atmosphere of hydrogen. Sample (1) yielded 0.17 c.c. of gas from 1 gram of silver, of which four-fifths was oxygen and one-fifth carbon monoxide. Sample (2) yielded 0.027 c.c. of gas from 1 gram of the metal, which was all carbon monoxide, and also water vapour equivalent to 0.01 c.c. of a perfect gas at  $0^\circ$  and 760 mm. The bubbling of hydrogen

through the silver had thus eliminated the whole of the oxygen, leaving the volume of carbon monoxide practically unaltered.

W. G.

**The Absorption of Nitrogen by Calcium.** RICHARD BRANDT (*Zeitsch. angew. Chem.*, 1914, 27, 424).—Contrary to statements in the literature, metallic calcium in the compact form is found to absorb nitrogen rapidly and almost quantitatively with formation of the nitride,  $\text{Ca}_3\text{N}_2$ . Absorption commences at about  $300^\circ$ , and attains a maximum velocity at  $440^\circ$ . Above  $650^\circ$  it once more gradually falls off to zero, but commences again above the melting point of calcium. The nitride retains the form of the original piece of metal, but it can readily be converted into chestnut-brown powder.

G. F. M.

**The Dehydration of Gypsum.** C. GAUDEFRY (*Compt. rend.*, 1914, 159, 263—264).—The passage from the hemihydrate to the soluble form of anhydrous calcium sulphate at  $120$ — $130^\circ$  is not accompanied by any change in form or size of the crystals. The anhydrous salt is, however, less refractive than, and has a birefraction almost double, that of the hemihydrate.

W. G.

**Tellurium as Colouring Agent for Soda Glass.** P. FENAROLI (*Chem. Zeit.*, 1914, 38, 873—874).—Tellurium, like selenium, in the oxidised state does not impart a colour to glass, but if elementary tellurium is added to an ordinary soda glass and fused under reducing conditions, for example, in the presence of charcoal, glasses are obtained of colours varying according to the amount of tellurium used. Some contain colloidal solutions of the element, and others polytellurides. The former correspond completely with the tellurium hydrosols, and are, like them, of two fundamental colours, blue and brown, analogous to the red selenium glass. The blue glass contains larger colloidal particles than the brown. The glass containing polytellurides is red, or violet-red, and has an absorption spectrum which corresponds exactly with that of aqueous solutions of polytellurides, showing an absorption from the green to the violet, with a distinct maximum between 480 and  $490\ \mu$ .

G. F. M.

**Glucinum Sulphate and its Hydrates.** F. TABOURY (*Compt. rend.*, 1914, 159, 180—182).—The progressive dehydration, by heating, of the tetrahydrate of glucinum sulphate confirms the existence of the di- and mono-hydrates, the former being obtained at  $55$ — $60^\circ$  and the latter at  $100^\circ$ , and indicates the existence of a hemihydrate obtainable at  $150$ — $160^\circ$ . The anhydrous salt obtained at  $250^\circ$  is stable up to  $530$ — $540^\circ$ , and thus allows of the estimation of glucinum in the form of its sulphate. Glucinum sulphate does not form acid salts even when dissolved in sulphuric acid.

W. G.

**The Corrosion of Metals by Water.** A. T. STUART (*Trans. Roy. Soc. Canada*, 1913, 7, 183—188).—Comparisons have been made



of the relative corrosivity of "raw" Ottawa River water, and the same water which had been treated either by "mechanical filtration" or with alum or magnesia. The metals were employed in the form of wire, and were suspended in the water for seven days, some at ordinary temperatures and others at 60°. The corrosion was measured in terms of the loss in weight after the products of corrosion had been rubbed off with a cloth. In addition to the "pure" metals, the effect of couples of two unlike metals in contact was also studied. It was found that raw waters, although corroding iron to practically the same extent as treated waters, retained most of the product in colloidal solution, and did not coat the metal with as much flocculent material, nor allow it to settle out, as was the case with treated waters, which became very murky and opaque even at the ordinary temperature. A rise in temperature greatly accelerated the corrosion. The contact of aluminium with iron or with lead diminished the corrosion observed with the iron or lead alone, and increase in temperature produced a further decrease. Contact with copper caused exactly the reverse effects, and in the case of copper and lead an enormous increase of corrosion was observed. It was noticed that the iron wires carried a large number of tubercles, at the centre of which the metal was nearly eaten away. These were possibly the seats of colonies of iron-dissolving bacteria or algæ. Water treated for clarification with magnesium oxide had a considerably smaller corrosive action than the raw or otherwise treated water. This suggests the possible use of this substance as a pigment in anti-corrosive paint.

G. F. M.

**Ternary Alloy, Zinc-Silver-Lead.** B. BOGITCH (*Compt. rend.*, 1914, 159, 178—180).—On melting together lead, silver, and zinc, two layers are generally formed, and the author has studied the distribution of the three metals between the two layers at the temperature of solidification of the top layer, this being the poorer in lead, and consequently less fusible. Some twenty fused mixtures were studied, and a curve is given showing the proportions of the three metals which give two layers, and those which can exist without liquation. These results only hold good for temperatures near to the solidification point.

W. G.

**The Reduction of the Oxides of Copper, Lead, and Nickel.** PAUL SABATIER and LÉO ESPIL (*Compt. rend.*, 1914, 159, 137—142).—Copper oxide undergoes reduction by dry hydrogen at 120°. The curve showing the rate of reduction is formed by one branch only, the velocity being small at first, then increasing rapidly up to a certain point, after which it diminishes regularly. This oxide is reduced directly to the metal without the intermediate formation of cuprous oxide.

The reduction of lead peroxide by a stream of dry hydrogen is first manifest at 150°, it being reduced to the protoxide without the intermediate formation of red lead (compare Glaser, A., 1903, ii, 646). The protoxide, litharge, is first visible at 190°, it being

slowly transformed at this temperature, and more rapidly at  $240^{\circ}$  into the suboxide,  $Pb_2O$ , this oxide being, in its turn, slowly reduced to metallic lead at  $250^{\circ}$ , and rapidly at  $300^{\circ}$ .

The authors have repeated their work, already described (this vol., ii, 276), on the reduction of nickel oxide, and maintain their opinion that the unstable, intermediate suboxide formed has the constitution  $Ni_4O$ , and not  $Ni_2O$  as given by Berger (this vol., ii, 656).

W. G.

**The Chemical Composition of Alkaline Bordeaux Mixtures and the Soluble Copper which they Contain.** V. VERMOREL and E. DANTONY (*Compt. rend.*, 1914, 159, 266—268).—If concentrated milk of lime is poured rapidly into a dilute solution of copper sulphate, using an amount of lime such as to give 1 gram per litre in excess, a blue precipitate is formed, which consists mainly of Peligot's stable hydrated oxide, together with a little of the unstable hydrate and a small proportion of basic sulphates. On boiling, only a portion of this precipitate is dehydrated. On filtering off the precipitate, the filtrate is found to contain both copper and lime in solution. The copper is precipitated on boiling or by the passage of carbon dioxide, but dissolves in excess of this gas. The amount of copper in solution expressed as copper sulphate may amount to as much as 0.23 gram per litre. Using the same proportions, but pouring the milk of lime slowly into the copper sulphate solution, a green precipitate is formed, which consists almost entirely of basic sulphates, which are not affected by the presence of free lime, except on boiling the mixture. The filtrate from the green precipitate also contains both lime and copper in solution, the latter, expressed as copper sulphate, reaching as much as 0.41 gram per litre.

W. G.

**Simple Method for the Purification of Mercury.** C. MARGOT (*Arch. Sci. phys. nat.*, 1914, [iv], 38, 46—52).—The method for the purification of mercury consists in placing the mercury in an inclined iron tube 160 cm. long and 3 cm. diameter. The tube is fitted with three vertical iron side-tubes, one at each end and one in the middle; the upper side-tube is connected through a Woulfe's bottle with a water pump, the lower side-tube is fitted with a funnel, and the tube in the centre carries a thermometer. The tube is heated midway between the lower and centre side-tubes by means of a Bunsen burner until the temperature has reached  $150$ — $160^{\circ}$ , and then a current of air is drawn through. In this way a very rapid oxidation of the impurities is brought about, and any volatilised mercury is condensed in the Woulfe's bottle. By this means very dirty mercury can be completely purified in twenty-four hours. After the current of air has been stopped and the mercury allowed to cool, it is necessary to filter through fine linen to remove the oxides. With an apparatus of the dimensions stated above, about 12 kilos. of mercury can be treated at once.

J. F. S.

**Isolation of Neoytterbium.** J. BLUMENFELD and G. URBAIN (*Compt. rend.*, 1914, 159, 323—326).—The authors have submitted the earths of the ytterbium group, in the form of their nitrates, to a process of fractional crystallisation (compare Urbain, A., 1907, ii, 956; 1908, ii, 108), following the stages in the purification by measuring the coefficients of magnetisation of each fraction. After four thousand crystallisations they have obtained eight successive fractions having the same coefficient, indicating the isolation of a definite compound. The metal of the nitrate corresponding with these fractions they call "neoytterbium." The paramagnetism of its oxide is 33·6, and the atomic weight of the metal is 173·54. The spectra of these fractions show but very feebly the strongest rays of lutecium (compare Urbain, *loc. cit.*), or of thulium (compare Soret, A., 1880, 7, and Cleve, *ibid.*). The spectra do not contain the rays of aldebaranum, as indicated by Auer von Welsbach (compare this vol., ii, 130).  
W. G.

**Reversible Hydrosols Derived from Aluminium Hydroxide.** R. PHILLIPS ROSE (*Koll. Chem. Beihefte*, 1914, 6, 1—7).—In the course of experiments on the adsorption of barium salts by precipitated aluminium hydroxide, it was found that a reversible gel was precipitated on the addition of hydrochloric acid to a solution of aluminium hydroxide in dilute acetic acid. The conditions which determine the formation of the sol and gel forms have been examined in detail.

Aluminium hydroxide, precipitated by the addition of ammonia to a solution of aluminium chloride or nitrate, varies very markedly in its solubility in dilute acetic acid (8%) according to the extent to which it is dehydrated. The hydroxide, dehydrated at low temperatures, yields the sol if its composition lies between  $\text{Al}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 1\cdot9\text{H}_2\text{O}$ . The maximum amount of sol is formed when the composition is between  $\text{Al}_2\text{O}_3 \cdot 4\cdot5\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 2\cdot7\text{H}_2\text{O}$ . From experiments on the solubility of a hydroxide of the approximate composition  $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  in acetic acid solutions of varying concentration, a maximum sol formation was found for solutions containing 6—8% of acid. Solutions of propionic, butyric, hydrochloric, hydrobromic, hydriodic, and nitric acid also gave rise to the sol, and the most favourable concentrations have been determined for each of these acids.

The sol is coagulated by the addition of aluminium salts, by hydrochloric and other acids, and this process is reversible. Irreversible coagulation occurs on the addition of potassium or sodium sulphate. The observations are discussed from a theoretical point of view.  
H. M. D.

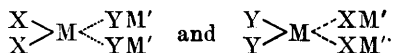
**Iron-Zinc Alloys.** F. TABOURY (*Compt. rend.*, 1914, 159, 241—243).—The author has examined the crystals which are formed in galvanising tanks, where the zinc is kept at a temperature slightly above its melting point for several months. He finds that they are identical with the mixed crystals containing 7·3% of

iron, as indicated by Vegesack (compare A., 1907, ii, 170). His determinations of the *E.M.F.* of the metal in which they are embedded agrees with the results obtained by Vigouroux, Ducelliez and Bourbon (A., 1912, ii, 648), the metal being zinc, and not an alloy of low iron content (compare Vegesack, *loc. cit.*). W. G.

**Iron-Zinc Alloys.** H. LE CHATELIER (*Compt. rend.*, 1914, **159**, 356—357).—The author points out that Berthier (1840) and himself (1889) published the results of work on iron-zinc alloys far earlier than Vigouroux (A., 1912, ii, 648) or Vegesack (A., 1907, ii, 170), the only workers referred to by Taboury (compare preceding abstract). The author had proved the composition of the alloy to correspond with  $\text{FeZn}_{10}$ , and had shown that chromium gave a similar compound,  $\text{CrZn}_{10}$ . His results have been elaborated and confirmed by Wologdine (compare *Rev. Metal.*, 1906, **3**, 701). The author does not consider that the measurements of *E.M.F.* permit of an exact determination of the formula of a chemical compound. W. G.

**The Solid Chromic Sulphates.** A. SÉNÉCHAL (*Compt. rend.*, 1914, **159**, 243—246).—The author agrees with Colson (compare A., 1907, ii, 177) that the green chromium sulphate obtained by Recoura from the violet sulphate by heating it at  $90^\circ$  (compare A., 1896, ii, 27) has the composition  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ . This dehydration commences in a dry vacuum at  $30^\circ$ , the salt gradually turning green, and being composed then of two phases. The green sulphate dissociates slowly in dry air at  $80^\circ$ , giving, finally, a new hydrate,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ . All the substances of composition intermediate between this and the hexahydrate are soluble in water, their solubility diminishing with their water content. This trihydrate slowly loses water at  $150^\circ$ , but a temperature of  $400^\circ$  is necessary in order to obtain the anhydrous salt, this and the intermediate hydrates being insoluble even in boiling water. For the hydrates from  $\text{Cr}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  to  $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  their molecular volume is an additive property, and can be calculated knowing the molecular volume of any one of them and of water in the solid state. The molecular volumes of the salts obtained by the dehydration of the trihydrate diminish more rapidly than would be the case if they followed a law of additivity. W. G.

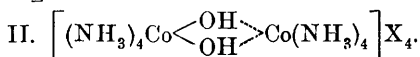
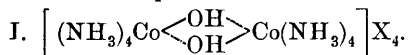
**Neutralisation of the Affinity of Main and Subsidiary Valencies in Compounds of a Higher Order.** J. V. DUBSKY (*J. pr. Chem.*, 1914, [ii], **90**, 61—118).—According to Werner's original theory of main and subsidiary valencies, additive compounds of the general formula  $\text{MX}_2 \cdot 2\text{M}'\text{Y}$ , produced by the union of two different haloid salts, should exist in two isomeric forms,



Up to the present, however, no well-established instance of the existence of valency isomerides of this type has been recorded.

With the object of gaining further information on this point, the author has examined the additive compounds formed by the union of haloid salts of papaverine with cadmium and zinc haloids, but has failed to obtain any evidence of the existence of such isomerides. The additive compounds of papaverine hydrochloride, for example, with zinc and cadmium bromides, proved to be identical in solubility, melting point, crystalline form, and optical rotation with those obtained by the combination of papaverine hydrobromide with zinc and cadmium chlorides. These results thus confirm Werner's recent conclusion (this vol., i, 18) that there is no essential difference between main and subsidiary valencies.

Further evidence in support of Werner's view is furnished by the behaviour of octamminedioldicobaltic salts which are formed by the loss of water from two molecules of hydroxoaaquotetramminecobaltic salts,  $\left[ (\text{NH}_3)_4\text{Co} \begin{smallmatrix} \text{OH} \\ \text{OH}_2 \end{smallmatrix} \right] \text{X}_2$ , and, therefore, receive the symmetrical constitution I. On the other hand, the diol-salts are quantitatively resolved by the action of halogen acids into *cis*-diaquotetrammine- and *cis*-dihalogenotetramminecobaltic salts, a result which can only be satisfactorily interpreted on the assumption that the octamminedioldicobaltic salts have the unsymmetrical constitution represented in II.



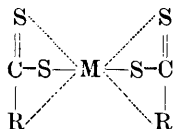
In view of the pronounced tendency of the acetato-group to enter into bridge-formation in multinuclear metallic complex salts, the behaviour of a number of ol-salts towards acetic anhydride has been studied.

Although hydroxopentamminecobaltic salts are readily converted into the corresponding acetato-salts by the action of acetic anhydride at the ordinary temperature, the dioldicobaltic and dioldichromic salts remain unchanged, even when heated for several hours with this reagent. Hydroxoaaquotetrammine salts, on the other hand, are quantitatively converted into diol-salts. Thus, hydroxoaaquodiethylenediamminecobaltic and -chromic salts,  $[\text{en}_2 \text{M}(\text{OH})(\text{OH}_2)]\text{X}_2$ , when warmed with acetic anhydride yield the corresponding tetraethylenediamminediol salts.

Attempts have been made to apply this method of preparing diol-salts to the preparation of heterogeneous dioldimetallic salts of the type  $\left[ \text{Y}_4\text{Co} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \text{CrY}'_4 \right] \text{X}_4$  (where  $\text{Y}_4$  and  $\text{Y}'_4 = 4\text{NH}_3$  or  $\text{en}_2$ ) by the action of acetic anhydride on equimolecular proportions of hydroxoaaquotetramminecobaltic and -chromic salts. These attempts, however, were unsuccessful, a mixture of the octamminedioldicobaltic and -dichromic salts being obtained.

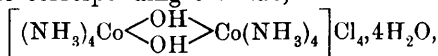
The author also discusses the constitution of the complex salts of chromium and iron with carboxylic acids, and gives an account of the preparation and properties of the ferric, chromic, and

cobaltic salts of xanthic acid. The xanthates exhibit the characteristic properties of internal complex salts, and are represented by the formula

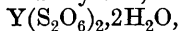


(R=OEt); a similar constitution is assigned to the salts of bi- and ter-valent metals with dithiocarbamic acid (R=NH<sub>2</sub>) and its dialkyl derivatives.

When heated with acetic anhydride, hydroxo-aquotetrammine-cobaltisulphate is converted into *octamminedioldicobaltisulphate*, from which the corresponding *chloride*,



small, lustrous, dark ruby-red crystals, and *dithionate*,



lustrous, light violet crystals, were obtained by treatment with ammonium chloride and sodium dithionate respectively.

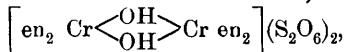
*Hydroxo-aquotetramminechromic sulphate*,



prepared by the addition of pyridine to an aqueous solution of chloro-aquotetramminechromic sulphate, forms violet-red crystals, and when heated with acetic anhydride is transformed into octamminedioldichromic sulphate, from which the bromide and dithionate,  $\left[ (\text{NH}_3)_4\text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr}(\text{NH}_3)_4 \right] (\text{S}_2\text{O}_6)_2, 4\text{H}_2\text{O}$  (Grodsenski, *Diss.*, Zürich, 1910), were obtained in the usual manner.

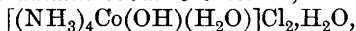
The action of acetic anhydride on both *cis*- and *trans*-hydroxo-aquodiethylenediamminecobaltic dithionate gives rise to the same tetraethylenediamminedioldicobaltic salts (Werner, *Annalen*, 1910, **375**, 85). The following new salts of this series are described ( $\text{Y} = \left[ \text{en}_2 \text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co} \text{en}_2 \right]$ ): *dithionate*,  $\text{Y}(\text{S}_2\text{O}_6)_2$ ; *chloride*,  $\text{YCl}_4, 4\text{H}_2\text{O}$ , lustrous, ruby-red crystals; and *iodide*,  $\text{YI}_4$ .

*cis*-Hydroxo-aquodiethylenediamminechromic dithionate yields *tetraethylenediamminedioldichromic dithionate*,



from which the following new salts were prepared: *chloride*,  $\text{YCl}_4, 2\text{H}_2\text{O}$ , microscopic, dark bluish-violet crystals; *thiocyanate*,  $\text{Y}(\text{SCN})_4$ ; *nitrate*,  $\text{Y}(\text{NO}_3)_4, 2\text{H}_2\text{O}$ ; and *chromate*,  $\text{Y}(\text{CrO}_4)_2, 4\text{H}_2\text{O}$ , brownish-red crystals.

*Hydroxo-aquotetramminecobaltic chloride*,



prepared by dissolving octamminedioldicobaltic chloride in strong aqueous ammonia, crystallises in slender, violet-red leaflets.

Hydroxopentamminechromic dithionate,  $[(\text{NH}_3)_5\text{Cr}(\text{OH})]\text{S}_2\text{O}_6$ , separates with  $2\text{H}_2\text{O}$  in carmine-red crystals, which decompose slowly at the ordinary temperature with evolution of ammonia;

when dissolved in acetic acid or treated with acetic anhydride at the ordinary temperature, it is converted into *aquopentammine-chromic dithionate*,  $[(\text{NH}_3)_5\text{Cr}(\text{OH}_2)]_2(\text{S}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$ , which forms light, brownish-red crystals, and is reconverted into the hydroxo-salt on treatment with aqueous ammonia. When heated with acetic anhydride, the anhydrous hydroxo-salt undergoes decomposition.

Hydroxo-aquatetramminecobaltic sulphate, on solution in acetic acid, yields Jörgensen's diaquatetramminecobaltic sulphate, to which the author assigns the formula  $[(\text{NH}_3)_4\text{Co}(\text{OH}_2)_2]_2(\text{O} \cdot \text{SO}_3)_3$ , the latter compound loses  $7\text{H}_2\text{O}$  at  $110-120^\circ$ , and passes into an intensely violet sulphatotetramminecobaltic salt. Unsuccessful attempts to prepare diol-salts by the action of acetic anhydride on dihydroxodiaquodiamminechromic bromide and hydroxo-aquodipyridinediamminecobaltic dithionate are also recorded.

*Ferric benzenesulphonate*,  $[\text{Fe}(\text{OH}_2)_6](\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 3\text{H}_2\text{O}$ , prepared from ferric hydroxide and an aqueous solution of the free acid or by the interaction of ferric sulphate and barium benzenesulphonate, crystallises from ethyl acetate in light yellow leaflets or plates, which sinter at  $56^\circ$ , melt at  $60^\circ$  to a turbid liquid, which becomes clear at  $80^\circ$ , and resolidifies at  $160^\circ$ .

*Ferric benzenesulphinate*,  $\text{Fe}(\text{C}_6\text{H}_5 \cdot \text{SO}_2)_3$ , is obtained as a voluminous, orange-yellow precipitate by adding an alcoholic solution of benzenesulphinic acid to aqueous ferric chloride.

[With S. VRETOS.]—The additive *compound* of papaverine hydrochloride and cadmium bromide,  $2\text{C}_{20}\text{H}_{21}\text{O}_4\text{N} \cdot 2\text{HCl} \cdot \text{CdBr}_2$ , separates in lustrous, white, silky crystals when the two anhydrous salts are brought together in alcoholic solution. It becomes yellow at  $100^\circ$ , m. p.  $185^\circ$ , and is identical with the compound formed by the union of papaverine hydrobromide and cadmium chloride; if the components are not anhydrous, the additive compound separates in crystals containing  $1\text{H}_2\text{O}$ .

The following additive *compounds* were prepared in a similar manner ( $\text{B} = \text{C}_{20}\text{H}_{21}\text{O}_4\text{N}$ ):  $2\text{B} \cdot \text{H}_2\text{CdCl}_2\text{I}_2$ , aggregates of slender leaflets, m. p.  $176^\circ$ ;  $2\text{B} \cdot \text{H}_2\text{CdBr}_2\text{I}_2$ , m. p.  $188^\circ$ ;  $2\text{B} \cdot \text{H}_2\text{ZnCl}_2\text{Br}_2$ , m. p.  $177^\circ$ .

*Ferric xanthate*,  $\text{Fe}(\text{CS}_2 \cdot \text{OEt})_3$ , prepared from ferric chloride and potassium xanthate in aqueous solution, separates from carbon disulphide in small, brownish-black crystals. Its solution in pyridine, on dilution with water, deposits lustrous, golden-yellow leaflets, having the composition  $\text{Fe}(\text{CS}_2 \cdot \text{OEt})_3 \cdot 3\text{C}_5\text{NH}_5$ .

The *cobalt* salt (small, blackish-green needles, m. p.  $117^\circ$ ) and *chromic* salt (dark blue crystals) differ from the ferric salt in that they do not yield additive compounds with pyridine. All three xanthates give normal molecular weights in ethylene dibromide or benzene solution. F. B.

**Reduction of Uranium Oxide.** ERIC K. RIDEAL (*J. Soc. Chem. Ind.*, 1914, 33, 673–676).—In view of the increasing quantities of uranium salts produced as by-products, several

methods have been investigated which might be suitable for the industrial production of metallic uranium. From uranous salts, the best procedure was found to be the preparation of the tetrachloride by the action of chlorine on an intimate mixture of uranium dioxide and carbon heated at a low red heat, and the subsequent treatment of this substance with sodium and sodium chloride in a steel cylinder heated at  $800^{\circ}$  in a resistance furnace for forty-five minutes. A brown powder was obtained containing 99.3% of uranium. The electrolysis of uranium tetrachloride, using a mercury cathode, was also tried, but with unsatisfactory results, and the industrial preparation of uranium by either of these methods does not appear feasible. Several methods for the reduction of urano-uranic oxide,  $U_3O_8$ , were investigated. Electrolysis in the solid state in an atmosphere of hydrogen gave under all conditions of pressure a black, crystalline product consisting of the dioxide, and a repetition of Stavenhagen's experiments, using magnesium or aluminium, yielded only a regulus of magnesia or alumina with the dioxide and unburnt metal. An electrothermal process, involving the use of magnesium powder, yielded, however, uranium of 98–99% purity. The oxide with 20% of magnesium was pressed into rods and placed in a tube of magnesia in contact with the carbon electrodes of an arc furnace. Hydrogen was passed through the apparatus, which was heated in a granular carbon resistor until the rods were hot enough to conduct the main current, which produced an arc of magnesium vapour, which effectively reduced the uranium oxide. The freshly prepared metal was spontaneously inflammable in air. Reduction of the oxide can also be effected by heating with magnesium and sodium in presence of calcium chloride as a catalyst, and an impure metal was obtained by Moissan's method of reducing with carbon in the arc furnace. The melting point of uranium containing 0.4% of carbon lay between  $1300^{\circ}$  and  $1400^{\circ}$ .

G. F. M.

**Removal of Iron from Oxygenated or Roasted Tin Sulphide Ores by Lixiviation with Acid.** MARCO CHIAPPONI and ROBERT HESSE (D.R.-P. 271594).—The oxygenated ore is treated at  $300$ – $500^{\circ}$  with a reducing agent, preferably gaseous in nature, so as to avoid introduction of impurities in the form of ash. Under these conditions the stannic oxide undergoes no, or but slight, reduction, and remains insoluble in acid, whereas the iron oxides are converted principally into ferrous oxide, which can be extracted readily by aqueous hydrochloric or sulphuric acid, or, better, by hydrogen chloride at  $400$ – $500^{\circ}$  in a counter-current apparatus, the iron then distilling off as volatile chloride.

T. H. P.

**Influence of Manganese Compounds on the Surface Alteration and Secondary Enrichment of Gold Deposits.** W. H. EMMONS (*Zeitsch. Kryst. Min.*, 1914, 54, 74; from *Trans. Amer. Inst. Min. Engin.*, 41, 768–837).—Ferric, manganic, and cupric salts present in natural waters, together with chlorides, liberate free chlorine, and gold may thereby be dissolved. It may



afterwards be deposited (principally by the agency of ferrous sulphate) in some other situation where there is no oxidation. Solutions containing 0·1% chloride, together with manganese, are capable of dissolving gold in the cold.

L. J. S.

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## Mineralogical Chemistry.

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**Organic Matter in Oil Shales.** JOHN B. ROBERTSON (*Proc. Roy. Soc. Edin.*, 1914, **34**, 190—201).—The results of analysis of thirteen shales showed that the ratio C/H varies from 6 to 8 and above. The yield of oil from shales varies directly as the percentage of organic matter, and inversely as a function of the carbon-hydrogen ratio. In all the shales examined, the ratio C/H is lower than in ordinary bituminous coals. The richer varieties may, however, approach cannel coals in properties. The organic matter of oil-shales is mainly insoluble in organic solvents. From torbanite and Broxburn shale, pyridine dissolved 4.92 and 3.29% respectively of the ash-free dry substance; the amount of resinous substances present is therefore quite small.

By the action of concentrated nitric acid on some of the shales, acids were obtained of a similar nature to those obtained by Anderson from coal (*J. Soc. Chem. Ind.*, 1898, **17**, 1018). The acids form a series, beginning with lycopodium acid, in which the hydrogen is relatively highest, and ending with ordinary coal acids, in which it is relatively lowest. Torbanite, Broxburn shale, peat, and cannel coal yield intermediate acids in the order as given, and they probably represent different stages in the alteration of vegetable matter. There is no evidence of the presence of animal residues; phosphates could not be detected, and the amounts of lime in the ash varied from a trace to 1.55%. The conclusion is drawn that the organic matter is derived from algæ, spores, or concretions of macerated organic material similar to that found in peat and cannel coal.

N. H. J. M.

**Empressite, a New Silver-Tellurium Mineral from Colorado.** W. M. BRADLEY (*Amer. J. Sci.*, 1914, [iv], **38**, 163—165).—This mineral was found as finely granular masses with metallic lustre in the Empress-Josephine mine, Kerber Creek district, Colorado. On the small, conchoidal and uneven surfaces of fracture, the colour is pale bronze; the streak is greyish-black. The mineral is brittle to friable, and has H 3—3½, D 7.510. It is readily fusible, and is soluble in hot dilute nitric acid. Analysis agrees with the formula AgTe.

Ag.	Te.	Fe.	Insol.	Total.
45.17	54.75	0.22	0.39	100.53

L. J. S.

**Bilinite, a New Bohemian Mineral.** J. SEBOR (*Jahrb. Min.*, 1914, i, ref. 395—396; from *Sborník Klubu přírodovědeckého, Prag*, 1913, No. II, 2 p.).—A mineral resembling coquimbite occurs in a lignite mine at Schwaz, near Bilin. It is white to yellowish, with a fine, radially-fibrous structure. Hardness about 2, D 1·875. The optical characters resemble those of halotrichite, of which the new mineral is the iron analogue. Analysis I is of the surface material, and II from the interior:

	SO <sub>3</sub> .	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	C.	Total.
I.	32·80	5·86	15·95	0·04	0·90	39·82	2·11	97·48
II.	34·87	6·93	15·88	0·13	0·29	41·77	—	99·87

These give a formula  $\text{Fe}''\text{Fe}'''_2\text{S}_4\text{O}_{16}, 24\text{H}_2\text{O}$ , analogous to that of halotrichite ( $\text{Fe}''\text{Al}_2\text{S}_4\text{O}_{16}, 24\text{H}_2\text{O}$ ). The mineral has been deposited from acid solutions resulting from the oxidation of pyrites.  
L. J. S.

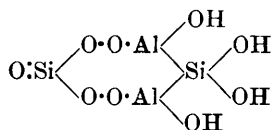
**Precious Stones from Lower California, Mexico.** ERNST WITTICH (*Centr. Min.*, 1914, 449—456).—Pale rose-red lithia-tourmaline (rubellite), occurring in biotite-schist in the mountain ranges between Calamahi and San Borja, gave the following results on analysis:

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	B <sub>2</sub> O <sub>3</sub> .	Total.
37·54	2·60	43·46	0·64	0·27	9·12	0·12
Li <sub>2</sub> O.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.		
0·56	1·58	2·51	1·87	100·27		

Embedded in this rubellite are sometimes crystals of sapphire. Other gem-minerals described from Lower Californian localities include beryl, garnet (hessonite and spessartite), and turquoise.

L. J. S.

**Chemical Structure of Kaolin.** J. V. SAMOILOV (*Bull. Acad. Sci. St. Pétersbourg*, 1914, [vi], 8, i, 779—794).—The author has studied the heat effects observed when kaolin is heated in an electric furnace. From the results obtained, taken in conjunction with those given under similar combined by opal, bauxite, diaspor, aluminium hydroxide, allophane, andalusite, disthene, and sillimanite, the conclusion is drawn that the two mols. of silica present in kaolin are differently combined with the alumina (compare Simmonds, T., 1903, **83**, 1469). The structural formula



is proposed for kaolin. Complete removal of water is accompanied by resolution into silica and the silicate,  $\text{Al}_2\text{SiO}_5$ . T. H. P.

**Mineral Waters of Moncatini Owned by the Crown.** R. GUARESCHI (*Ann. Chim. Applicata*, 1914, 1, 506—514).—These

waters exhibit ordinary physical and chemical characters, the temperature varying widely with the different springs, but being in all cases appreciably above that of the atmosphere. Their principal saline constituent is sodium chloride, which occurs, together with magnesium and potassium chlorides, sulphates of the alkali and alkaline-earth metals, and magnesium and calcium carbonates; certain of them contain also iodides, bromides, and salts of lithium, manganese, and cæsium. All contain considerable proportions of dissolved gas, which begins to escape when the water reaches the surface of the earth, and consists largely of carbon dioxide.

T. H. P.

**Manganese in Some Springs of the Central Rock System.** F. JADIN and A. ASTRUC (*Compt. rend.*, 1914, 159, 332—333. Compare A., 1913, ii, 870; this vol., ii, 378).—The authors have determined the manganese content of the water from seventy-two springs spread over eighteen different places in the central plateau. The waters of this system are, on the whole, richer in manganese than those of the Vosges Mountains, this being expected, as these springs are richer in hydrogen carbonates than those in the Vosges Mountains. As in the previous cases, very marked variations were found in the manganese content of springs at the same place, this variation being relative to the variation in iron content. W. G.

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### Analytical Chemistry.

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**Panel for Electro-Analysis.** HENRY ZIEGEL (*J. Amer. Chem. Soc.*, 1914, **36**, 1450—1452).—A convenient form of supply and switch-board is described; the various connexions allow the use of the current from a 6-volt accumulator or from a 110-volt lighting circuit.  
W. P. S.

**Method for the Preparation of Dry Starch, Soluble in Cold Water, for Use as an Indicator.** ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1914, **6**, 649—650).—Four hundred grams of potato starch, 2300 c.c. of water, and 80 c.c. of *N*/1-hydrochloric acid are mixed in a flask and heated in a boiling water-bath for 1·5 hours. The mixture is then cooled to 50°, rendered ammoniacal, 800 c.c. of 95% alcohol are added, the solution is strained through coarse muslin, and, while still warm (45°), is poured slowly, with continuous stirring, into 4 litres of 95% alcohol. After forty-eight hours the alcohol is decanted, the residue is washed with 95% alcohol, and spread out in a thin layer to dry. The powdered starch thus obtained dissolves readily in cold water.  
W. P. S.

**Apparatus for Controlling the Rate of Flow of Reagents into Solutions, etc.** GEORG PANOPULOS (*Chem. Zeit.*, 1914, **38**, 922).—A cover-glass for beakers is provided with a conical hole in its centre; a conical glass rod fits into this hole and extends to the bottom of the beaker. The reagent to be added is poured into the upper or concave side of the cover-glass, and flows slowly into the beaker when the rod is raised slightly. The reagent may also be contained in a graduated vessel fitted over the upper part of the rod, so that a definite amount is admitted to the beaker when the rod is raised.

W. P. S.

**A Pipettometer.** W. D. FROST (*J. Amer. Chem. Soc.*, 1914, **36**, 1785—1787).—This apparatus consists essentially of a vertical, graduated glass tube, to the upper end of which non-graduated pipettes may be attached by means of rubber tubing. At the lower end of the graduated tube another tube is attached by means of a flexible rubber joint. This tube has a bulb at its outer end, and is so arranged that this end can be readily raised or lowered. The vertical tube and the movable arm with the bulb are partly filled with mercury. The whole apparatus is supported by a suitable frame so arranged on a stand that its height can be varied. By moving the bulb up or down, the height of the mercury in the vertical tube can be altered. When the mercury column is lowered, the pipette draws up the liquid in which its tip is immersed, and when it is raised the liquid is expelled. The quantity of liquid taken up or discharged is measured by reading the position of the mercury in the graduated tube.

The apparatus is very useful for the accurate measurement of small volumes of liquids. It was devised for use in bacteriological work, and is recommended for handling poisonous or infectious material. It can also be employed for calibrating pipettes.

E. G.

**Analysis of Very Small Quantities of Gas; Application to the Analysis of Air.** PH. A. GUYE and F. E. E. GERMANN (*Compt. rend.*, 1914, **159**, 154—157).—A description of a volumeter by means of which it is possible to analyse very small quantities of gas. The apparatus consists essentially of a volumeter of comparatively small capacity (25—50 c.c.) used in conjunction with a MacLeod vacuum gauge. The measurements are all made at constant volume under a pressure of 7—8 mm., the gauge being sensitive to 1/100 mm. of mercury. The sensitiveness of the apparatus can be considerably augmented by reducing the capacity of the volumeter and increasing the accuracy of the gauge. Absorption and reaction chambers are sealed on to the volumeter, and separated from it by glass taps. The apparatus is figured in the text, and can be used for the analysis of the atmosphere at different heights or of gases evolved on heating solids. Two analyses of the same sample of air, 0.25 c.c. being used in each case, gave exactly the same percentage of oxygen.

W. G.

**Gas Analysis by Fractional Distillation at Low Temperatures.** G. A. BURRELL and F. M. SEIBERT (*Chem. News*, 1914, **110**, 2—5, 14—16; *J. Amer. Chem. Soc.*, 1914, **36**, 1537—1548).—A process is described for the separation of a natural gas into its constituent paraffin hydrocarbons by means of fractional distillation of the liquefied gas under low pressures. A measured volume of gas (about  $1\frac{1}{2}$  litres is sufficient) is transferred to a condensing tube immersed in liquid air in a Dewar flask. This tube is also connected with a Töpler pump fitted with a mercury manometer and with vessels for trapping the gas fractions over mercury as they are removed. The entire sample having been liquefied, the methane can be removed between  $-185^{\circ}$  and  $-190^{\circ}$  at 22 mm. At this temperature ethane has so small a vapour-pressure that none could be detected in the distillate within the limits of analytical error. After thrice-repeated distillation of the residue, no more methane could be removed, and the manometer pressure sank to zero. In a similar way ethane was removed at  $-140^{\circ}$  to  $-145^{\circ}$ . At this temperature, a small quantity of propane also passed over, and was removed by liquefaction and repeated distillation. Propane was separated from the butanes at  $-120^{\circ}$  to  $-135^{\circ}$  by a repetition of the above processes. The final fractions of each gas that were obtained were analytically pure, and the process, although tedious, is therefore applicable for the satisfactory separation of a gaseous mixture into its constituents when this is unattainable by other means. G. F. M.

**Penot's Chlorometric Method.** J. CLARENS (*Compt. rend.*, 1914, **159**, 183—185).—Penot's method of estimating hypochlorites gives results which are lower and less correct than those obtained by Mohr's modification of this method. The following is the simplest and quickest method of carrying out an estimation. A first determination is made by Penot's method of the volume of sodium arsenite solution required. The volume of liquid, thus determined, is poured into a flask, and the solution of the hypochlorite added, the mixture being shaken. A further quantity of sodium arsenite is then added drop by drop until the end of the action is reached, as indicated by starch-iodide paper. The addition of a small amount of potassium bromide to the hypochlorite solution is advantageous in that the end-point can be found without the use of the starch-iodide paper. W. G.

**Direct Iodometric Estimation of Soluble Iodides.** W. STÜWE (*Chem. Zentr.*, 1914, i, 2121; from *Apoth. Zeit.*, 1914, **29**, 382).—The estimation depends on the reaction between iodides and iodates in acid solution, according to the equation  $5\text{HI} + \text{HIO}_3 = 6\text{I} + 3\text{H}_2\text{O}$ . Ten c.c. of an aqueous solution containing 0.2 gram of potassium iodide are treated with 10 c.c. of 3% potassium iodate solution, 10 c.c. of alcohol and 2 c.c. of nitric acid are added, and 2 grams of barium carbonate mixed with water are then introduced. When the evolution of carbon dioxide has ceased, potassium iodide is added to dissolve the liberated iodine, the

solution is diluted to 100 c.c., and, after settling, 50 c.c. of the clear solution are titrated with *N*/10-thiosulphate solution. The presence of chlorides does not interfere with the estimation, but the method cannot be used when the iodide contains bromide.

W. P. S.

**Estimation of Total Sulphur in Caoutchouc.** URZ (*Chem. Zentr.*, 1914, i, 2068—2069; from *Gummi-Zeit.*, 1914, 28, 631—632).—A method described recently by Kaye and Sharp (*India Rubber Journal*, 1912), in which the caoutchouc is ignited with a mixture of zinc oxide and potassium nitrate, yields trustworthy results. The crucible containing the mixture should be heated first on an iron plate, and then over a flame which is raised gradually. Experiments with pure sulphur showed that there is no loss under these conditions.

W. P. S.

**Estimation of Dissolved Oxygen in Waters, Effluents, etc.** PERCY KAY (*Chem. News*, 1914, 110, 49).—Two methods are described, and depend on the oxidation of ferrous or manganese salts in alkaline solution. A 500 c.c. bottle is filled with the water under examination, 1 gram of ferrous sulphate and 3 grams of potassium hydroxide are added, the closed bottle is shaken occasionally for two hours, the mixture being then acidified with sulphuric acid, and the excess of ferrous sulphate titrated with permanganate solution. In the second method, the water is similarly treated with 1 gram of manganous sulphate, a small quantity of potassium hydroxide, and a few crystals of potassium iodide; after two hours the mixture is acidified with hydrochloric acid, and the liberated iodine is titrated.

W. P. S.

**Volumetric Estimation of Sulphurous Acid in Wines.** L. FERRÉ (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, 31, 959—963).—The wine (100 c.c.), with 2 c.c. of phosphoric acid, is gently boiled for half an hour in a reflux apparatus connected with two Strauss and Wurtz's absorption vessels containing, respectively, solutions of iodine (40 c.c.) and sodium thiosulphate (5 c.c.). Carbon dioxide is passed through the whole apparatus for some minutes before the wine is heated and during the heating. The two solutions are then transferred to a beaker and titrated with thiosulphate solution, with soluble starch as indicator (Mathieu, A., 1910, ii, 747). The iodine solution contains 3.968 grams of iodine per litre, 1 c.c. corresponding with 1 mg. of sulphur dioxide. The thiosulphate solution contains 7.740 grams per litre.

The combined sulphurous acid is estimated, in a similar apparatus, in 100 c.c. of the wine, an amount of iodine solution equivalent to the total sulphurous acid, as previously estimated, and the same amount of a solution of sodium arsenite. The amount of combined sulphur dioxide =  $10[40 - (n + 5)]$ , *n* being the number of c.c. of iodine solution added to the wine.

The sodium arsenite solution is prepared by dissolving about 1 gram of arsenious acid and 3 grams of crystallised sodium



carbonate in 500—600 c.c. of water. The solution is then made equivalent to the iodine solution. N. H. J. M.

**Apparatus for the Estimation of Hydrogen Sulphide in Water.** GEO. B. FRANKFORTER (*J. Ind. Eng. Chem.*, 1914, 6, 676—677).—The apparatus is all in one piece, and consists of a burette and a flask, or bulb, holding 500 c.c.; a three-way tap is provided between the burette and the flask, a side-tube on the neck of the flask being also fitted with a three-way tap. Both these taps are turned so that the flask is in communication with the air; the apparatus is then immersed in the water of which a sample is to be taken, and, on withdrawing the apparatus, a portion of the water flows out of the tap on the side-tube, leaving the flask filled to a definite level. Starch solution is then admitted through the side-tube, and the water is titrated with iodine solution contained in the burette. In a modification of the apparatus the flask is provided with a tap at the bottom, and a tube extends from this tap to a definite height in the flask. A tap or stopper is provided at the top of the burette so that the contents of the flask may be shaken during the titration without loss of solution from the burette. W. P. S.

**Micro-Kjeldahl Estimations.** A. V. SAHLSTEDT (*Chem. Zentr.*, 1914, i, 2121; from *Skand. Arch. Physiol.*, 1914, 31, 367—380).—The method proposed by Pilch (A., 1911, ii, 225) was found to be more trustworthy than that described by Folin and Farmer (A., 1912, ii, 702). W. P. S.

**Detection of Nitric Acid with Ferrous Sulphate.** I. BELLUCCI (*Ann. Chim. Applicata*, 1914, 1, 549—558).—In presence of ferrous sulphate and sulphuric acid, selenious acid in small proportion undergoes reduction to selenium, which at first forms a purple coloration. This cannot, however, be confused with the coloration given by nitric acid, since the selenium rapidly settles to the bottom of the liquid in a finely divided state.

In the reaction with nitric acid, this is first reduced to nitric oxide, and if the latter acts on aqueous ferrous sulphate, in the presence or absence of a small proportion of sulphuric acid, the dark-brown cation,  $\text{Fe}(\text{NO})^{++}$ , is formed; here the iron remains bivalent, and the nitric oxide functions as a neutral molecule. When the solution contains sulphuric acid, the salt  $\text{Fe}(\text{NO})\text{SO}_4$  is formed. The complex cation is readily dissociated, and the nitric oxide may be completely eliminated from the solution and the coloration destroyed by heating. In testing for nitric acid, it is therefore necessary to prevent excessive rise of temperature of the liquid.

When, however, nitric oxide acts on a solution of ferrous sulphate containing sulphuric acid in sufficient concentration, the liquid assumes an intense amethyst-red coloration, which changes to brown on slight dilution with water, the reverse change being subsequently effected by addition of concentrated sulphuric acid.

Under the influence of an electric current, the coloured zone of the red solution migrates towards the anode, whilst that of the brown liquid moves to the anode. In the case of the red solution, the colour is due to the anion,  $\text{Fe}(\text{SO}_4)_x\text{NO}$ .

If the nitric acid is mixed with the ferrous sulphate and sulphuric acid, there is a risk of the immediate oxidation of the ferrous iron by the acid and of the prevention of the formation of the cation  $\text{Fe}(\text{NO})$ . When, however, the liquids are in layers, the nitric acid is in excess only at the zone of contact, so that time is allowed for the manifestation of the coloration (see below); a further advantage of this procedure is the possibility of using concentrated sulphuric acid and an excess of ferrous sulphate together, the limited solubility of the salt in the acid otherwise coming into play.

The reduction of the nitric acid by the ferrous sulphate takes place rapidly in presence of concentrated sulphuric acid, and only slowly, or not at all, if the proportion of sulphuric acid present is small. The volume of acid taken should be at least as great as that of the liquid to be tested, and the nitrate should either be dissolved in a little water or, when this is not possible, be added in the solid state to the sulphuric acid.

The best results are obtained by mixing the nitrate solution with the sulphuric acid, and by pouring the cold, saturated ferrous sulphate solution carefully on to the surface of the mixture while the latter is still hot. Equal rapidity of action is obtained by introducing a mixture of the ferrous sulphate and the nitrate solutions on to the surface of the sulphuric acid, but the intensity of the coloration and the thickness of the ring are less than in the former case, whilst the coloration disappears more rapidly. When the nitrate solution forms the upper layer, and the mixture of ferrous sulphate and sulphuric acid the lower one, the test is considerably less delicate.

When attention is paid to the above points, 1 part of nitric acid can be detected in 250,000 parts of sulphuric acid. If, however, small traces of nitric acid are to be sought, the use of strata loses its objects, and the best results are obtained by mixing the solutions. For this end, 2.5 grams of ferrous sulphate are dissolved in 6—8 c.c. of water containing a few drops of dilute sulphuric acid, and the solution added to 1000 grams of 90% sulphuric acid (compare Manchot and Huttner, A., 1910, ii, 414). This reagent remains unchanged for a long time in a closed vessel, and allows of the detection of 1 part of nitric acid in 500,000 of sulphuric acid.

T. H. P.

**Fresenius' Method for Estimating Small Quantities of Nitrites and its Sensitiveness Compared with the *m*-Phenylenediamine Reaction.** E. A. LETTS and FLORENCE W. REA (*Analyst*, 1914, 39, 350—352).—The zinc iodide-starch solution described by Fresenius for the colorimetric estimation of nitrites was found to be capable of detecting as little as 0.00025 mg. of nitrite-nitrogen, and to be about twenty times more sensitive than

the *m*-phenylenediamine reaction. A freshly prepared zinc iodide-starch reagent appears to be less sensitive than a similar solution one year old.

W. P. S.

**Use of Ammonium Citrate in the Estimation of Phosphoric Acid [in Slags].** A. QUARTAROLI and A. ROGAI (*Chem. Zentr.*, 1914, ii, 263—264; from *Staz. sperim. agrar. ital.*, 1914, 47, 410—426).—The chief sources of error in the estimation of phosphoric acid in Thomas slag lie in the precipitation of magnesium iron compounds and in the incomplete precipitation of the phosphoric acid with magnesia mixture. When the magnesium pyrophosphate is not quite white, the presence of iron is indicated; this may be removed by treatment with “cupferron.” The citrate method cannot be used when iron and aluminium phosphates are present.

W. P. S.

**Estimation of Arsenic in Organic Substances.** MARIAM VINOGRAD (*J. Amer. Chem. Soc.*, 1914, 36, 1548—1551).—For the oxidation of organic matter previous to the estimation of arsenic in such substances as blood, tissue, etc., it is recommended that the substance be heated with nitric acid at 260° in a sealed tube. One c.c. of nitric acid is sufficient to oxidise 3 c.c. of blood serum, the residue obtained on evaporating 100 c.c. of spinal fluid, or 0.5 gram of dry tissue. After the oxidation, the contents of the tube are diluted, evaporated to a small volume, and heated with sulphuric acid until all nitric acid has been expelled. The arsenic is then estimated by Sanger and Black’s modification of the Gutzeit method (A., 1908, ii, 64).

W. P. S.

**Estimation of Potassium and Magnesium by Physico-chemical Volumetric Methods. Application to the Analysis of Wines.** MARCEL DUBOUX (*Compt. rend.*, 1914, 159, 320—323. Compare Dutoit and Duboux, A., 1908, ii, 781, 892).—Potassium can be estimated in wines by determining the conductivity of the solution after the repeated additions of small amounts of chloroplatinic acid, after the addition of eighteen times its volume of alcohol. A change in the direction of the conductivity curve indicates the end of the precipitation. It is necessary to wait some time for the conductivity to become constant after each addition of the reagent, and also to destroy the organic matter in the wine by evaporation and ignition prior to the estimation. For the estimation of magnesium, the conductivity is measured in a solution containing 0.02% of ammonia and 0.06% of ammonium chloride after the addition of measured small quantities of *N*/2-phosphoric acid. Before performing the titration, the organic acids in the wine must be destroyed and the phosphoric acid and lime removed by precipitation. Fifty c.c. of the wine are treated with 3 c.c. of *N*-sulphuric acid and 100 c.c. of alcohol. After two hours the calcium sulphate is filtered off, and to the filtrate is added 3.5 c.c. of *N*-ammonia and 7 c.c. of a 16% solution of lead nitrate, which precipitates the phosphates. The whole is warmed on the water-

bath, filtered, and to the filtrate 5 c.c. of *N*-sulphuric acid are added and the lead sulphate filtered off. The solution is evaporated to dryness and calcined, the residue is dissolved in 5 c.c. of *N*/10-HCl, 50 c.c. of *N*/10-ammonia are added, and the liquid titrated with the phosphoric acid. W. G.

**Estimation of Calcium in Urine and Fæces.** R. von DER HEIDE (*Biochem. Zeitsch.*, 1914, **65**, 363—380).—A detailed investigation is made of the estimation of calcium by Aron's method, according to which the metal is precipitated as sulphate by alcohol in the liquid obtained after the destruction of organic matter by Neumann's wet-ashing method. It is shown that this method of precipitation of calcium has many sources of error, due to the fact, chiefly, that other substances are carried down with the calcium sulphate precipitate. The author recommends the following modification. The calcium sulphate precipitate is collected on a Gooch filter, and then dissolved in hot concentrated hydrochloric acid. The solution is neutralised to methyl-orange with ammonia, and ferric chloride (two to three drops of 10% solution) and acetate are added. In the hot filtrate from the precipitate thus produced, the calcium is precipitated as oxalate.

S. B. S.

**Estimation of Magnesia in Magnesite.** HENRYK WDOWISZEWSKI (*Chem. Zeit.*, 1914, **38**, 949—950).—In the estimation of magnesia by Mayrhofer's method (A., 1908, ii, 431), it is essential that the mixture be kept at 0° for two hours after the ammonium magnesium phosphate has been precipitated. The precipitate is then collected, washed with ammonia, dissolved in hydrochloric acid, reprecipitated by the addition of ammonia, and again cooled for two hours before being finally collected, dried, ignited, and weighed. W. P. S.

**Estimation of Copper as Cuprous Sulphide.** ERNST MURMANN (*Chem. Zentr.*, 1914, i, 2016; from *Oesterr. Chem. Zeit.*, 1914, [ii], **17**, 96).—A reply to C. Beck (A., 1913, ii, 1077), maintaining that the conversion of cupric into cuprous sulphide by ignition in a current of carbon dioxide should be rejected.

N. H. J. M.

**Estimation of Copper in Open Hearth and Alloy Steel or in Cast Iron.** E. D. KOEPPING (*J. Ind. Eng. Chem.*, 1914, **6**, 696).—From 3 to 10 grams of the steel are dissolved in 35 c.c. of hydrochloric acid (1:1), the solution is diluted with 35 c.c. of water, and boiled for twenty minutes after the introduction of a strip of sheet aluminium. The solution is then filtered, the precipitated copper is washed with hot water, and dissolved in a mixture of 3 c.c. of nitric acid and 7 c.c. of water; this acid solution is first poured over the strip of aluminium to dissolve adhering copper. The solution and washings are boiled for fifteen minutes to expel nitrous fumes, 7 c.c. of ammonia are added, and the boiling continued until only a small quantity of free ammonia remains.

Ten c.c. of 80% acetic acid are now added, the mixture is boiled for one minute, cooled, potassium iodide is added, and the liberated iodine titrated with thiosulphate solution.

W. P. S.

**Estimation of Iron by Permanganate in the Presence of Hydrochloric Acid.** O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1914, **36**, 1429—1448).—Sodium sulphate, acid phosphate mixtures, manganese sulphate with sulphuric acid or phosphoric acid, and cerous sulphate, may be employed in the titration of a hydrochloric acid solution of ferrous salts in order to prevent the action of the hydrochloric acid on the permanganate used for the titration.

W. P. S.

**Estimation of Iron in the Presence of Phosphoric Acid.** C. E. CORFIELD and W. R. PRATT (*Pharm. J.*, 1914, **93**, 131—133).—The gravimetric estimation of iron in the presence of even small quantities of phosphate is untrustworthy, the results obtained being too high and not concordant. Volumetric methods are preferable; the iodometric process and reduction by stannous chloride may be employed in the presence of phosphoric acid, but the former process is liable to give slightly high results, owing to oxidation of the hydriodic acid on contact with air. Reduction of ferric salts by zinc or zinc-couples has the disadvantage that the subsequent titration with dichromate solution cannot be carried to completion.

W. P. S.

**Estimation of Chromium and Manganese in Iron and Steel.** FRED C. T. DANIELS (*J. Ind. Eng. Chem.*, 1914, **6**, 658—659).—The metals are estimated by the persulphate method. Chromium is estimated by dissolving 1 gram of the sample in 100 c.c. of nitric acid (D 1.135), boiling the solution to expel nitrous fumes, and then adding 75 c.c. of a 0.2% silver nitrate solution and 5 grams of ammonium persulphate. The mixture is boiled for one minute, and hydrochloric acid is added drop by drop until the permanganate has been reduced. The boiling is continued for one minute, the solution is then cooled, an excess of  $N/10$ -ferrous ammonium sulphate is added, and the mixture titrated with  $N/10$ -permanganate solution. The number of c.c. of  $N/10$ -ferrous ammonium sulphate solution oxidised by the chromate is multiplied by 0.00174 to obtain the quantity of chromium in the sample. Chromium and manganese are then estimated together in a separate portion of the sample. The same procedure is adopted, except that, after the addition of the persulphate, the solution is heated just to boiling, then cooled immediately, and treated with an excess of ferrous ammonium sulphate solution.

W. P. S.

**Volumetric Estimation of Titanium and Chromium by means of a Modified Reductor.** C. VAN BRUNT (*J. Amer. Chem. Soc.*, 1914, **36**, 1426—1429).—The reductor described is of the type proposed by Shimer and Shimer (A., 1913, ii, 723), but has a height

of about 20 cm., and is heated electrically by passing a current through a length of resistance ribbon wrapped round the exterior of the tube. For the analysis of a mixture containing iron, chromium, and titanium, the metals are brought into solution as their sulphates; a portion of the solution is treated with bismuth oxide, passed through the reductor, and the reduced solution is titrated; this gives the quantity of iron. A second portion is then reduced and titrated, the result giving the quantity of the three metals together. Chromium is estimated in another portion of the solution, by titration with a ferrous salt solution, after it has been converted into chromate by heating with ammonium persulphate.

W. P. S.

**Anomalies in the Analysis of Platinum Minerals.** H. C. HOLTZ (*Ann. Chim.*, 1914, [ix], 2, 56—63. Compare this vol., ii, 144).—Polemical. A reply to Wunder and Thüringer (*A.*, 1913, ii, 883).

W. G.

**Estimation of Iridium in Platinum-Iridium Alloys.** C. O. BANNISTER and E. A. DU VERGIER (*Analyst*, 1914, 39, 340—346).—Two methods are given; in the first, the platinum-iridium is alloyed with silver and parted, whilst in the second it is alloyed with lead and parted. *Method 1*: A quantity of 0.25 gram of the alloy is cupelled with 1.5 grams of pure silver and 10 grams of assay lead; when the last traces of lead have disappeared, the button is parted twice with 40 c.c. of concentrated sulphuric acid, and the insoluble residue washed with water, annealed at a high temperature, then digested with *aqua regia*, diluted with water, and the insoluble residue of iridium collected on a filter. After being washed with ammonia to remove traces of silver chloride, the iridium is ignited at a high temperature and weighed. If desired, the platinum may be estimated in the *aqua regia* solution. *Method 2*: 0.5 Gram of the alloy is melted in a carbon crucible with 5 grams of lead, the lead button is repeatedly digested with hot dilute nitric acid, and the insoluble residue then treated with *aqua regia* as described in method 1. Both methods yield trustworthy results.

W. P. S.

**Estimation of Organic Matter in Water.** PERCY KAY (*Chem. News*, 1914, 110, 13).—Potassium ferricyanide is recommended as an oxidising agent in preference to the method of Tidy usually employed, where the oxygen absorbed is much below the quantity actually needed to oxidise the organic matter. The procedure is as follows: About 500 c.c. of the water with 1.1 gram of ferricyanide and 3.5 c.c. of concentrated potassium hydroxide solution are boiled for an hour, and, after cooling, the excess of ferricyanide is determined by the addition, after acidification, of potassium iodide and excess of zinc sulphate, and titration of the liberated iodine with thiosulphate in slightly alkaline solution. The difference between the observed reading and a blank experiment is a measure of the oxygen absorbed by the organic matter.

A water giving an oxygen absorption of 2.56 per million by this process gave 2.34 by Wanklyn's moist combustion method, and only 0.72 by the ordinary method. G. F. M.

**Detection of Methyl Alcohol.** A. RINCK (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 98—99).—A small quantity of the alcoholic solution to be tested is distilled slowly, and the vapours are passed through a silica tube containing a copper spiral, which is maintained at a red heat by a flame placed below the tube. The distillate is collected in a cooled receiver, and a portion of it is tested with sulphuric acid and morphine for the presence of formaldehyde. W. P. S.

**Application of Physico-chemical Methods in the Analysis of Wines.** G. LO PRIORE (*Ann. Chim. Applicata*, 1914, **1**, 494—502).—The author discusses, and gives a bibliography of, the physico-chemical methods used in estimating the alcohol and acidity of wines, and in determining the distribution of the bases among the acids. T. H. P.

**Capillary Method of Estimating the Acidity of Wines.** R. DUBRISAY and X. ROCQUES (*Ann. Falsif.*, 1914, **7**, 341—346).—The method described previously by one of the authors (A., 1913, ii, 388) yields satisfactory results when applied to certain wines, but its usefulness is limited. It may be employed as a control method in comparing the acidity of two samples of wine. W. P. S.

**Estimation of Organic Phosphorus Compounds in Concentrated Musts and Wines.** CESARE FINZI (*Chem. Zentr.*, 1914, ii, 88; from *Staz. sperim. agrar. ital.*, 1914, **47**, 337—346).—One hundred c.c. of the must are evaporated at 47° under reduced pressure to a syrup; this is mixed with sand, dried over sulphuric acid under reduced pressure, and then extracted in a Soxhlet apparatus for twelve hours with anhydrous ether. The extraction is then continued for twelve hours with absolute alcohol, the pressure being reduced so that the temperature does not exceed 48°. The alcoholic extract is evaporated under reduced pressure, the residue fused with a mixture of potassium nitrate and sodium carbonate, and the resulting phosphate estimated by the molybdate method. In the case of wine, 500 c.c. of the sample are evaporated to dryness under reduced pressure, the residue extracted five times with anhydrous ether, then five times with absolute alcohol at 45°, and the alcoholic extract is treated as described. When the molybdate precipitate is converted into ammonium magnesium phosphate and weighed as magnesium pyrophosphate, the weight of the latter multiplied by 7.2703 gives the quantity of lecithin present. The organic phosphorus compounds appear to be derived from the juice and fleshy portions of the fruit, and, whilst there is no definite relation between the quantities of organic and inorganic phosphorus, a certain relation exists between the organic phosphorus and the protein-content. W. P. S.

**Estimation of Glycerol in Industrial Glycerins and in Soap Lyes.** M. TORTELLI and A. CECCHERELLI (*Ann. Chim. Applicata*, 1914, 1, 514—548).—The authors have investigated the "acetic" method recommended for the estimation of glycerol in crude glycerins by the International Committee in their publication of January, 1911. They find: (1) that this method is subject to a fundamental error, and must yield somewhat inaccurate results; (2) that Hehner's dichromate method, when slightly modified, gives exact results. Full details of this modified process, in its application to crude glycerins and to soap lyes, are given, together with the necessary tables. T. H. P.

**The Estimation of Esters in Essential Oils.** JEAN NIVIÈRE (*Bull. Soc. chim.*, 1914, [iv], 15, 677—680).—The author considers that the standard method for estimating esters in essential oils, using a long glass condenser, is accurate and gives concordant results, and that Béhal's modification, using a closed tube at 100° (compare this vol., ii, 686), is unnecessary. Further, the high results obtained in the case of oils of lavender and of bergamot when using a closed tube are not due to linalool. W. G.

**Cupropotassic Solutions, Barreswill's and Fehling's Solutions.** H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, 31, 978—981).—More than fifty cupropotassic solutions are known. They may be divided into four groups, in which (1) potassium hydrogen tartrate, (2) potassium sodium tartrate, (3) potassium tartrate, and (4) tartaric acid are employed. As the original process for estimating sugar in this manner was published by Barreswill (in 1843), and was, for several years, known as Barreswill's method, it is suggested, in accordance with the proposal recently made by Lindet, that the name "Barreswill solution" should be employed instead of "Fehling solution." N. H. J. M.

**Different Methods of Inversion.** A. GILLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, 31, 992—1033).—A study of the methods of Clerget, Herzfeld, Andrlík, Pellet, Saillard, and Ogilvie. As regards direct acid polarisation, both Pellet's and Andrlík's methods may be employed for molasses. Pellet's method is, however, preferred, and it is applicable to all sugar products.

Methods in which direct alkaline polarisation is compared with indirect acid polarisation should not be employed.

As regards beet juice, the different methods of inversion give less regular results than in the case of molasses. Pellet's and Andrlík's methods seem, however, to give the same results.

N. H. J. M.

**Polarimetric Estimation of Lactose in Milk.** E. FEDER (*Zeitsch. Nahr. Genussm.*, 1914, 28, 20—29).—The use of mercuric iodide and sulphuric acid, as in Scheibe's method, for precipitating casein and fat from milk previous to the estimation of lactose cannot be recommended, owing to the difficulty of ascertaining the



volume of the resulting precipitate; moreover, the rotatory power of the lactose is considerably influenced by the mercuric iodide and sulphuric acid mixture. When, however, the milk is curdled by the addition of asaprol, the precipitate consists essentially of proteins and fat, and its volume is approximately equal to the quantity of the total solids of the milk, less lactose and mineral matter. The following process is described for the estimation: Seventy-five c.c. of the milk are treated in a 100 c.c. flask with 6 c.c. of a reagent prepared by dissolving 75 grams of asaprol and 75 grams of citric acid in hot water, and diluting the solution to 250 c.c. The treated milk is then diluted to 100 c.c., shaken, filtered after fifteen minutes, and the filtrate polarised at  $20^{\circ}$  in a 200 mm. tube; under these conditions, each degree of rotation observed is equivalent to 0.9518 gram of lactose. The reading found is multiplied by 0.9518; let the result be  $a$ , then the actual quantity of lactose,  $L$ , is calculated from the equation

$$L = a\{100.8 - t + (96.7 - f)a/75\}/75,$$

where  $t$  is the percentage of total solids and  $f$  the percentage of fat in the milk. W. P. S.

**Estimation of Dextrin and Sugars in Foods.** C. F. MUTTELET (*Ann. Falsif.*, 1914, 7, 372—380).—In a solution, containing from 5 to 10 grams (total) per 100 c.c., of sucrose, dextrose, lævulose, and dextrin, the following estimations are made: (1) The reducing power of the solution is estimated, and the result expressed as grams of invert sugar per 100 c.c.,  $p$ . (2) The reducing power is estimated after inversion, and the result expressed in the same terms,  $q$ . (3) The reducing power is estimated after inversion in an autoclave at  $110^{\circ}$ , the result being also calculated into grams of invert sugar per 100 c.c.,  $m$ . (4) The rotation of the solution is determined at  $20^{\circ}$  in a 200 mm. tube; let  $D$  be the reading observed. Then the quantity of sucrose,  $S$ , present per 100 c.c. is  $0.95(q - p)$ , having a rotation,  $c$ , equal to  $1.33 \times S$ . The amount of dextrin,  $\Delta$ , is  $0.90(m - q)$ , having a rotation,  $\delta$ , of  $3.90 \times \Delta$ . The sum of the weights of the dextrose,  $G$ , and the lævulose,  $L$ , is equal to  $p$ , and the corresponding rotation,  $d$ , is  $D - (c + \delta)$ . The quantity of lævulose is, therefore,  $(1.06 \times p) - d$  grams, and of dextrose,  $(p - L)$  grams. W. P. S.

**Criterion for the Genuineness of Vinegar.** N. TARUGI (*Boll. Chim. Farm.*, 1914, 53, 129—137).—After its acidity has been determined, the vinegar is diluted so as to contain 0.6% of acetic acid ( $V=10,000$ ), and its electrical conductivity measured at  $25^{\circ}$ . Examination of a series of thirty-three samples of genuine vinegar gave 7.92, 9.81, and 11.36 as the minimal, mean, and maximal values of the molecular conductivity,  $M$ . Under similar conditions, the value for pure acetic acid was found to be 5.69, and that for a commercial sample containing 31.8% of acid 5.70; the molecular conductivity of vinegar would therefore be appreciably lowered by the addition of any considerable proportion of acetic acid. Commercial samples which had been adulterated with from

0.5% to 3.8% of sodium chloride, or with 2.0% of potassium sulphate, gave molecular conductivities varying from 11.81 to 18.88. The addition of small proportions of mineral acids also increases the conductivity. Thus, for diluted vinegars containing 0.59% of acetic acid and 0.01% of hydrochloric, sulphuric, and nitric acid respectively, the values of the molecular conductivity were 14.99, 14.20, and 12.27, the value for the original vinegar being 11.10.

The vinegar was next neutralised with sodium hydroxide prepared from the metal, diluted to  $V=10,000$ , and the conductivity again measured at  $25^{\circ}$ . After this treatment, a series of nineteen samples of genuine vinegar gave values for the molecular conductivity,  $M'$ , varying between 59.4 and 88.05. The ratio  $M':M$  has the minimal, mean, and maximal values 6.66, 7.94, and 9.98 respectively. The corresponding value for pure acetic acid is 12.14, whilst the vinegars adulterated with sodium chloride or potassium sulphate gave values between 4.17 and 5.72, and those containing 0.01% of hydrochloric, sulphuric, and nitric acids the values 4.82, 4.77, and 5.67 respectively. A sample of vinegar which was suspected to contain added acetic acid gave  $M=7.65$ ,  $M'=82.1$ , and  $M':M=10.7$ .

No relation exists between the value of the ratio  $M':M$  and the proportion of dry extract present in a vinegar. T. H. P.

**Estimation of Ricinoleic Acid in Oil Preparations.** FRANZ ERBAN (*Chem. Zentr.*, 1912, ii, 358; from *Seifenfabrikant*, 1914, 34, 493—495, 525—527, 556—557, 585—587).—Owing to the tendency of ricinoleic acid to form polymerides, the acid number does not indicate the quantity of this acid in fatty acid mixtures; for instance, whilst the acid number of ricinoleic acid is 188, that of di-ricinoleic acid is 96.8. The polymeric acids are, however, converted into the normal acid when submitted to saponification, and the acid number of the fatty acids obtained from the soap gives the proportion of ricinoleic acid present provided that the alteration in weight of the fatty acid mixture is taken into account. Formulæ are given in the original paper for calculating the composition of a mixture of ricinoleic acid and diricinoleic acid, of ricinoleic acid, diricinoleic acid, and neutral fat, of ricinoleic acid, lactide, and diglyceride, etc. W. P. S.

**Estimation of Lactic Acid in Wine by Moslinger's Barium Chloride Method.** W. I. BARAGIOLA and O. SCHUPPLI (*Zeitsch. Nahr. Genussm.*, 1914, 27, 841—881).—The following modification of the method is proposed, since the process as described originally (A., 1902, ii, 180) is liable to give untrustworthy results, owing to the reduction of barium chloride by carbon, to the retention of lactic acid by the alcohol-insoluble substances, and to the conversion of a portion of the lactic acid by malic acid into a compound in which the former acid is not estimated. Twenty-five c.c. of the wine are mixed with 25 c.c. of water, and distilled with steam until 200 c.c. of distillate have been collected; this distillate is treated with 5 c.c. of 10% barium chloride solution, and neutralised with

saturated barium hydroxide solution. In case any lactic anhydride is present, an excess of barium hydroxide may be added, the solution heated for ten minutes on a water-bath, and then neutralised with hydrochloric acid, using azolitmin paper as the indicator. The neutral solution is evaporated to 15 c.c., transferred to a 100 c.c. cylinder, diluted with water to 25 c.c., and 95% alcohol is added drop by drop while the mixture is shaken. The mixture is now diluted to 100 c.c. with alcohol, filtered after twenty-four hours, and 75 c.c. of the filtrate are treated with 25 c.c. of 5% sodium sulphate solution. The barium sulphate is removed by filtration, and 75 c.c. of the filtrate are evaporated to dryness; the residue is incinerated, the ash dissolved in water, and the boiling solution titrated with *N*/10-acid. W. P. S.

**Colour Reaction of Citric Acid.** E. P. HÄUSSLER (*Chem. Zeit.*, 1914, **38**, 937).—The solution to be tested is mixed with a few c.c. of an alcoholic vanillin solution and evaporated to dryness; the residue is then heated on a water-bath for fifteen minutes with four drops of dilute sulphuric acid, diluted with water, and rendered ammoniacal. A bright, red coloration is obtained if as little as 0.002 gram of citric acid is present. Tartaric, malic, oxalic, malonic, benzoic, salicylic, acetic, lactic, or succinic acids do not yield the reaction, and their presence does not greatly affect that given by citric acid. The test may be applied to fruit juices after the organic acids have been precipitated with lead acetate and separated as their calcium salts. W. P. S.

**Estimation of Refractivity and Dispersion in Fats and Oils.** K. SZALÁGYI (*Biochem. Zeitsch.*, 1914, **66**, 149—153).—These factors were determined in the cases of thirty-eight fats and oils at 45°. For the measurement of the dispersion, the light of a hydrogen spectrum was employed. It was found that these factors were not constant for any given oil, depending on the composition, method of preparation, and age of the various samples. S. B. S.

**Examination of Various Methods for the Estimation of the Iodine Number of Fats.** ST. WEISER and H. G. DONÁTH (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 65—73).—Winkler's potassium bromate method is recommended for the estimation of the iodine number of fats, oils, and fatty acids. A weighed quantity of the fat is dissolved in 10 c.c. of carbon tetrachloride, and 50 c.c. of *N*/10-potassium bromate solution, 1.5 grams of potassium bromide, and 10 c.c. of 10% hydrochloric acid are added. After one to four hours (ordinary fats require from one to two hours' contact, fish oils four hours), potassium iodide solution is added, and the liberated iodine is titrated. The results agree with those found by the Hübl, Wys, and Waller methods (compare A., 1910, ii, 1122). W. P. S.

**Preservation of Milk Samples for Analysis.** J. TILLMANS, A. SPLITTGERBER, and H. RIFFART (*Zeitsch. Nahr. Genussm.*, 1914, **27**, 893—901).—Mercuric chloride was found to be the most suitable

substance for preserving milk samples for subsequent analysis. The addition of 0.04% of mercuric chloride keeps the milk quite fresh for 120 hours, has no influence on the usual methods used in milk analysis, and does not interfere with the detection of nitrates in milk. Various objections are adduced against the use of thymol, phenol, chloroform, mustard oil, sodium fluoride, and potassium dichromate for the purpose mentioned. W. P. S.

**Detection of Acetone in Urine by Sobel's Method.** BEUTTNER (*Chem. Zentr.*, 1914, i, 2207; from *Schweiz. Apoth. Zeit.*, 1914, 52, 293—294).—Sobel's method (this vol., ii, 592) is untrustworthy; in the presence of nitric acid, a portion of the silver iodide, resulting from the decomposition of the iodoform with nitric acid, is converted into silver iodate, which is fairly soluble in dilute nitric acid. Iodine is also lost when the silver iodide containing iodate is ignited. The factor for converting silver iodide into acetone should be 0.082, and not 0.1171 as given by Sobel. W. P. S.

**Microchemistry of Some Anthraquinones.** EMAN. SENFT (*Chem. Zentr.*, 1914, ii, 82—83; from *Zeitsch. Allg. Osterr. Apoth.-Ver.*, 1914, 52, 165—166, 181—183, 201—202).—Rhodocladonic acid dissolves in sodium carbonate solution, yielding a reddish-brown colour, and the solution reduces potassium permanganate in the cold, with the formation of a red precipitate; the latter is only slightly soluble in the usual solvents, but nitric acid dissolves it to a colourless solution, whilst with sulphuric acid it gives a purple-red coloration. This coloration changes quickly to yellow, and the solution deposits red crystals. The author has detected the presence of rhodocladonic acid in members of the *Cladonia* species by means of these reactions. When heated considerably above its melting point, solorinic acid gives off yellow vapours, and yields a dichroic (greenish-yellow and red), crystalline sublimate, which dissolves in sulphuric acid to a violet solution; this colour changes to yellow, and an amorphous, yellow precipitate is formed; the precipitate crystallises gradually. The crystals thus obtained are coloured first red and then violet when treated with cold 10% potassium hydroxide solution, but are not dissolved; on heating, the alkali converts the crystals into an amorphous, violet precipitate. Solorinic acid is only slightly soluble in hot petroleum. Rhodophyscin, contained in the lichen, *Physcia endococcinea*, separates from boiling acetic acid in the form of orange-red crystals; it does not yield a sublimate. With sulphuric acid it yields a purple-red solution, from which a brown precipitate separates. Potassium hydroxide solution dissolves the substance, yielding a red solution, which afterwards deposits an amorphous, violet precipitate. Rhodophyscin is insoluble in hot petroleum. Blastenin, contained in *Blastenia arenaria* and *B. percrecata*, is soluble in chloroform, and yields a yellow sublimate, which is coloured red, but not dissolved, by potassium hydroxide solution. The sublimate gives a red solution with sulphuric acid; the solution changes to yellow, and lemon-yellow crystals are deposited.

Blastenin dissolves in hot petroleum, and the solution yields orange-yellow crystals. W. P. S.

**Detection of Small Quantities of Phloridzin Alone and in the Presence of Phlorin.** ERNST GRIESE (*Chem. Zentr.*, 1914, ii, 88—89; from *Beitr. Physiol.*, 1914, 1, 23, 52).—Traces of phloridzin may be detected by means of reactions with ferric chloride, Millon's reagent (brownish-red precipitate), or mercurous nitrate (white precipitate). With ferric chloride and Millon's reagent a reaction is obtained with 1 c.c. of a 0.002% phloridzin test solution; the mercurous nitrate is about five times more sensitive. Phlorin free from phloridzin may be obtained by taking advantage of the slight solubility of the latter in ether and amyl alcohol (compare A., 1912, i, 885). W. P. S.

**Estimation of Acetanilide.** A. MIRKIN (*Amer. J. Pharm.*, 1914, 86, 354—355).—The method proposed depends on the conversion of the acetanilide into aniline, and the titration of the latter with sodium nitrite solution. One gram of acetanilide is boiled for four hours with a mixture of one part of sulphuric acid (D 1.84) and five parts of water. The solution is then cooled, neutralised with sodium hydrogen carbonate, hydrochloric acid is added (6 mols. to 1 mol. aniline), the mixture cooled to  $-10^{\circ}$ , and titrated with standardised sodium nitrite solution. Potassium iodide-starch paper is used as the indicator; the diazotising reaction proceeds slowly, and several minutes should elapse after the addition of each quantity of the nitrite solution before a drop of the solution is placed on the test paper. W. P. S.

**Estimation of Acetanilide and Phenacetin in Admixture.** W. O. EMERY (*J. Ind. Eng. Chem.*, 1914, 6, 665—669).—The process described depends on the formation of an insoluble iodine additive compound, or periodide, when phenacetin in aqueous solution is added to an iodine solution containing hydrochloric acid; in the case of acetanilide, the iodine compound is soluble. A quantity of 0.2 gram of the phenacetin-acetanilide mixture is dissolved by warming with 2 c.c. of acetic acid and 40 c.c. of water, and the solution is rinsed into 25 c.c. of *N*/5-iodine solution, previously heated to  $40^{\circ}$ ; 3 c.c. of concentrated hydrochloric acid are then added, and, when a crystalline precipitate has formed, the mixture is cooled and diluted with water to about 98 c.c. After eighteen hours the solution is diluted to 100 c.c., filtered, and 50 c.c. of the filtrate are titrated with *N*/10-thiosulphate solution. Each c.c. of *N*/10-iodine solution which has entered into combination corresponds with 0.00889 gram of phenacetin. The phenacetin may also be estimated gravimetrically by collecting the precipitate, washing it with iodine solution, then with a small quantity of water, transferring it to a separating funnel, and, after the addition of sodium sulphite, extracting the phenacetin with chloroform. The acetanilide is estimated by treating 30 c.c. of the filtrate from the iodine compound with sodium sulphite and

an excess of sodium hydrogen carbonate, shaking the solution with chloroform, and heating the chloroform solution for one hour on a water-bath with 10 c.c. of dilute sulphuric acid. Ten c.c. of concentrated hydrochloric acid are then added, and the mixture is titrated with standardised potassium bromide-bromate solution.

W. P. S.

**New Method for the Estimation of Phenolphthalein.** A. MIRKIN (*Amer. J. Pharm.*, 1914, 86, 307—308).—The method depends on the formation of an oxime when phenolphthalein is treated with hydroxylamine. One gram of phenolphthalein, 0.8 gram of hydroxylamine hydrochloride, and 0.52 gram of sodium hydroxide are dissolved in 40 c.c. of absolute alcohol, and the solution is boiled for about three hours under a reflux apparatus until the liquid turns yellow. Water is then added, 10 c.c. of 10% sulphuric acid are introduced, and the solution is diluted to 250 c.c. In 50 c.c. of this solution the acid is neutralised, using methyl-orange as indicator, and the excess of hydroxylamine then titrated with *N*/10-potassium hydroxide solution, phenolphthalein being the indicator in this case. A blank experiment, using the same quantities of sodium hydroxide, hydroxylamine, and alcohol, is run at the same time, and the difference between the number of c.c. of *N*/10-alkali solution required in the two titrations is multiplied by 316 to give the quantity of phenolphthalein. For the estimation of phenolphthalein in medicinal tablets, the latter are crushed, extracted with alcohol, and a portion of the alcoholic solution used for the estimation. These tablets frequently contain lactose and sucrose; the latter does not yield an oxime, and lactose is practically insoluble in alcohol.

W. P. S.

**A Method of Estimating Urea.** A. DESGREZ and R. MOOG (*Compt. rend.*, 1914, 159, 250—253. Compare A., 1912, ii, 104).—A description of a modified form of ureometer (*loc. cit.*), by means of which it is possible to make a rapid and accurate estimation of the amount of urea in urine or serum, 1 c.c. of urine being used. The apparatus is figured in the text, and only requires the use of a small amount of chloroform as compared with the earlier pattern (*loc. cit.*). The reagent used is prepared by dissolving 1 gram of mercury in 2 grams of nitric acid (D 1.3322), and diluting this with an equal volume of a liquid prepared by shaking 1 gram of infusorial earth with 100 c.c. of water, leaving one minute, and then decanting. This suspension acts as a catalyst, and renders the decomposition of the urea complete at 17°. The only other nitrogenous constituent of urine decomposed under these conditions is allantoin, and this only at the rate of 0.015 gram in twenty-four hours. The actual estimation takes about forty-five minutes.

W. G.

**Gravimetric Estimation of Small Quantities of Urea at Dilutions Greater than 1 in 1000.** R. FOSSE (*Compt. rend.*, 1914, 159, 253—256. Compare this vol., i, 859; ii, 593).—In

order to estimate the amount of urea in solutions containing 1 gram or less of urea in 1 litre, the following process should be adopted. The solution of urea (1 c.c.), exactly measured, is diluted with twice its volume of glacial acetic acid, and then to it is added one-twentieth of its volume of a solution of xanthhydrol in methyl alcohol, this addition being repeated twice at intervals of ten minutes. After one hour, the precipitate is collected in the usual way. An alternative process is as follows. To a mixture containing one volume of the urea solution and two volumes of glacial acetic acid, one-twentieth of its total volume of xanthhydrol solution is added, the whole allowed to remain one hour, and the precipitate collected. W. G.

**Estimation of Small Quantities of Urea by Sodium Hypobromite.** W. MESTREZAT (*J. Pharm. Chim.*, 1914, [vii], 10, 100—108).—Four c.c. of blood or other liquid to be analysed, 2 c.c. of water, and 5 c.c. of sodium hypobromite solution are introduced successively into a small, graduated tube provided with a tap at each end, and filled previously with mercury. The lower part of the tube, below the graduated portion, is slightly enlarged. After the contents of the tube have been well shaken, the apparatus is immersed in water at a definite temperature, and the volume of the gas is then observed, the mercury level having been adjusted. The author finds that mercury does not liberate any gas from sodium hypobromite in the absence of urea. It is recommended that the hypobromite solution be submitted to a low pressure before use, in order to remove dissolved oxygen. W. P. S.

**Gravimetric Estimation of Urea in Blood.** R. FOSSE, A. ROBYN, and F. FRANÇOIS (*Compt. rend.*, 1914, 159, 367—369. Compare Hugounenq and Morel (*Compt. rend. Soc. Biol.*, 1913, 1914).—Ten c.c. of the blood serum are mixed with 10 c.c. of Tanret's solution of potassium mercuriodide in acetic acid and centrifuged. The clear liquid measures about 17 c.c., and of this an aliquot portion, 15 c.c., is taken; to it is added 30 c.c. of glacial acetic acid and three portions of 0.75 c.c. of a 10% solution of xanthhydrol in methyl alcohol. After one hour the precipitate is collected, dried, and weighed. The urea present is equal to one-seventh of the weight of the precipitate, and the volume of defecated serum may be taken as equivalent to one-half its volume of fresh serum for purposes of calculation. W. G.

**Estimation of Caffeine in Coffee.** G. FENDLER and W. STÜBER (*Zeitsch. Nahr. Genussm.*, 1914, 28, 9—20).—Although the methods described by Lendrich and Nottbohm (A., 1909, ii, 449), and by Katz (A., 1903, ii, 250), are trustworthy, they are somewhat tedious, and the following process is therefore recommended; the results obtained agree with those yields by the methods mentioned above. Ten grams of the powdered sample are shaken for thirty minutes with 10 grams of 10% ammonia and 200 grams of chloroform; the solution is then poured on a large filter, and 150 grams

of the filtrate are evaporated to dryness. The residue is digested for ten minutes with 80 c.c. of hot water, cooled, and 20 c.c. of 1% potassium permanganate solution are added (10 c.c. are sufficient in the case of raw coffee). After fifteen minutes a slight excess of hydrogen peroxide (3% hydrogen peroxide containing 1% of glacial acetic acid) is added, the mixture is heated for fifteen minutes on a water-bath, more hydrogen peroxide is added until the solution becomes clear, and then cooled and filtered, the filter and its contents being washed with cold water. The filtrate is shaken first with 50 c.c. of chloroform, then with three successive quantities of 25 c.c. of the solvent; the united chloroform extracts are evaporated to dryness, the residue of caffeine is dried at 100°, and weighed. A method proposed by Keller was found to be untrustworthy.

W. P. S.

**Characterisation of Morphine and Phenols by means of Uranium Salts.** J. ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1914, [iv], 15, 680—682. Compare 1903, ii, 581; 1905, ii, 616).—Morphine in the free state or in the form of its hydrochloride can be detected as follows. To a small amount of the alkaloid in a test-tube a few drops of methyl alcohol and a crystal of uranyl nitrate are added, when the liquid becomes coloured red. If the base is present as its hydrochloride, uranyl acetate is used instead of the nitrate, and on evaporating the liquid to dryness a red residue is left. The test will show the presence of 0.1 mg. of the alkaloid. Phenols give a similar reaction, and where they are soluble in water the alcohol can be omitted and water used in its place. The greater the number of hydroxyl groups present, the more intense is the red coloration. The presence of other groups does not, as a rule, interfere with the test, except in the case of sulphonic or nitr-groups. The colouring matter is soluble in water, and is not extracted from aqueous solution by organic solvents. It is destroyed both by acids and bases.

A red liquid is also obtained by warming uranium oxide with an aqueous solution of resorcinol, or with a solution of morphine in methyl alcohol, and from the latter solution addition of ether causes a voluminous precipitate containing uranium.

W. G.

**Estimation of Morphine in Pills, Tablets, Etc.** J. B. WILLIAMS (*Amer. J. Pharm.*, 1914, 86, 308—312).—A number of pills or tablets, equivalent to from 0.1 to 0.2 gram of morphine, are dissolved in a few c.c. of dilute acid, the solution is transferred to a separator, 25 c.c. of a solvent consisting of 1 volume of alcohol and 2 volumes of chloroform are added, the mixture is rendered distinctly alkaline with ammonia, and shaken for three minutes. The chloroform layer is drawn off, and the extraction twice repeated with the alcohol-chloroform solvent. The extracts are evaporated to dryness, the residue dissolved in a definite quantity of *N*/10-acid, and the excess of acid is titrated with *N*/50-alkali solution, using cochineal as indicator. Each c.c. of *N*/10-acid is equivalent to 0.0301 gram of morphine.

W. P. S.



**Estimation of Strychnine in the Presence of Brucine.** D. B. DORT (*Pharm. J.*, 1914, 93, 120).—In the method of estimating strychnine in the presence of brucine by destroying the latter with dilute nitric acid, and then extracting the strychnine with an immiscible solvent, the best results are obtained when 1 c.c. of concentrated nitric acid is added to every 20 c.c. of the sulphuric acid solution of the two alkaloids; the action of the nitric acid should proceed for twenty minutes at the ordinary temperature. Under these conditions, 1 c.c. of nitric acid will destroy 0.25 gram of brucine without having any effect on the strychnine.

W. P. S.

**Diascopy of Traces of Blood.** ANGELO DE DOMINICIS (*Boll. Chim. Farm.*, 1914, 53, 162—163).—The following procedure serves to detect traces of blood in cases where all other methods fail, and is especially valuable where a very small quantity of blood is present on heavily rusted iron.

With dried blood adhering to a substrate, a scarcely visible particle is introduced into a trace of origanum oil on a microscope slide placed on a white background, and is thoroughly disintegrated by means of the rounded end of a glass rod. After the addition of a drop of a saturated or more dilute solution of eosin in paracetaldehyde, the preparation is examined in artificial light passing through a suitable diaphragm. A drop of euparal may be employed subsequently to render the preparation permanent. Where the blood has penetrated the substrate, the latter and the blood are scraped off by means of a sharp knife in the form of a fine powder, which is treated as above. Particles of blood appear wholly or partly coloured, and the red corpuscles, in groups or isolated, may be distinguished; the diameter of the corpuscles can be measured.

T. H. P.

**The Analysis of Meat Extract.** J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1914, 92, 214—220. Compare A., 1913, i, 1132).—The author compares four different methods for the quantitative separation of the bases from the same extract of beef: (1) precipitation of the bases with mercuric sulphate without previous treatment with lead acetate, the precipitate being then decomposed by hydrogen sulphide, and the bases isolated by means of phosphotungstic acid; (2) precipitation with phosphotungstic acid after preliminary treatment with lead acetate; (3) precipitation with phosphotungstic acid in the presence of 5% sulphuric acid; (4) direct precipitation with phosphotungstic acid without any preliminary treatment.

Expressing the results in percentages of fresh ox muscle, the first method furnished the largest amount of purine (0.062), carnosine (0.318), and carnitine (0.037), but only 0.048% of methylguanidine, as against 0.066% obtained by methods (2) or (3). The preliminary treatment with lead acetate is quite superfluous, and, indeed, leads to twice the quantity of expensive phosphotungstic acid being subsequently required, on account of the

inhibiting action of acetates on the precipitation of the phosphotungstates. Method (1) is therefore recommended from all points of view. H. W. B.

**Estimation of the Acidity of Leather.** PAUL NICOLARDOT (*Ann. Chim. anal.*, 1914, 19, 250—259).—The leather is extracted with chloroform to remove fatty substances, and is then boiled with water for three hours; the acidity of the filtered solution is estimated by titration, litmus paper being the indicator. Sulphuric acid and soluble sulphates are estimated in the solution in the usual way. Another portion of the leather may be boiled with the same volume of water and for the same length of time but in the presence of barium carbonate, and the acidity of the solution is estimated after filtration. In this case, the sulphuric acid and sulphates present are converted into barium sulphate. The total sulphur is best estimated by burning the leather in a bomb apparatus with oxygen under a pressure of 10 atmospheres. W. P. S.

**Analysis of Stabilised Cocoa.** L. REUTTER (*Chem. Zentr.*, 1914, ii, 169—170; from *Schweiz. Apoth. Zeit.*, 1914, 52, 308—312, 322—325, 335—339).—The usual method of submitting cocoa pods to fermentation in order to effect the ready removal of the husks has the disadvantage that the fermentation considerably affects the beans. The same object may be attained by immersing the pods for ten minutes in 1% sodium carbonate solution at 45°; the beans are then submitted to a sterilising process. Cocoa prepared in this way is known as stabilised cocoa; it does not contain pre-formed sugars or free theobromine. Caffeine is not present, but traces of essential oils can be detected. The following substances were separated from the methyl alcohol extract of the fat-free cocoa: cocoa red,  $C_{40}H_{60}O_{27}N$ ; cocoa brown,  $C_{76}H_{78}O_{34}N$ ; and cacaorin,  $C_{10}H_{20}O_6N_8$ . The theobromine is present in the cocoa in combination with other substances, and is set free when the cocoa is subjected to the action of ferments. W. P. S.

**Estimation of Certain Soluble Constituents of Soils.** A. HUTIN (*Ann. Chim. anal.*, 1914, 19, 259—263).—The water soluble substances are estimated by shaking 1 kilo. of the soil with 1 litre of water for thirty minutes, and filtering the mixture after twenty-four hours' contact. The filter should be partly filled with dried paper pulp. Two hundred and fifty c.c. of the filtrate are evaporated to dryness, and the residue is weighed. This residue is then incinerated, and the ash weighed to obtain the quantity of soluble mineral matter. The alkalinity of the soil is ascertained by titrating a definite volume of the filtrate, and the chlorides are estimated by the Charpentier-Volhard method. W. P. S.

## General and Physical Chemistry.

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**Wave-lengths of Hydrogen Lines and Determination of the Series Constant.** W. E. CURTIS (*Proc. Roy. Soc.*, 1914, [A], 90, 605—620).—The wave-lengths of the first six lines in the series spectrum of hydrogen have been measured with the greatest possible accuracy in order to determine the exact relationship between the wave-lengths of the series lines. The accuracy attained is of the order of 0.001 Å, but the actual accuracy depends on the time of exposure, increasing with the length of this period in consequence of changes in the temperature of the instrument.

The results obtained show that Balmer's formula does not afford an exact representation of the relation between the wave-lengths of the various lines. The numbers can, however, be accurately represented by a modified Rydberg formula,  $n = N/4 - N/(m + \mu)^2$ , in which  $N = 109679.22$  and  $\mu = 0.069$ . This formula gives the convergence frequency of the series as 27419.805, corresponding with a wave-length (in air) of 3645.981 international units.

Up to the present, the Balmer series of hydrogen lines has usually been regarded as of the diffuse type. It is suggested that in this case the sharp and diffuse series practically coincide, and that the Balmer series represents the superposition of the two.

H. M. D.

**Absorption Spectrum of Zinc Vapour.** J. C. McLENNAN (*Phil. Mag.*, 1914, [vi], 28, 360—363).—It has been found that zinc vapour shows an absorption band at  $\lambda$  2139.33, but no evidence of any absorption at  $\lambda$  3075.99 was obtained even at the highest temperatures employed in the experiments. The three lines, mercury  $\lambda$  1849.6, cadmium  $\lambda$  2288.79, and zinc  $\lambda$  2139.33, are homologous, and correspond with a value of  $m = 2$  in Paschen's single line series,  $n = 1.5$ ,  $S - mP$ . It is probable that these series of lines are to be attributed to atoms of the respective metals in the neutral state.

H. M. D.

**Absorption Spectra at Very Low Temperatures.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 953—959).—In view of the fact that the bands of the phosphorescence spectra of uranyl salts become narrower and more clearly defined at very low temperatures, the author has investigated the absorption spectra of uranyl sulphate, chloride, bromide, iodide, and *o*- and *p*-hydroxybenzoates at temperatures somewhat above  $-180^\circ$ . At such temperatures solutions of the salts in ethyl alcohol solidify to transparent, glassy masses suitable for observation; addition of glycerol or methyl alcohol to the ethyl alcohol lowers the solidifying point considerably, but the solutions then give either an opaque mass or a transparent one, which rapidly disintegrates. The absorption

bands are found to become clearer, and to be appreciably displaced at the low temperatures used; in some cases new bands make their appearance.

Examination of various colouring matters in the same manner shows that at about  $-180^{\circ}$  the absorption bands differ but very slightly in position and clearness from those observed at ordinary temperatures. It seems, therefore, that the influence of low temperatures on the absorption bands is pronounced only with compounds, the selective absorption of which is a property of one of the constituent elements.

T. H. P.

**Action of Radium Emanation on Explosive Gas.** OTTO SCHEUER (*Compt. rend.*, 1914, 159, 423—426. Compare this vol., ii, 649).—Hydrogen and oxygen readily combine under the influence of radium emanation, and in one case the combination was accompanied by an explosion. The products of the reaction are water and hydrogen peroxide, the water probably being formed as a decomposition product of the hydrogen peroxide. No ozone could be detected, and but little is formed when working with oxygen alone under the same conditions (compare Lind, A., 1911, ii, 841).

W. G.

**Immutability of the Uranium Radiation.** W. P. JORISSEN and J. A. VOLLGRAFF (*Chem. Weekblad.*, 1914, 11, 832—837).—Exposure to cathode rays produces no change in the activity of uranoso-uranic oxide. The increase noted by Jorissen and Ringer (A., 1907, ii, 422, 731) was due to changes in the surface-area of the preparations employed.

A. J. W.

**Electrification at Liquid-Gas Surfaces.** H. A. McTAGGART (*Phil. Mag.*, 1914, [vi], 28, 367—378).—The velocity with which small bubbles of air move through various liquids under the influence of an electric field has been examined in a series of experiments with aqueous solutions of various alcohols and fatty acids. In particular, the dependence of the velocity on the size of the bubble and on the concentration of the solution was investigated.

The addition of alcohols (or fatty acids) reduces the velocity of the bubbles, and therefore the electrification at the liquid-gas surface, the effectiveness of any alcohol in this respect corresponding with its effectiveness in reducing the surface tension of water. This reduction of surface tension is caused by a positive adsorption of alcohol into a surface layer of small thickness. The fact that the difference between the velocities for pure water and a given solution diminishes as the diameter of the gas bubble decreases, indicates that the degree of adsorption is dependent on the curvature of the surface. At the moment of disappearance of the bubble, the concentration of the surface layer is equal to that of the surrounding solution.

Experiments with air bubbles in pure alcohols show that there is no electrification at the surface of contact with the liquid. This and other evidence indicates that the electrification phenomena

observed in "water-fall" experiments are not due to the potential differences which come into play in the cataphoresis experiments.

H. M. D.

**Emission of Electric Charges by Salts Non-radioactive at the Ordinary Temperature.** D. PACINI (*Nuovo Cim.*, 1914, [vi], 7, i, 267—290).—Further study of the phenomenon already described by the author (A., 1907, ii, 425) and others with ammonium, sodium, potassium and barium sulphates, ammonium nitrate and potassium bromide gives results which indicate that the property of emitting electric charges is to be attributed to the action, probably an electrochemical one, of water-vapour on these salts. The charges seem to be carried by ions, and the hypothesis is advanced that the phenomenon is one of molecular dissociation, the nucleus of the predominating positive ions being an atom of the metal or, more probably, one of hydrogen generated by the dissociation of the water-vapour. The effects of change of pressure, temperature, and intensity of field were studied. Indications of a "fatigue" of the phenomenon could not be corroborated.

T. H. P.

**Conductivity of Salt Vapours.** S. J. KALANDYK (*Proc. Roy. Soc.*, 1914, [A], 90, 634—647).—The conductivity exhibited by the vapours of the halogen salts of zinc and cadmium has been investigated. It is shown that the conductivity is mainly due to processes occurring in the vapours themselves, and is practically independent of the emission of charges from the surface of the heated salt. The vapours of carefully dried salts exhibit marked conducting power, although this is greatly increased in the presence of water-vapour. The greatest increase was observed in the case of zinc iodide, which is the most hygroscopic of the substances examined.

Although previous experiments (compare Garrett, A., 1907, ii, 524) have shown that in ordinary circumstances the conductivity of the salt vapour seems to vary with the duration of the experiment, the author has found that carefully dried cadmium iodide gives rise to a steady current.

The connexion between the current  $i$  and the temperature  $\theta$  can be expressed with considerable accuracy by the formula  $i = a \cdot e^{-b/\theta}$ , in which  $a$  and  $b$  are constants. On the assumption that the conductivity is due to the ionisation of the vapours, the ionising potential has been calculated with the following results: cadmium iodide, 1.93; zinc iodide, 2.72; zinc bromide, 2.97 volts. These values are much smaller than the corresponding ionising potentials for the ordinary gases.

From experiments with phosphorus pentabromide and sulphur dichloride it has been found that these vapours are non-conducting. From this it follows that ionisation is not a consequence of chemical dissociation.

H. M. D.

**Disintegration of the Aluminium Cathode.** L. L. CAMPBELL (*Phil. Mag.*, 1914, [vi], 28, 347—354).—It has been supposed that the

aluminium cathode does not disintegrate to any marked extent except in the presence of the inert gases, but this view is shown to be untenable by the results which have been obtained in experiments with discharge tubes containing the halogens, certain metallic vapours, and other gases. It is probable that, under proper conditions, the aluminium cathode will disintegrate in all gases more or less rapidly. This has, at any rate, been found to take place in presence of the halogens, cyanogen, pentane, mercury vapour, cadmium vapour, mercury dimethyl, and carbon monoxide. In the case of the halogens, the rate of disintegration increases with the molecular weight of the gas.

The disintegration appears to take place most readily when the pressure in the discharge tube has reached the ordinary X-ray stage, and when the cathode dark-space has reached the walls of the tube surrounding the cathode.

Under certain conditions disintegration seems to be delayed, and experiments are described which indicate that a very small amount of water-vapour may in some cases be the cause of this phenomenon. It may also be due to a thin film of oxide or nitride on the surface of the cathode, which must first be removed by bombardment by the positively charged particles. H. M. D.

**The Rôle of Valency in the Additiveness of Diamagnetism.** PAUL PASCAL (*Compt. rend.*, 1914, 159, 429—431).—In organometallic compounds of the metals lead, tin, or mercury the diamagnetism of the metal in an homologous series of compounds varies from an upper limit at the lower end of the series to a lower limit at the upper end of the series. In the form of salts the atomic coefficients of magnetisation of quadrivalent lead and bivalent tin tend towards the inferior limit, of bivalent lead and quadrivalent tin towards the upper limit. Mercury, on the other hand, has the same atomic coefficient both in mercurous and mercuric salts, the value differing notably from that of pure mercury and approaching the upper limit in its series of organometallic compounds. The neighbourhood of several halogen atoms around the same central atom depresses the diamagnetism in inorganic chemistry as well as in organic chemistry, but it is impossible at present to give a rule for calculating the value of this diminution. W. G.

**Specific Heats of Liquids at Various Constant Pressures and Various Temperatures. II.** SILVIO LUSSANA (*Nuovo Cim.*, 1914, [vi], 7, i, 304—312. Compare A., 1912, ii, 1135).—Further measurements on ethyl ether at higher temperatures than those previously employed show that, as with ethyl and amyl alcohols, the diminution of  $c_p$  as the pressure rises tends to become lower at the higher temperatures and pressures; at a sufficiently high pressure the variation of  $c_p$  changes its sign. The value of  $c_p : c_v$  or  $\gamma$  diminishes as the temperature and pressure rise. If the external work effected in liquids during heating be neglected and the difference between the two specific heats be attributed solely to the internal work, these results and the variations of the coefficient of

dilatation at constant pressure with the pressure and temperature would show that the amount of internal work necessary during heating diminishes with increase of the pressure.

The conclusion is drawn that the diminution of the distance between the molecules of liquids, which is naturally accompanied by restriction of the liberty of movement of the molecules, carries with it a diminution in the value of  $\gamma$ , and hence tends to cause the heat consumed during heating to aid the molecular energy.

T. H. P.

**Freezing Point of Benzene as a Fixed Point in Thermometry.** THEODORE W. RICHARDS and JOHN W. SHIPLEY (*J. Amer. Chem. Soc.*, 1914, **36**, 1825—1832).—The most convenient and exact way of fixing points on the thermometric scale between  $0^\circ$  and  $100^\circ$  is probably by means of the transition temperatures of hydrated crystalline salts (compare A., 1898, ii, 555; 1899, ii, 354; 1903, ii, 411; 1906, ii, 727; 1908, ii, 16; 1911, ii, 695; this vol., ii, 244). The f. p. of a liquid can also be used for this purpose, and a careful study has therefore been made of the f. p. of benzene. Benzene of sufficient purity can be prepared without much difficulty, and yields a very definite and constant f. p.,  $5.483^\circ \pm 0.002^\circ$  on the international hydrogen scale. This fixed temperature, in conjunction with the f. p. of water, is of value for calibrating Beckmann thermometers.

E. G.

**Calculation of Chemical Constants.** UGO GRASSI (*Nuovo Cim.*, 1914, [vi], **7**, i, 313—320).—By means of measurements made on a series of fourteen compounds, Mündel (this vol., ii, 28) found that the values of the chemical constant,  $C$ , which give good agreement between the observed values of  $p$  and those determined by means of Nernst's equation,  $\log p = -\lambda_0/4.571T + 1.75 \log T - \epsilon T/4.571 + C$ , differ markedly from those previously calculated by Nernst himself. The latter made use of the equation,

$$\lambda = (\lambda_0 + 3.5T - \epsilon T^2)(1 - p_0/\pi_0),$$

in conjunction with that given above, but the thermochemical data at his disposal referred only to a restricted temperature interval, and the values of the constants  $\epsilon$  and  $\lambda_0$  were derived by a process of approximation. The author has determined these constants more exactly from the value of  $\pi$ , and that of  $p$  at two temperatures differing considerably from the critical temperature and from one another.

The following latent heats of evaporation at  $0^\circ$  were determined, the numbers being cal. per gram (compare this vol., ii, 184): methyl ethyl ketone, 124.2; diethyl ketone, 112.85; dipropyl ketone, 103.7; isopropyl alcohol, 192.2; pinacolin, 98.53. By means of Altschul's method the following critical pressures were measured: dipropyl ketone, 33.9; diethyl ketone, 42.5; and methyl ethyl ketone, 47.5 atmos. The values of the chemical constants calculated from the two above formulæ are as follows, those given by Trouton's rule being shown in brackets: acetone, 3.74 (3.08); methyl ethyl ketone, 4.50 (2.97); diethyl ketone, 4.54 (2.92);

dipropyl ketone, 5.59 (2.90); ethyl formate, 6.56 (2.92); propyl formate, 4.10 (3.14); methyl acetate, 5.73 (2.96); ethyl acetate, 5.05 (2.93); benzene, 4.37 (2.88); isopropyl alcohol, 4.94 (3.71).

T. H. P.

**Trouton's Rule.** CARLO SONAGLIA (*Nuovo Cim.*, 1914, [vi], 7, i, 321—328).—Cederberg's objection to Nernst's equation (A., 1911, ii, 854), on the ground that it contains no constants relative to the particular compound, is invalid, since the boiling point enters into the equation. Cederberg claims for his own equation that it contains no empirical constants; since, however, it is derived by combining other relations with van der Waals' equation, and the values of  $a$  are not the same, but different for different compounds, this claim is open to criticism.

The author has investigated the values of Trouton's constant for ethyl and propyl formates, methyl and ethyl acetates, acetone, methyl ethyl ketone, diethyl ketone, and dipropyl ketone at various temperatures, which exactly correspond. Use is made of Nernst's formula,  $\lambda = (\lambda_0 + 3.5T - \epsilon T^2)(1 - p/\pi_0)$ , in which  $\epsilon$  is a constant and  $\lambda_0$  the latent heat of evaporation at absolute zero. Accurate measurements of  $\lambda$  at two different temperatures give the values of  $\lambda_0$  and  $\epsilon$ , and hence the value of  $\lambda$  at any other temperature, so long as  $p$  is small compared with the critical pressure,  $\pi_0$ . For reduced temperatures equal to or greater than 0.5 this condition is not satisfied, and in these cases  $p$  was calculated by means of Nernst's formula,  $\log p = \lambda_0/4.571T + 1.75 \log T - \epsilon T/4.571 + C$ .

The results show that the values of Trouton's constant for the esters become equal at a reduced temperature of about 0.5, whilst at lower temperatures marked variations occur. Nernst's observation, that the values at the boiling point increase with rise of temperature, is not confirmed for the values at corresponding temperatures.

On the other hand, the curves representing the variation of Trouton's constant with temperature for the last three ketones are similar, but do not meet; the behaviour of acetone is complicated by the tendency of its molecules to associate.

T. H. P.

**Rapid Laboratory Method of Measuring the Partial Vapour Pressures of Liquid Mixtures.** M. A. ROSANOFF, C. W. BACON, and R. H. WHITE (*J. Amer. Chem. Soc.*, 1914, 36, 1803—1825).—The usual method of obtaining partial pressure data by distilling off a small quantity of the liquid and determining its composition (Zawidzki, A., 1901, ii, 6) gives good results. A simpler and more rapid method has now been devised, which has been applied to both binary and ternary mixtures, and is recommended as the easiest means of ascertaining the composition of vapours in equilibrium with liquid mixtures. Instead of allowing the distillate to accumulate in the receiver, seven or eight consecutive small fractions are removed and analysed separately. The composition and weights of these fractions being known, a curve can be constructed indicating the composition of the distillate when its weight has



attained any definite amount within the range of the curve. A moderate extrapolation backwards leads to the point at which the weight of the distillate is zero. The point of intersection indicates the composition of the first indefinitely small amount of vapour evolved by the liquid mixture.

Apparatus is described for carrying out determinations by this method, and the results of measurements are given for mixtures of carbon disulphide and carbon tetrachloride, chloroform and toluene, acetone and toluene, and ethyl iodide and ethyl acetate. The measurements were carried out isopiastically under ordinary atmospheric pressure. The method can be employed in cases in which the amount of substance available is too small to yield accurate results by the older methods. E. G.

**Apparatus with Ground-joints for the Distillation in Vacuum of Substances Attacking Cork.** HENRI VIGREUX (*Ann. Chim. anal.*, 1914, 19, 220—221).—A glass apparatus consisting of distilling flask, fractionating column, and receiver, in which all joints are ground, is figured and described; it may be used for distillation under ordinary or reduced pressure. A glass tube supporting the thermometer is ground into the top of the fractionating column, and contains mercury, to secure rapid equalisation of the temperature. C. S.

**Thermoelement Installations, Especially for Calorimetry.** WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1914, 36, 1856—1868).—The greatest precision in calorimetric work is obtainable by the use of electrical thermometers. The most satisfactory of these, and the most accurate for small intervals, is the multiple thermoelement, when used with a small difference between its two ends. An account is given of the methods and apparatus employed in thermoelectric procedure, and a type of auxiliary installation for thermoelements is described which is convenient, rapid, and capable of the high precision often required for calorimetry. A precision of 0.1 microvolt can be obtained with the use of a suitable eliminating switch and an appropriate potentiometer. For the former, a common copper knife switch is serviceable. Satisfactory potentiometers are described in a separate paper (following abstract). E. G.

**Potentiometers for Thermoelectric Measurements, Especially in Calorimetry.** WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1914, 36, 1868—1885).—Potentiometers are described which are particularly adapted for high-temperature measurements in cases in which the sensitiveness and precision of the thermoelement is much in excess of the requirements. Split circuit and combination potentiometers are satisfactory and easily obtainable, but the slide wire and Feussner potentiometers of a range of 1 volt or more are not suitable for thermoelement work. The potentiometer system is convenient for simultaneous measurements of different and differently varying *E.M.F.*'s, and also enables the last two

figures of any reading to be taken directly from the galvanometer scale. It increases speed, simplifies manipulation, diminishes errors, and gives calorimetric data in a convenient form for further treatment.

E. G.

**Surface Tensions of Liquids in Contact with Different Gases.** ALLAN FERGUSON (*Phil. Mag.*, 1914, [vi], 28, 403—412).—From observations of the maximum pressure required to release a bubble of gas from the end of a vertical capillary tube immersed in the liquid, the author has determined the surface tension of benzene, chloroform, water, methyl alcohol, ethyl alcohol, ethyl ether, and turpentine in contact with (1) air, (2) carbon dioxide. In all cases, the liquid was found to have a smaller surface tension in contact with carbon dioxide; the largest difference, amounting to 2.05%, is shown by chloroform, and the smallest difference, 0.46%, by turpentine.

The observed effect is not only influenced by the nature of the gas, but also by its solubility in the liquid. Since the gases are, however, only sparingly soluble in the liquids examined, it is probable that the values obtained differ only very slightly from the values for gas-free liquids.

H. M. D.

**Absorption of Dextrose by Bone-black.** HAROLD A. MORTON (*J. Amer. Chem. Soc.*, 1914, 36, 1832—1838).—In the course of certain work on the sugars, it was necessary to purify a large quantity of dextrose. During this purification it was observed that a considerable amount of the dextrose was removed by the bone-black from the aqueous solution. In order to investigate this phenomenon, solutions of dextrose of concentrations from 4.63% to 50.58% were treated with purified bone-black, and afterwards examined polarimetrically. The results show a regularity, indicating that the absorption of dextrose by bone-black follows a principle resembling the distribution law. The ratios of the weight of dextrose per gram of solution to that per gram of bone-black are almost identical for all the concentrations. The data obtained in these experiments show that the bone-black takes part of the water from the solutions as well as the dextrose, and that the absorption of the water takes place according to some principle similar to that followed in the absorption of dextrose. When equilibrium has been attained, the solution of dextrose within the bone-black is at least twice as concentrated as the solution outside.

E. G.

**Morphological Studies of Benzene Derivatives. VII. The Correlation of the Forms of Crystals with their Molecular Structure and Orientation in a Magnetic Field in the Case of Hydrated Sulphonates of Dyad Metals.** H. E. ARMSTRONG and E. H. RIDD (*Proc. Roy. Soc.*, 1914, [A], 90, 463—492. Compare this vol., i, 1062; ii, 443).—The work recorded in this paper has particular reference to the behaviour of crystals, especially those of salts of the magnetic and other dyad metals, when sus-

pended in a strong magnetic field. Salts of these metals with benzenesulphonic, toluene-*p*-sulphonic, *p*-chloro-, *p*-bromo-, *p*-iodo-, and 2·5-dichloro-benzenesulphonic acids have been prepared, and the following new crystallographic data are given. All the salts crystallise in the monoclinic system, the last two in the hemimorphic class.

	$\alpha : b : c.$	$\beta.$
$(C_6H_5\cdot SO_3)_2Fe, 6H_2O$ .....	3·5690 : 1 : 1·1058	86°18'
$(C_6H_5\cdot SO_3)_2Co, 6H_2O$ .....	3·5560 : 1 : 1·1086	86 7
$(C_6H_5\cdot SO_3)_2Ni, 6H_2O$ .....	3·5476 : 1 : 1·1076	86 9
$(C_6H_5\cdot Me\cdot SO_3)_2Fe, 6H_2O$ .....	3·9972 : 1 : 1·1051	88 37
$(C_6H_5\cdot Me\cdot SO_3)_2Co, 6H_2O$ .....	3·9903 : 1 : 1·1080	88 17
$(C_6H_5\cdot Me\cdot SO_3)_2Ni, 6H_2O$ .....	3·9949 : 1 : 1·1039	88 31½
$(C_6H_4\cdot Cl\cdot SO_3)_2Fe, 6H_2O$ .....	3·6781 : 1 : 0·9094	94 21½
$(C_6H_4\cdot Cl\cdot SO_3)_2Co, 6H_2O$ .....	3·6603 : 1 : 0·9071	93 46½
$(C_6H_4\cdot Br\cdot SO_3)_2Fe, 6H_2O$ .....	3·7293 : 1 : 0·9104	94 26½
$(C_6H_4\cdot Br\cdot SO_3)_2Co, 6H_2O$ .....	3·7103 : 1 : 0·9087	93 59
$(C_6H_4\cdot Br\cdot SO_3)_2Ni, 6H_2O$ .....	3·7316 : 1 : 0·9139	94 34
$(C_6H_4\cdot I\cdot SO_3)_2Fe, 6H_2O$ .....	3·7856 : 1 : 0·9085	93 35
$(C_6H_3\cdot Cl_2\cdot SO_3)_2Fe, 8H_2O$ .....	1·7543 : 1 : 2·1053	78 40
$(C_6H_3\cdot Cl_2\cdot SO_3)_2Co, 8H_2O$ .....	1·7456 : 1 : 2·1034	78 15½

The benzenesulphonates, toluenesulphonates, and *p*-halogen-benzenesulphonates form three distinct isomorphous series, between all of which, however, there is a close morphotropic relationship; the salts of the dichloro-series, however, show no obvious connexion with those of the other three. When the salts of any one metal of the first three series are considered, their crystals are found to correspond in magnetic behaviour as they do in geometrical structure, that is to say, corresponding directions set in the same manner in the magnetic field. The salts of different metals, however, differ totally in magnetic behaviour. In the case of all the iron salts, the axis *a* is the direction of greatest magnetic permeability, whilst in the cobalt salts this direction is that of least permeability. The nickel salts differ from both those of iron and cobalt, but appear to be similar to those of copper, manganese, and magnesium. Similar differences are found between the sulphates of the magnetic metals and between the double salts which these form with ammonium sulphate. The relation between the molecular and crystalline structure of the sulphonates is discussed from the Barlow-Pope point of view, and also the use which may be made of the magnetic property of crystals for determining the correct setting.

In an appendix, data are given for the crystalline form of potassium *p*-chlorobenzenesulphonate, which is found to be in close morphotropic relationship with the corresponding iron and cobalt salts. The salt, which is anhydrous, crystallises in the monoclinic system,  $\alpha : b : c = 1·4394 : 1 : 0·9049$ ;  $\beta = 97°11'$ . The behaviour of azobenzene in the magnetic field is also considered in the light of the suggestion that there may be some connexion between magnetic susceptibility and the colour of the crystals. E. H. R.

**Growth of Metallic Eutectics.** F. E. F. LAMPLUGH and J. T. SCOTT (*Proc. Roy. Soc.*, 1914, [A], 90, 600—604).—The influence of

undercooling on the structure of certain binary alloys has been examined. It has been supposed that the formation, around the primary crystals of an alloy, of an envelope of the second constituent separating the primary crystals from the banded eutectic, is due to undercooling in the process of solidification. The experiments which have been made by the authors indicate that this is not the case, and there appears to be no connexion whatever between the undercooling at the first moment of solidification and the formation of such a halo or envelope.

From the examination of a large number of alloys, it has been found possible to classify eutectics according to their structure. The majority of eutectics fall into two classes, which are characterised, respectively, (1) by spherical radiating growths, and (2) by well-defined crystal contours, showing in section a herring-bone structure.

H. M. D.

**Hermannus Follinus and the Law of the Indestructibility of the Elements.** W. P. JORISSEN (*Chem. Weekblad.*, 1914, 11, 822—826).—In 1613, Follinus observed that a given weight of mercury could be transformed into mercuric sulphide, and that the product could be oxidised to mercury without change in the weight of the metal.

A. J. W.

**History of Condensers.** MAX SPETER (*Chem. Zentr.*, 1914, i, 1798; from *Chem. Appar.*, 1914, 1, 65—70).—A critical discussion regarding the history of condensers. The author suggests that the Liebig condenser should be known by the name of its inventor, Weigel.

W. P. S.

**Simple Method of Making Dewar's Tubes.** HENRI VIGREUX (*Ann. Chim. anal.*, 1914, 19, 293—294).—A glass tube of suitable diameter is drawn out to a fine tube at one end, whilst the other end is rounded, like the bottom of a test-tube. This end is then heated, the end is drawn in so as to form a concave cap, and, while the end of the tube is kept in the flame, an iron rod is pressed into the cup so as to force it into the outer tube to a sufficient depth. The tube is then silvered and exhausted.

W. P. S.

**Device to Aid in Freeing a Precipitate from Mother-liquor when Filtering by Suction.** ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1914, 36, 1967).—When a precipitate has been collected and drained in a Büchner funnel, a further quantity of the mother-liquor can be removed from it by placing a piece of thin sheet rubber over the top of the funnel and securing it by means of a rubber band. The suction draws the rubber down over the sides of the funnel and on to the top of the precipitate. The surface of the rubber may now be firmly pressed either by hand or with a pestle, and in this way the precipitate can be obtained in a comparatively dry condition.

E. G.

## Inorganic Chemistry.

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**Reduction of Chlorates to Chlorides by Hydrazine Salts with the Aid of a Catalytic Substance.** W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1914, 33, 815).—Solutions of alkali or other chlorates (bromates or iodates) and hydrazine salts may be mixed together in any proportion and boiled without any reaction taking place. If, however, a piece of tarnished copper wire or a fragment of copper oxide is introduced into a cold solution of potassium chlorate and hydrazine nitrate, an action commences at the surface of the solid, nitrogen being evolved. The reaction is accelerated by warming, and is quantitative, in accordance with the following equation,  $2\text{KClO}_3 + 3\text{N}_2\text{H}_4 \cdot \text{HNO}_3 = 6\text{H}_2\text{O} + 3\text{N}_2 + 3\text{HNO}_3 + 2\text{KCl}$ . The amount of copper dissolved is very small; various copper salts produce a like result. When used for the estimation of chlorates, bromates, or iodates, the slight excess of hydrazine salt used is destroyed by permanganate mixed with nitric acid; the chloride, bromide, or iodide present in the solution is then estimated.

Hydrazine sulphate and oxalate do not react so well as the nitrate with copper and its salts; in the presence of metallic iron or an iron salt, the reaction with the sulphate is violent, whereas it is very slow with the nitrate and oxalate.

Reference is also made to the action of hydrazine salts on dichromates, arsenates, persulphates, osmates, molybdates, tungstates, and tantalates. Perchlorates are not reduced in the same way as are chlorates; ammonium perchlorate and hydrazine nitrate may be melted together without decomposition. T. S. P.

**Existence of Free Thiosulphuric Acid.** C. BONGIOVANNI (*Gazzetta*, 1914, 44. i, 624—627).—When an aqueous-alcoholic solution of methylene-blue is added to an acidified solution of a thio-sulphate, it is decolorised. Sulphurous acid does not effect this reduction, which is an indication of the presence of free thio-sulphuric acid in the solution. R. V. S.

**The Crystal Form of Some of the Hydrated Haloid Salts of the Alkali Metals.** C. W. COOK (*Amer. J. Sci.*, 1914, [iv], 38, 142—144).—The majority of these hydrated haloids effloresce rapidly at the ordinary temperature, in consequence of which the crystallographic data recorded are incomplete, and of only approximate accuracy. The salts were not analysed, the formulæ being based on that given by Mitscherlich for the sodium bromide.

$\text{KF} \cdot 2\text{H}_2\text{O}$ ?; monoclinic prismatic;  $a : b : c = 1.0565 : 1 : 0.70608$ ;  $\beta = 109^\circ 15'$ .

$\text{LiBr} \cdot 2\text{H}_2\text{O}$ ?; monoclinic prismatic;  $a : b : c = 0.83665 : 1 : 1.1188$ ;  $\beta = 107^\circ 18\frac{1}{2}'$ .

$\text{NaBr} \cdot 2\text{H}_2\text{O}$ ; the constants for this salt could not be determined; the value of the angle  $(1\bar{1}0) : (110)$  is  $61^\circ 24'$ . E. H. R.

**Isomorphism between Perchlorates and Permanganates.** G. SCAGLIARINI and A. MARANGONI (*Atti R. Accad. Lincei*, 1914, [v], 23, ii, 12—14).—The action of sodium perchlorate on a concentrated ammoniacal solution of silver nitrate yields the compound  $\text{AgClO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ , which forms acicular crystals sensitive to the influence of light. The analogous compound,  $\text{AgMnO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$  (compare Klobb, A., 1886, 983), forms dark, acicular crystals with metallic lustre. These two salts form mixed crystals, which may contain up to about 25% of the permanganate compound.

The compounds  $\text{Mg}(\text{MnO}_4)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 8\text{H}_2\text{O}$  and  $\text{Ni}(\text{MnO}_4)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 8\text{H}_2\text{O}$  have also been prepared by the action of hexamethylenetetramine on magnesium and nickel permanganates. T. H. P.

**Synthetic Celite and Large Crystals of Tricalcium Silicate.** EDWARD D. CAMPBELL (*J. Ind. Eng. Chem.*, 1914, 6, 706—710).—Celite consists essentially of a calcium aluminate, m. p. slightly above  $1400^\circ$ ; it has the formula  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , and is capable of dissolving, when liquid, calcium orthosilicate and calcium oxide. If the concentration of the calcium oxide is sufficient and solution complete, pure tricalcium silicate crystallises out when the mixture is cooled slowly. This suggests a new theoretical formula for Portland cement. The Le Chatelier formula first proposed was  $x(3\text{CaO} \cdot \text{SiO}_2) + y(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$ , requiring calcium oxide by weight equal to  $2 \cdot 8\text{SiO}_2 + 1 \cdot 6\text{Al}_2\text{O}_3$ ; in practice this gives a large excess of free calcium oxide. In the Newberry formula,

$x(3\text{CaO} \cdot \text{SiO}_2) + y(2\text{CaO} \cdot \text{Al}_2\text{O}_3)$ , the calcium oxide is equivalent to  $2 \cdot 8\text{SiO}_2 + 1 \cdot 1\text{Al}_2\text{O}_3$ , and still gives an excess of free lime in the cement. The formula now suggested would be  $x(3\text{CaO} \cdot \text{SiO}_2) + y(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3)$ , where the calcium oxide by weight would be equal to  $2 \cdot 8\text{SiO}_2 + 0 \cdot 9\text{Al}_2\text{O}_3$ . Such a formula would conform more closely with the results obtained in the best practice. W. P. S.

**The Dissolution Faces of Dolomite.** P. GAUBERT (*Compt. rend.*, 1914, 159, 486—488).—When a cleavage rhombohedron of dolomite is attacked by boiling nitric acid, scalenohedral facets appear. The positions of these facets can be determined, and are found to vary in a regular manner with the rate of attack of the acid on the crystal, the indices ranging from (11,1,0) to (410). In the same manner, the form of the corrosion figures on different faces of the crystal varies with the rate of attack. Specimens of dolomite are attacked more slowly by acid of a given concentration the more iron they contain, and the position of the dissolution facets varies accordingly. E. H. R.

**The Ternary System. Diopside-Forsterite-Silica.** N. I. BOWEN (*Amer. J. Sci.*, 1914, [iv], 38, 207—264).—An account is given of the equilibrium relationships in the ternary system  $\text{CaMg}(\text{SiO}_3)_2$ - $\text{Mg}_2\text{SiO}_4$ - $\text{SiO}_2$  which represents that part of the more general ternary system  $\text{CaO}$ - $\text{MgO}$ - $\text{SiO}_2$ , which is of greatest interest to the petrologist.

The method of experiment consisted in heating mixtures of specially purified silica, magnesia, and calcium carbonate at known temperatures in an electrical resistance furnace until equilibrium was attained, when the mixtures were rapidly cooled, and afterwards examined under the microscope.

The binary system  $\text{Mg}_2\text{SiO}_4\text{--SiO}_2$  has been described in a previous paper (Bowen and Andersen, this vol., ii, 562). The system  $\text{CaMg}(\text{SiO}_3)_2\text{--SiO}_2$  shows the simple eutectic relation. Diopside melts at  $1391^\circ$ , and the eutectic temperature  $1362^\circ$ , at which diopside and tridymite co-exist, corresponds with the composition 84% diopside and 16% silica. A break on the silica liquidus is shown at  $1470^\circ$ , and this in all probability corresponds with the transformation of tridymite into cristobalite. The system  $\text{CaMg}(\text{SiO}_3)_2\text{--Mg}_2\text{SiO}_4$  also shows the eutectic relation. The eutectic point, at the composition 88% diopside and 12% forsterite, is only  $4^\circ$  to  $5^\circ$  lower than the melting point of diopside.

The above three binary systems give rise to five solid phases—diopside, cristobalite, tridymite, clino-enstatite, and forsterite. In the normal ternary equilibrium diagram there would be five corresponding surfaces, six boundary curves, and three ternary invariant points. The experimental results indicate, however, that diopside and clino-enstatite form an unbroken series of solid solutions (monoclinic pyroxenes), with the result that diopside, clino-enstatite, and the intermediate pyroxenes have but one surface in common. There are, consequently, only three boundary curves and only one ternary point, namely, that corresponding with the co-existence of cristobalite, tridymite, and pyroxene.

The optical properties of the various crystalline phases have been examined, and it has been found that the properties of the pyroxenes vary continuously with the composition. In considering the bearing of the results on petrologic problems, attention is called to the resorption of forsterite in the artificial mixtures and its probable connexion with the resorption of olivine in natural rocks.

H. M. D.

**Oxy-haloids of Lead.** G. SANDONNINI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 959—965).—Thermal and micrographic study of the system  $\text{PbO--PbBr}_2$  confirms the existence of the compound  $\text{PbBr}_2\cdot\text{PbO}$  at high temperatures, and of  $\text{PbBr}_2\cdot 2\text{PbO}$ , and indicates also the existence of the compound  $\text{PbBr}_2\cdot 4\text{PbO}$ , which decomposes on melting. No formation of solid solutions between these various oxybromides is observed.

The system  $\text{PbO--PbF}_2$  does not form a compound, but a simple eutectic, m. p.  $494^\circ$ , containing about 54 mol. % of  $\text{PbO}$ , is observed.

T. H. P.

**Arsenates of Lead.** HERMAN V. TARTAR and R. H. ROBINSON (*J. Amer. Chem. Soc.*, 1914, 36, 1843—1853).—The extensive use of the lead arsenates as insecticides has rendered a knowledge of their constitution and properties of considerable importance, and the present investigation was therefore undertaken.

Lead hydrogen arsenate can be obtained in a fairly pure condition by the following method. The precipitate produced by the interaction of lead nitrate and disodium hydrogen arsenate is washed with water and dissolved in just sufficient nitric acid to effect solution. Dilute ammonia is added gradually to this solution until about three-fourths of the nitric acid has been neutralised. The precipitate of lead hydrogen arsenate thus obtained is left in contact with the solution for some hours, and is then collected, washed with freshly boiled water, and dried at  $110^{\circ}$ . The product contains a small quantity of water, which is not expelled below  $200^{\circ}$ . When heated somewhat above  $200^{\circ}$  it is converted into lead pyroarsenate.

Attempts to prepare lead orthoarsenate by the action of ammonium hydroxide on lead hydrogen arsenate, as suggested by Volck (*Science*, 1911, **33**, 868), resulted in the formation of the basic compound,  $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$ , as a white, amorphous powder. Pure lead orthoarsenate could not be obtained.

Lead hydrogen arsenate has  $D_4^{20}$  5.786, and basic lead arsenate  $D_4^{20}$  7.105. Both compounds are very little, if at all, soluble in water.

The precipitates obtained by the reactions of lead acetate and lead nitrate with disodium hydrogen arsenate are mixtures of lead hydrogen arsenate and the basic lead arsenate in proportions varying with the conditions of the experiments. E. G.

**Atomic Weight of Copper by Electrolysis.** ALBERT G. SHRIMPTON (*Proc. physical Soc. London*, 1914, **26**, 297—312).—The relative quantities of copper and silver deposited by the same current have been determined in order to obtain the atomic weight of copper.

For the production of an uniform coherent deposit of pure metal it was found necessary to maintain the current density at the cathode below a certain limiting value. This limiting value was determined in a series of preliminary experiments, and found to depend on the form of the electrolytic cell, the concentration of the electrolyte, the presence of acid and other impurities, the presence or absence of a porous pot, and in the case of a rotatory cathode on the speed of rotation. In order to prevent the formation of loose crystalline clusters, it was also found necessary to regulate the current density according to the weight of the metal to be deposited. Empirical formulæ are given from which the limiting current density can be calculated.

In the actual experiments four copper cells, placed between two silver cells, were run in series. The surfaces of the copper cathodes varied from 10 to 50 cm.<sup>2</sup>, and the actual weights of the deposits were plotted against the corresponding cathode surfaces in order to eliminate the effect of cathodic dissolution by extrapolation to zero cathode surface. Ten values obtained in this manner give for the atomic weight of copper  $63.563 \pm 0.003$ , when silver is taken as 107.88. H. M. D.



**The Crystalline Structure of Copper.** W. LAWRENCE BRAGG (*Phil. Mag.*, 1914, [vi], 28, 355—360).—The author has applied the X-ray method of investigation to the study of natural crystals of copper. The surfaces of these crystals reflect the rays satisfactorily after being etched with nitric acid, and although the faces are considerably distorted, a good standard of accuracy is obtainable with the X-ray spectrometer. The results show that in a copper crystal the atoms are arranged on a face-centred cubic lattice, identical with the close-packed lattice suggested by Barlow and Pope for elementary substances. E. H. R.

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### Mineralogical Chemistry.

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**Octahedral Crystals of Sulphohalite.** HOYT S. GALE and W. B. HICKS (*Amer. J. Sci.*, 1914, [iv], 38, 273—274).—Octahedral crystals, obtained from drillings in the saline deposits at Searles Lake, California, gave on analysis numbers which agree with those represented by the formula for sulphohalite,  $2\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaF}$ . Measurements of the density and refractive index gave  $D=2.5$  and  $n_D=1.455$ . H. M. D.

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## Analytical Chemistry.

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**Some Natural Indicators.** H. W. BRUBAKER (*J. Amer. Chem. Soc.*, 1914, 36, 1925—1928).—An account is given of the behaviour of the colouring matters of the petals of various flowers towards alkalis and acids. These substances are usually acid, but sometimes neutral in character, and generally change colour in acids and alkalis, thus acting as indicators. Many of the colouring matters are very sensitive to the action of light and air. E. G.

**Electro-volumetric Method and its Application to General Analytical Chemistry.** F. H. HESSELINK VAN SUCHTELEN and ARAO ITANO (*J. Amer. Chem. Soc.*, 1914, 36, 1793—1803).—The difficulties encountered in the use of indicators in volumetric analysis, such as the personal equation and the interference of the colour of the liquid with that of the indicator, have led the authors to study the conductivity method of estimation (compare Küster, Grütters and Geibel, A., 1905, ii, 55; Hall and Bell, A., 1911, ii, 657). This method has been applied to the estimation of acids, bases, salts, and mixtures of salts, and has been found very satisfactory. Curves have been constructed by plotting the conductivities as ordinates and number of c.c. of the reagent as

abscissæ. The method is also of service for the estimation of chlorine and phosphates in urine. E. G.

**Apparatus for the Analysis of Mixed Gases.** A. C. WILSON (*Analyst*, 1914, 39, 391—392).—A modification of Stead's apparatus is described. Mercury is used as the confining medium, and the absorption bottles are each provided with a side-tube, to which is attached a thin gas-bag. Combustion of the gas mixture is effected in a graduated eudiometer tube fitted with platinum terminals, or a palladium tube may be employed. W. P. S.

**Apparatus for Exact Gas Analysis.** E. MAUGUIN (*Ann. Chim. anal.*, 1914, 19, 298—300).—A measuring burette is connected by means of a three-way tap with a gas vessel and an absorption pipette, which is provided at the top and bottom with three-way taps. The burette is also in connexion with a levelling tube. The apparatus and the capillaries between the pipette and the burette are filled with mercury, and, when the gas has been introduced into the burette and driven over into the pipette, the absorption solution is admitted to the latter. When absorption has taken place, the solution is withdrawn from the pipette by connecting the latter with an exhaust pump, and the gas is then passed back again into the burette. W. P. S.

**Absorption Vessel for Gas Analysis.** E. MAUGUIN (*Ann. Chim. anal.*, 1914, 19, 219—220).—A modified form of absorption vessel for the Orsat apparatus, in which intimate contact with the absorbing liquid is obtained, the gas on entering the vessel being caused to pass through the liquid in very small bubbles, and then remaining in contact with broken glass moistened with the absorbent. Two automatic valves cause the gas to pass in the required directions when entering or leaving the vessel.

L. DE K.

**Estimation of Iodine and Bromine in Halogen Salts by Means of Telluric Acid.** HARRIET ISABELLE COLE (*Amer. J. Sci.*, 1914, [iv], 38, 265—272. Compare this vol., ii, 379).—Quantities of iodine or bromine up to 0.3 gram when associated in their halogen salts with 0.25 gram of chlorine may be estimated as follows. Weighed amounts of the three salts, for instance, 0.5 gram each of iodide, bromide, and chloride, are introduced into a graduated tubular flask and dissolved in 50 c.c. of water; the flask is connected with a receiver containing 200 c.c. of 1.5% potassium iodide solution, and cooled in ice-water. After the addition of 1 gram of telluric acid, dissolved in 15 c.c. of sulphuric acid (D 1.015) and 35 c.c. of water, the solution in the flask is heated to boiling, and a current of carbon dioxide and steam is passed through it until all the liberated iodine has been distilled, the volume of the solution being kept at 100 c.c. The steam supply is then diminished, and the solution concentrated to 65 c.c. The iodine in the distillate is now titrated with thiosulphate solution,

the receiver is recharged with potassium iodide solution, and, after the addition of 10 c.c. of sulphuric acid (1:1) to the contents of the tubular flask, the distillation with steam and carbon dioxide is continued, the volume being kept constant until all bromine coloration has been expelled; the solution is then concentrated slowly to 30 c.c., next rapidly to 24 c.c., and the distillate is titrated with thiosulphate solution; the iodine thus titrated is equivalent to the quantity of bromine distilled. W. P. S.

**Volumetric Method of Estimating Sulphurous Acid.** GEORGE S. JAMIESON (*Amer. J. Sci.*, 1914, [iv], 38, 166—168).—The method is based on the titration of sulphurous acid with potassium iodate solution in the presence of 15 to 20% of hydrochloric acid and a small quantity of an immiscible solvent, such as chloroform. The sulphurous acid solution is added to a cooled mixture of 30 c.c. of concentrated hydrochloric acid, 20 c.c. of water, and 6 c.c. of chloroform, and the solution is then titrated with standardised potassium iodate solution. The latter is at first run in rapidly until the iodine which is liberated reaches a maximum, and then nearly disappears. The mixture is now shaken thoroughly, and the titration continued, the end-point being denoted by the disappearance of the violet colour from the chloroform. When dealing with quantities of sulphurous acid or sulphite equivalent to more than 0.1 gram of sulphur dioxide, it is advisable to add iodine monochloride solution to the hydrochloric acid mixture before the sulphurous acid is introduced; this prevents loss of sulphur dioxide before the titration is carried out. W. P. S.

**A Simplification of the Estimation of Total Nitrogen by Colorimetry.** ADDISON GULICK (*J. Biol. Chem.*, 1914, 18, 541—547).—An improvement on the Folin-Farmer colorimetric method for estimating total nitrogen in urine (A., 1912, ii, 702) is described by the author which avoids the necessity of separating the ammonia by aspiration from the products of oxidation. This is achieved by oxidising the urine with a very small quantity of sulphuric acid in the presence of potassium sulphate and mercuric chloride, so that the subsequent colour reaction with a modified Nessler's reagent is not interfered with. The resulting method is stated to be expeditious and accurate, and requires less apparatus than the microchemical methods now employed. H. W. B.

**Reduction of Disodium Phosphate by the Alternating Current.** P. WENGER and L. HEINEN (*Ann. Chim. anal.*, 1914, 19, 209—211).—Tables (compare A., 1912, ii, 624, 1038) are given showing the effect on the reduction of disodium phosphate of the alternating current under various conditions, such as the period of the experiment, the concentration of the liquid, the number of amperes, the periodicity of the current, and the temperature. The phosphites formed during the experiments are estimated very satisfactorily by means of Rupp and Finck's process (with standard iodine in the presence of sodium hydrogen carbonate).

L. DE K.

**Hypothetical Combinations in Water Analysis.** R. B. DOLE (*J. Ind. Eng. Chem.*, 1914, 6, 710—714).—In view of an effort which is being made by committees of the American Chemical Society, the American Public Health Association, and the Association of Agricultural Chemists to agree on a uniform manner of reporting results of water analyses, the author discusses the present confusing methods of expressing results of analyses, and draws attention to the advantages of reporting the constituents in ionic form.

W. P. S.

**Estimation of Silver and Base Metal in Precious Metal Bullion.** FREDERIC P. DEWEY (*J. Ind. Eng. Chem.*, 1914, 6, 650—658, 728—736).—The cadmium-thiocyanate method (fusion of the metal with lead and cadmium in potassium cyanide, solution of the button in nitric acid, and titration of the silver with thiocyanate solution) for the estimation of silver in gold was found to be quite as trustworthy as the ordinary cupellation method.

W. P. S.

**Separation and Estimation of Small Quantities of Lead in Solders, Tinfoil, etc.** PIERRE BRETEAU and PAUL FLEURY (*J. Pharm. Chim.*, 1914, [vii], 10, 147—152).—The authors point out sources of error when, after dissolving the alloy in nitric acid, the lead is separated by precipitation as sulphide, sulphate, or chromate, or estimated electrolytically or colorimetrically, and will give in a subsequent paper details of a method for the accurate estimation of small quantities of lead in these alloys.

W. P. S.

**Detection of Lead in Bismuth Subnitrate.** G. GUÉRIN (*J. Pharm. Chim.*, 1914, [vii], 10, 22—23).—In a previous communication (A., 1913, ii, 1076) a test has been described which depends on the insolubility of bismuth subnitrate in 5% ammonium nitrate solution, whilst lead sulphate, carbonate, etc., are soluble. The author now finds that certain specimens of heavy bismuth subnitrate, which are free from lead, but possibly incompletely washed, are partly soluble in boiling ammonium nitrate solution, and that the filtered solution gives a yellow precipitate of bismuth chromate after addition of potassium chromate. It is therefore necessary to test the precipitate by adding sodium hydroxide in slight excess. If it consists solely of lead chromate, a clear solution is obtained, from which reprecipitation occurs after addition of a slight excess of acetic acid; the mixed precipitate of lead and bismuth chromates, on the other hand, is only partly dissolved by the alkali, and the filtrate then yields lead chromate after acidification with acetic acid.

H. W.

**Estimation of Mercuric Iodide in Tablets.** A. W. BENDER (*J. Ind. Eng. Chem.*, 1914, 6, 753—754).—A quantity of the powdered tablets, equivalent to about 0.15 gram of mercuric iodide, is heated under a reflux apparatus with 20 c.c. of hydrochloric acid (1:1) and 0.5 gram of potassium chlorate until all the iodide has dis-

solved. The solution is then cooled, diluted with water to 100 c.c., freed from chlorine by means of a current of air, and filtered. The filtrate is rendered ammoniacal, the mercury precipitated immediately with hydrogen sulphide, and the mercury sulphide is collected, dried at 100°, and weighed. The weight of the precipitate is multiplied by 1.995 to give mercuric iodide.

W. P. S.

**Volumetric Estimation of Titanium by means of Ferric Chloride.** T. R. BALL and G. MCP. SMITH (*J. Amer. Chem. Soc.*, 1914, **36**, 1838—1843).—Knecht and Hibbert (*A.*, 1903, ii, 509) have described a method for the volumetric estimation of ferric iron by means of titanium trichloride, potassium thiocyanate being used as an indicator. It is now shown that the same reaction can be employed for estimating titanium.

The solution of the titanium salt is reduced with zinc in presence of dilute sulphuric acid, and filtered; potassium thiocyanate is then added, and the solution titrated rapidly with standard ferric chloride solution. The reduction is allowed to proceed for about two hours. In order to protect the resulting titanous salt solution from oxidation, the filtration and titration are carried out in an atmosphere of carbon dioxide. A special form of apparatus for effecting the reduction and filtration is described. The method gives trustworthy results, and is much more rapid than Gooch's gravimetric method. Such metals, however, as tin, chromium, vanadium, tungsten, and molybdenum must be absent when the solution is reduced.

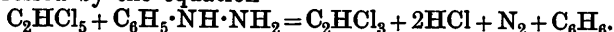
E. G.

**Separation of Zirconium from Iron and Aluminium with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron").** WILLIAM M. THORNTON, jun., and E. M. HAYDEN, jun. (*Amer. J. Sci.*, 1914, [iv], **38**, 137—141. Compare this vol., ii, 583).—One hundred c.c. of a solution containing zirconium, iron, and aluminium salts are neutralised with ammonia, 2 c.c. of dilute sulphuric acid (1:1) are added, and the iron is reduced with hydrogen sulphide. The solution is then rendered slightly ammoniacal, and treated with hydrogen sulphide until all the iron has been precipitated as sulphide. This is collected on a filter and washed thoroughly with dilute ammonium sulphide solution. The filtrate is boiled to expel hydrogen sulphide, acidified with 60 c.c. of dilute sulphuric acid, cooled in ice-water, and the "cupferron" reagent is added. The precipitate which forms is collected on a filter, washed twenty times with dilute hydrochloric acid, dried at 110°, ignited, and the residue of zirconium oxide weighed. In the case of phosphatic minerals, the phosphoric acid must be removed by fusion with sodium carbonate before the zirconium is separated as described.

W. P. S.

**Properties of Some Chlorohydrocarbons and their Uses in Chemical Analysis. II. Estimation of the Chloroethanes.** I. GOWING-SCOPES (*Analyst*, 1914, **39**, 385—388. Compare this vol., ii, 141).—When tetra-, penta-, or hexa-chloroethane is treated with

phenylhydrazine, a precipitate of phenylhydrazine hydrochloride is formed, together with nitrogen and benzene. The reaction may be expressed by the equation



The reaction, however, varies with the conditions of the experiment, and the estimation of any one of the substances formed does not give a measure of the chloro-hydrocarbon. Further experiments showed that tetrachloroethane or pentachloroethane can be estimated in the following way, even in the presence of chloroethylenes, chloroform, or carbon tetrachloride. Ten c.c. of an alcoholic *N*/10-potassium hydroxide solution and 20 c.c. of xylene are placed in a stoppered flask and weighed; a few drops of the chlorohydrocarbon are then introduced, and the flask is again weighed. After a few minutes water is added, the solution is acidified with nitric acid, and the chloride is estimated by titration with silver nitrate and thiocyanate. One c.c. of *N*/10-silver nitrate solution is equivalent to 0.0168 gram of tetrachloroethane or 0.0202 gram of pentachloroethane. The amount of hexachloroethane in tetrachloroethane and pentachloroethane may be estimated by the method. When hexachloroethane is boiled with xylene and alcoholic potassium hydroxide solution, a deep, orange coloration is produced. This reaction may afford a means for the colorimetric estimation of hexachloroethane, since the coloration is not given by other chlorohydrocarbons.

W. P. S.

**Detection of Methyl Alcohol in Spirits.** R. VIVARIO (*J. Pharm. Chim.*, 1914, [vii], 10, 145—147).—The method depends on the formation of hydrogen cyanide when methyl alcohol, or a derivative, is treated with potassium hydroxide and hydroxylamine hydrochloride; ethyl alcohol, acetaldehyde, acetal, and amyl alcohol do not yield hydrogen cyanide. One hundred c.c. of the spirit to be tested are distilled, and the first 30 c.c. of distillate are boiled for seven hours under a reflux apparatus with 15 grams of potassium hydroxide and 1 gram of hydroxylamine hydrochloride. The mixture is then cooled, acidified with sulphuric acid, and distilled with steam. The distillate is tested for hydrocyanic acid by the Prussian-blue test.

W. P. S.

**Estimation of Alcohol in the Tropics.** K. C. BROWNING and C. T. SYMONS (*J. Soc. Chem. Ind.*, 1914, 33, 819—821).—Systematic investigations on the estimation of alcohol in the Tropics have led the authors to the conclusion that the brass Sikes's hydrometer, using the tables supplied by the makers of the instrument, gives quite inaccurate results, especially at low strengths; at no strength are the tables even approximately satisfactory. Bedford's tables, used with glass hydrometers, give the most satisfactory readings, except at low strengths. The brass hydrometer, used with Bedford's tables, gives very fair results.

The authors consider that the standard tables published in 1913 by the United States Bureau of Standards are the most accurate, and all alcoholic work should be based on these.

A table is given showing the relation between the refractive index at 30° and the percentage of alcohol for various mixtures of alcohol and water. The refractive index reaches a maximum at about 78·25% by weight of alcohol (compare Holmes, T., 1913, 103, 2165). T. S. P.

**Verification of the Methods of Analysis of Glycerophosphates and their Preparations.** M. FRANCOIS and E. BOISMENU (*J. Pharm. Chim.*, 1914, [vii], 10, 5—14, 51—57).—The methods used in the analysis of glycerophosphates are discussed, and a scheme is given for the investigation of pure and granulated calcium glycerophosphate, of the sodium salt, and also of commercial products.

Calcium glycerophosphate should be completely soluble in cold water (1 gram in 100 grams), and the solution should be neutral or slightly alkaline to phenolphthalein. It should not give a yellow precipitate with silver nitrate (mineral phosphates), neither should it be darkened by pure sulphuric acid (various organic matters). It should not yield a residue after extraction with 95% alcohol and evaporation of the solvent (glycerol, citric acid).

Water is determined by desiccation at 150°. The residue left after calcination (pyrophosphate) is estimated by ignition in a muffle, the last traces of carbon being oxidised, if necessary, by nitric acid. Phosphorus is estimated by fusing the salt with eight times its weight of potassium nitrate in a nickel dish, dissolving the cold fusion in water, precipitating the phosphoric acid with ammonium molybdate, and converting the latter precipitate into magnesium pyrophosphate. Calcium is precipitated as the oxalate from a solution of the salt which has been acidified with dilute acetic acid; the precipitate is ignited and weighed as calcium sulphate. The proportion of pure monoethereal salt is determined by Astruc's method of titration with *N*/10-sulphuric acid in the presence of helianthin as indicator. Test analyses give good results.

Granulated calcium glycerophosphate should be completely soluble in five times its weight of cold, distilled water, yielding a clear solution without acid reaction. It should not give a precipitate with silver nitrate.

Calcium pyrophosphate is estimated by ignition in a muffle furnace, the temperature of which must be raised gradually. The results may be rendered useless by the presence of mineral impurities. It is therefore preferable to determine the glycerophosphate as magnesium pyrophosphate. For this purpose, the product is mixed with four times its weight of potassium nitrate, and brought in very small, successive portions into a nickel crucible heated to dull redness. The determination is completed in the manner given for calcium glycerophosphate.

Sodium glycerophosphate is analysed in much the same manner as the calcium salt. The qualitative tests are the same; moisture is determined by desiccation at 150°, and sodium pyrophosphate by



ignition. Phosphorus is estimated through the phosphomolybdate. For the estimation of sodium, the salt is converted by ignition into sodium pyrophosphate; the latter is dissolved in water, and the solution warmed until conversion into orthophosphate is complete. The latter is precipitated by addition of barium hydroxide solution in slight excess. After filtration, the solution is neutralised by sulphuric acid in the presence of litmus; the barium sulphate is removed, the filtrate evaporated to dryness, and the residual sodium sulphate weighed. Test analyses give excellent results.

The authors are led to the following conclusions. The results obtained in the analyses of pure sodium and calcium glycerophosphates by their methods (which are similar to the methods of the Codex) show these methods to be exact, and also to be applicable to commercial products. Nevertheless, determination of residue left on calcination, of phosphorus and of metal are insufficient by themselves for the evaluation of commercial specimens, and Astruc's method should also be employed for the estimation of the monoethereal salt, which is the official product. The method of examination of granulated calcium glycerophosphate given in the Codex is insufficient, whilst Astruc's method loses its value on account of the presence of sugar. The content of calcium glycerophosphate can, however, be accurately determined from the estimation of phosphoric acid on the assumption that the latter is calculated to the salt,  $C_3H_5(OH)_2 \cdot PO_4Ca, H_2O$ . H. W.

**The Fachini-Dorta Method of (Approximately) Separating Liquid from Solid Fatty Acids in Oils and Fats.** ARMAND DE WAELE (*Analyst*, 1914, 39, 389—391).—The following method of applying this process was found to have advantages in manipulation over the older process. About 10 grams of the dry fatty acids are placed in a flask, dissolved in 90 c.c. of anhydrous acetone, the solution is warmed to  $25^\circ$ , and 10 c.c. of *N*/1-potassium hydroxide solution are added. The mixture is then cooled in ice-water for four hours, the precipitated soaps are collected on a filter, washed with acetone at  $0^\circ$ , dissolved in warm water, and the fatty acids liberated from the solution in the usual way, collected, dried, and weighed. The liquid acids may be separated from the acetone filtrate by adding an equal volume of water, 50 c.c. of ether, and hydrochloric acid. The ethereal solution is separated, washed with water containing a small quantity of acid, then evaporated, and the residue weighed. Unless precipitation of saturated fatty acids has occurred through the employment of lead as a drier, no diminution in the quantity of saturated fatty acids takes place when an oil is oxidised. W. P. S.

**The Insoluble Bromide Value of Oils.** JOHN A. L. SUTCLIFFE (*Analyst*, 1914, 39, 388—389).—With regard to a method suggested by the author (*Analyst*, 1914, 39, 28), and criticised by Gemmell (this vol., ii, 684), it is mentioned that the temperature of cooling before and during precipitation ( $11^\circ$ ) was stated simply to prevent formation of substituted bromine compounds. A direction to cool

to below  $5^{\circ}$  before filtration might have been inserted; the precipitate must be washed with cooled ether, and, unless the bromides when dried are white and crumbly, the estimation is to be rejected. It is not claimed that the precipitate consists of pure hexabromide, but the method is trustworthy within a limit of 1%. W. P. S.

**Production of  $\omega$ -Hydroxy-5-Methyl-2-furfuraldehyde from Carbohydrates and its Influence on the Estimation of Pentosans and Methylpentosans.** MARY CUNNINGHAM and CHARLES DORÉE (*Biochem. J.*, 1914, 8, 438—447).—The authors find that when dilute hydrochloric acid acts on hexoses, starch and cellulose,  $\omega$ -hydroxy-5-methyl-2-furfuraldehyde is formed in amounts varying from 1 to 2%. Although it is precipitated by phloroglucinol, it does not interfere with the accuracy of pentosan estimations made by the Kröber phloroglucinol method, provided aniline acetate is used as the indicator. This is accounted for on the ground of the slowness with which the  $\omega$ -hydroxymethylfurfuraldehyde is produced. The recognition of this substance, however, renders previous estimations of methylpentosan of doubtful value. H. W. B.

**Estimation of Sugar in Blood.** ARTHUR DUNCAN GARDNER and HUGH MACLEAN (*Biochem. J.*, 1914, 8, 393—403).—A method is described for estimating the sugar in 2 c.c. or less of blood, involving the use of dialysed iron to precipitate the proteins and a modification of Bertrand's method for the determination of the sugar in an aliquot portion of the filtrate. The results agree closely with those obtained by Bang's micro-method (this vol., ii, 75), which takes considerably longer to carry out. H. W. B.

**New Copaiva Balsam and Investigation of Copaiva Balsam.** J. D. RIEDEL (*Chem. Zentr.*, 1914, i, 1886—1887; from *Riedel's Ber.*, 1914, 27—29).—The adulteration of copaiva balsam with so-called African or Illurian balsam can be detected, according to Caesar and Loretz, by an optical examination of the ethereal oil obtained from the balsam by distillation with steam. True balsams are strongly dextrorotatory, but yield a levorotatory oil and a dextrorotatory resin. African balsam, on the contrary, is only slightly optically active, but yields a strongly dextrorotatory oil and an approximately equally strongly levorotatory resin.

A copaiva balsam obtained from Amazona, Brazil, has the following properties. It is a pale yellow, mobile, non-fluorescent liquid having a normal odour and taste, and giving a turbidity with an equal volume, and a white precipitate with an excess, of absolute alcohol. It has  $D^{15}_D$  0.930, saponification number 23.8, ester value 42.1,  $\alpha^{20}_D$   $-40^{\circ}$ , and contains 20.4% of resin ( $\alpha^{20}_D$   $-55^{\circ}$ ); the ethereal oil has  $\alpha^{20}_D$   $-35^{\circ}20'$ . C. S.

**Detection of Saponin in Beverages.** NAZARETH CAMPOS (*Ann. Chim. anal.*, 1914, 19, 289—293).—The beverage is neutralised with magnesium carbonate, concentrated, and extracted with phenol; the phenol solution is then shaken with ether and water, the

saponin being thus obtained in aqueous solution. Substances other than saponin, however, also pass into the aqueous solution and interfere with the tests which are applied to the residue, obtained on evaporation, in order to identify it as saponin. The solution is, therefore, evaporated to 25 c.c. and shaken with 125 c.c. of saturated barium hydroxide solution; a compound of saponin and barium hydroxide is precipitated. After the liquid has been decanted, the precipitate is decomposed with carbon dioxide, the barium carbonate is separated by filtration, and the filtrate evaporated to dryness. The residue obtained, consisting of saponin mixed with barium carbonate, is extracted several times with boiling alcohol, and the alcoholic solutions are evaporated separately. The first extract may contain a quantity of colouring matters, but the subsequent solutions yield pure saponin on evaporation. The sulphuric acid test is recommended for identifying the saponin. The reaction with Nessler's reagent, described by Vamvakas (A., 1906, ii, 504), is untrustworthy, since a number of materials, particularly coffee extract, yield substances giving reactions which cannot be distinguished from that given by saponin. W. P. S.

**Defecation of Urine by Acid Mercury Nitrate.** CH. TANRET (*J. Pharm. Chim.*, 1914, [vii], 9, 602).—In a recent communication by Berner (this vol., ii, 587), the use of mercury nitrate for the defecation of urine is ascribed to Patein and Dufau. The author points out that this reagent was first employed by him, and that his priority has been recognised by Patein and Dufau. H. W.

[**Estimation of Allantoin.**] MAURICE H. GIVENS (*J. Biol. Chem.*, 1914, 18, 417—424).—See this vol., i, 1144.

**The Determination of the Lime Requirements of the Soil.** H. B. HUTCHINSON and K. MACLENNAN (*Chem. News*, 1914, 110, 61—62).—A brief review of methods previously suggested for the estimation of the lime requirements, or acidity, of the soil. Many of these are purely qualitative, while the quantitative methods are largely based on reactions having no relation to those obtaining in the field.

The one proposed by the authors consists in the treatment of the soil with an  $N/50$ -solution of calcium hydrogen carbonate for three hours, under constant agitation. The soil suspension is then filtered, an aliquot portion of the filtrate titrated with  $N/10$ -acid, using methyl-orange as indicator, and the amount of calcium absorbed is then calculated. Usually, 10—20 grams of soil, and 200—300 c.c. of solution, are taken for field soils, but these amounts must be adjusted so that the concentration of the final hydrogen carbonate solution is not less than approximately  $N/100$ -strength.

H. B. H.

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## General and Physical Chemistry.

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### Spectrum of the Oscillatory Discharge in Various Gases.

RITA BRUNETTI (*Nuovo Cim.*, 1914, [vi], 7, i, 390—410).—The author has investigated the spectra of the oscillatory discharge passing between magnesium electrodes in hydrogen, oxygen, nitrogen, and carbon dioxide. The first part of the discharge shows lines of the gas and of the metal of high and low excitation; in the second part, the metallic lines of low excitation remain, and are accompanied by the bands of the gas and of the compounds of the latter with the metal. The bands start from the positive electrode and cease at a distance from the negative one, whilst the gas lines traverse the whole space between the electrodes, and the metal lines are not found in the regions bordering on the electrodes. The first phase of the oscillatory discharge presents, indeed, those complex phenomena known as a spark; it opens the path by ionising the gas, carries with it occasional particles of the metal, and heats the electrodes to redness, being then replaced by the second phase of the discharge, namely, the arc. In the latter there is a localisation of the seat of emission of the various series of lines, the principal series originating in a stratum surrounding the accessory series emitted by the central regions. The heating of the electrodes during this second part of the discharge depends on the thermal conductivity of the surrounding medium; in hydrogen, the heating does not last so long as in nitrogen, oxygen, or carbon dioxide, whilst the discharge is extinguished sooner. The sudden change in potential at the electrodes falls off in the adjacent regions; for equal magnitudes of the auto-induction, the difference of potential at the electrode is greater in oxygen than in nitrogen, and is least in hydrogen. The luminous emission is subjected to the action of the gas in which the discharge takes place, since the gas modifies to some extent both the distribution of the electric field interposed between the electrodes and the temperature of the medium.

T. H. P.

### Spark Spectrum of Nickel under Moderate Pressures.

E. G. BILHAM (*Phil. Trans.*, 1914, [A], 214, 359—371).—The influence of pressure on the spark spectrum of nickel has been examined for pressures up to eleven atmospheres. One of the most striking results of the increase of pressure is the change in the character of the lines, which, according to the differences in behaviour, may be divided into five groups. These groups contain, respectively, (1) lines which show symmetrical reversion; (2) lines which reverse unsymmetrically; (3) lines which remain bright and sharp; (4) lines which remain bright, but are symmetrically broadened; (5) lines which are unsymmetrically broadened towards the red. The general effect of an increase of pressure on the relative intensi-

ties of the lines is similar to that produced by the inclusion of self-induction in a spark circuit.

All nickel lines are displaced towards the red, the average shifts being the same for lines of the first and second groups, whilst the shifts are larger for unreversed lines, and are greatest for lines which broaden unsymmetrically towards the red.

The observations point to the existence of two enhanced lines,  $\lambda 3514.14$  and  $\lambda 3608.98$ , the wave-lengths of which are practically identical with those of nickel arc lines. H. M. D.

**The Infra-Red Absorption Bands of Hæmoglobin.** H. HARTRIDGE and A. V. HILL (*Proc. physiol. Soc.*, 1914, li—liii; *J. Physiol.*, 48).—The absorption spectrum of reduced oxy- and carboxy-hæmoglobin was measured by means of a very sensitive spectrophotometer. It was found that the absorption by hæmoglobin was greatest, by oxyhæmoglobin less, and by the carboxy-complex less still. The differences are sufficiently great for it to be possible to employ the method for determining the amounts of these compounds present in a given solution. S. B. S.

**Simple and Complex Rotatory Dispersion.** T. MARTIN LOWRY and T. W. DICKSON (*Trans. Faraday Soc.*, 1914, 10, 96—102. Compare P., 1913, 29, 185).—All cases of rotatory dispersion may be represented by Drude's formula. Simple rotatory dispersion may be expressed by the equation  $\alpha = k/(\lambda^2 - \lambda_0^2)$ , whilst complex rotatory dispersion requires two or more terms, some of which may be negative. Anomalous dispersion is probably due in many instances to dynamic isomerism. C. H. D.

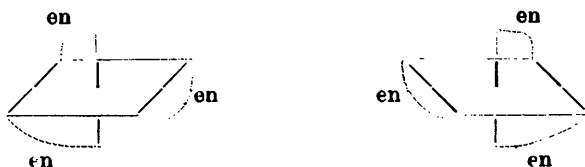
**An Enclosed Cadmium Arc for Use with the Polarimeter.** T. MARTIN LOWRY and H. H. ABRAM (*Trans. Faraday Soc.*, 1914, 10, 103—106).—For substances with simple rotatory dispersion (see preceding abstract), measurements with light of two wave-lengths, such as the green and violet mercury lines, are sufficient to determine the form of the dispersion curve. For more complex cases, a cadmium arc may be used. The arc passes between water-cooled electrodes of solid cadmium in a vessel exhausted by means of a Gaede pump. When the vacuum is good, the arc will sometimes start itself, but usually the passage of a spark from Leyden jars is necessary. There is a silica bridge between the electrodes, and the tube has two quartz windows.

$\alpha$ - and  $\beta$ -Methylglucoside show simple rotatory dispersion, the ratios for the violet and green mercury lines being the same as for the green and red cadmium lines. C. H. D.

**The Constitution of Liquid Mixtures and Their Rotatory Power.** A. COTTON (*Trans. Faraday Soc.*, 1914, 10, 91—95).—The determination of the optical rotatory power and of the magnetic birefractive of the same mixture of liquids is proposed as a means of determining whether complexes are present. C. H. D.

**Rotatory Power of Mixed Crystals,  $\text{NaClO}_3\text{-AgClO}_3$ .** ELIGIO PERUCCA (*Atti R. Accad. Sci. Torino*, 1914, 49, 1127—1134. Compare Retgers, A., 1890, 1208; Foote, A., 1902, ii, 453).—The composition of mixed crystals of sodium and silver chlorates varies sensibly among crystals from one and the same crystallisation, and also from sector to sector of an individual crystal. The crystals exhibit various optical anomalies, the double refraction of two sectors increasing with the content of silver chlorate. The specific rotations have been measured, and are found to be in accord with Bodländer's additive law. Monometric silver chlorate has an approximately constant specific gravity of about 4.20 in mixed crystals of all compositions, and its specific rotation is  $12.65^\circ$ , which is about four times that of sodium chlorate. T. H. P.

**The Optical Activity of Chemical Compounds without Carbon.** A. WERNER (*Compt. rend.*, 1914, 159, 426—429).—The author has prepared an optically active compound containing no carbon, but similar in composition to the cobalt triethylenediamine salts  $(\text{Co en}_3)\text{X}_3$ , en representing  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ . In place of each molecule of ethylenediamine there is in the new compounds one molecular complex  $[(\text{OH})_2\text{Co}(\text{NH}_3)_4]\text{X}$ , their asymmetric configuration being represented by



The salts prepared were the *bromides*, having the composition  $(\text{Co}[(\text{OH})_2\text{Co}(\text{NH}_3)_4]_3)\text{Br}_6\cdot 2\text{H}_2\text{O}$ , the active forms being prepared by precipitation from their  $\pi$ -bromocamphorsulphonates with sodium bromide. The active *d*-salt prepared in this way crystallises in small, greyish-brown plates and is very soluble. It has  $[\alpha]_{560}$  varying from  $4000^\circ$  to  $4500^\circ$ , its rotatory power diminishing rapidly in aqueous solution, the salt becoming inactive after two hours.

W. G.

**The Existence of Racemic Tartaric Acid in Solution.** E. DARMOIS (*Trans. Faraday Soc.*, 1914, 10, 80—83. Compare A., 1908, ii, 747).—When *d*- and *l*-tartaric acids are mixed in unequal proportions in solution, the measured rotatory dispersions are those which would be expected if the two acids remained uncombined. Mixtures of *d*-tartaric acid and racemic acid also behave in solution as if the latter compound were dissociated into its components.

C. H. D.

**The Rotatory Power of Tartaric Acid.** G. BRUHAT (*Trans. Faraday Soc.*, 1914, 10, 84—90).—The rotatory power of fused and undercooled tartaric acid has been observed at temperatures from  $180^\circ$  downwards, and for light of different wave-lengths. The dispersion is normal at  $180^\circ$ , but becomes anomalous below  $100^\circ$ .

The dispersion curves are plotted together with those determined by Arndtsen (*Ann. Chim. Phys.*, 1858, [iii], 54, 403) for aqueous solutions of various concentrations, and exhibit a complete similarity. The only hypothesis which will account for the phenomena is that of the presence of two compounds of opposite rotatory power, in proportions varying with the temperature and the concentration, in both the solutions and the undercooled acid. One of these compounds being ordinary tartaric acid, the other must be a complex aggregate.

Cryoscopic determinations in water by acetic acid show that the quantity of the polymeride cannot much exceed 2%, and it must have a rotatory power of from  $-80^{\circ}$  to  $-200^{\circ}$ . This is comparable with the rotatory power of solid rubidium tartrate.

C. H. D.

#### Discovery of the Sensitiveness of Silver Salts to Light.

ICILIO GUARESCHI (*Att. R. Accad. Sci. Torino*, 1914, 49, 1083—1088).—The author regards Homberg's observation in 1694 (compare Fritz, this vol., ii, 234) as of little importance, since it refers to silver nitrate in contact with organic matter, which accelerates the decomposition of the silver salt, and since also it was known much earlier, before the time of Boyle (1663), that silver salts blacken in the light or in the air. Of far greater importance to the development of photography were the investigations of Schulze (1727), and particularly those of Beccari (1757) and Scheele (1777). The invention of the dark chamber is due to G. B. Porta (Naples, 1540—1615).

T. H. P.

#### Radium Constants on the International Standard.

SIR ERNEST RUTHERFORD (*Phil. Mag.*, 1914, [vi], 28, 320—327).—A recalculation of the radioactive magnitudes in the author's "Radioactive Substances and their Radiations" is given on the basis of the International Standard. The equilibrium ratio of radium to uranium is now  $3.23 \times 10^{-7}$ , the yearly production of helium per gram of radium, calculated 163, found 164 cu. mm.; the total observed heating effect per gram of radium in equilibrium with its first four products is 134.7 calories per hour, made up of radium, 25.1; emanation, 28.6; radium-A, 30.5; -B and -C, 50.5; the equilibrium volume of emanation per gram of radium, calculated, 0.62, found 0.63 cu. mm.; number of  $\alpha$ -particles expelled per second per gram of radium, itself,  $3.57 \times 10^{10}$ , in equilibrium with first four products,  $14.3 \times 10^{10}$ ; the total positive charge in the latter case, 33.2 *E.S.U.*, or  $1.11 \times 10^{-9}$  *E.M.U.*; the total negative charge carried by the  $\beta$ -particles of radium-B and -C, 18.3 *E.S.U.*; the total saturation current due to  $\alpha$ -rays from 1 curie of emanation, itself,  $2.89 \times 10^6$  *E.S.U.*, and with its products,  $9.94 \times 10^6$ .

With regard to the heating effect of the emanation, calculated from the kinetic energy of the  $\alpha$ -particles expelled, which is 7% lower than the observed, the following explanation is suggested. The energy of the electronic distribution of an atom may

be expected to increase with increase of the nuclear charge, or the expulsion of the  $\alpha$ -particle may be expected to be accompanied by decrease of the energy of the electronic distribution, and the expulsion of the  $\beta$ -particle by the opposite effect. The relative heating effect of radium-*B* and -*C*, as compared with that of the emanation and radium-*A*, is less than the calculated, in agreement with this view, since  $\beta$ -rays as well as  $\alpha$ -rays result in the change of radium-*B* and -*C*. It is calculated that of the total heat effect in each of the  $\alpha$ -ray changes, some 90% is due to the kinetic energy of the  $\alpha$ -particle expelled and 10% to loss of internal atomic energy in the manner indicated.

From the value for  $nE = 1.11 \times 10^{-9}$  E.M.U., where  $n$  is the number of  $\alpha$ -particles per gram per sec. of radium itself, and  $E$  is the charge each particle carries, the half-period of radium on the International Standard is 1690 years. The experimental determinations give 2000 years (Boltwood), 1800 years (Keetman), 1730 years (Stefan Meyer). F. S.

**The Mass and Velocities of  $\alpha$ -Particles from Radioactive Substances.** SIR E. RUTHERFORD and H. ROBINSON (*Phil. Mag.*, 1914, [vi], 28, 552–572).—From the mean of recent determinations of the atomic weight of helium, 3.998, and the value of  $e/m$  for the hydrogen atom, 9570, the value of  $e/m$  for the  $\alpha$ -particle, or helium atom carrying two positive charges, should be 4826, whereas the previous experimental value is 5070. To test as thoroughly as possible whether the value of  $e/m$  for a high-speed positive particle agrees with the value from electrochemical data, experiments have been made, to an accuracy of  $\frac{1}{4}\%$ , on the value of  $e/m$  of the  $\alpha$ -particle, by measuring the deflexions of a narrow pencil of  $\alpha$ -rays in a vacuum by the photographic method, in very carefully determined electromagnetic and electrostatic fields. The final results for the value of  $e/m$  of the  $\alpha$ -particles of radium emanation, radium-*A* and radium-*C*, lay between 4813 and 4826, the mean value being 4820, which agrees with the calculated result within the limits of error. The initial value of the velocity of the  $\alpha$ -particles of radium-*C* is  $1.922 \times 10^9$  cm. per second, about 7% lower than the previously accepted value. On the new data, the development of heat calculated from the kinetic energy of the  $\alpha$ -particles for radium and its products is 7% less than the observed, and part of the heat effect is probably due to other sources (see preceding abstract).

A special search was made for atoms differing from the  $\alpha$ -particle either in mass or charge, and the conclusion is drawn that if any such exist their number is certainly less than 1 in 10,000 of the total number of  $\alpha$ -particles. F. S.

**Connexion between the  $\beta$ - and  $\gamma$ -Ray Spectra.** SIR ERNEST RUTHERFORD (*Phil. Mag.*, 1914, [vi], 28, 305–319).—Previous investigations on the  $\beta$ - and  $\gamma$ -rays are discussed from the point of view of the general problem of radiation, and tentative conclusions drawn. The results of Chadwick (this vol., ii, 408) show that even



the intense lines in the magnetic spectrum of radium-*B* represent a small fraction only of the total  $\beta$ -rays emitted. From this it seems that  $\beta$ -ray magnetic spectra are probably continuous, with a superimposed line spectrum. The continuous spectrum is ascribed to the escaping  $\beta$ -particle suffering in its ejection from the nucleus of the atom several collisions of the ordinary type with the electrons in the outer electronic distribution of the atom. In addition, it is supposed that certain well-defined regions in this part of the atom are set into definite vibration, whence the "characteristic"  $\gamma$ -radiations of the atom arise and one or more groups of  $\beta$ -rays of definite speed are expelled, which give the line spectrum observed. The conclusion that characteristic  $\gamma$ -rays and a line spectrum of  $\beta$ -rays must accompany one another is borne out by the evidence. Radium-*E*, which gives only a continuous  $\beta$ -ray spectrum, gives little or no  $\gamma$ -radiation.

To explain their absence in such particular cases, the conclusion is drawn that the direction of expulsion of the  $\beta$ -particle from the nucleus with regard to the structure of the atom must be fixed and be the same for all the atoms. Thus if this direction does not lie through one of the vibrating regions of the atom before postulated, neither  $\gamma$ -radiation nor "line"  $\beta$ -radiation is emitted. The same explanation covers the remarkable anomalies exhibited in the types and relative intensities of  $\gamma$ -rays emitted by the various radio-elements. In the bombardment of atoms by cathode rays of sufficient speed, however, the rays enter the atoms in all directions, and all types of characteristic *X*-rays have a chance of being excited.

Accepting Planck's relation between the frequency and energy of radiation and his values for the numerical constant and for the electronic charge, the experimental evidence is reviewed from a point of view differing from that before propounded. The primary effect of the ejection of the  $\beta$ -particle from the nucleus is the excitation of  $\gamma$ -rays at one vibrating region of frequency  $\nu_1$ , and the energy of these  $\gamma$ -rays suffers partial or complete conversion into energy of "line"  $\beta$ -radiation in the same region or in another vibrating region of frequency  $\nu_2$ . The energy of the  $\beta$ -particle in these cases will be either  $p h \nu_1$  or  $p h \nu_1 - q h \nu_2$ , where  $p$  and  $q$  are integers and  $h$  is Planck's constant. On comparing the energy of the lines in the  $\beta$ -ray spectrum of radium-*B* and -*C* with the frequency of the  $\gamma$ -rays, numerous close agreements are observed which can hardly be accidental. Thus the unit of energy,  $0.4284 \times 10^{13}e$ , which enters as an integral multiple in the lines Nos. 1 to 29 (A., 1913, ii, 899) of the  $\beta$ -ray spectrum of radium-*C* is, within the experimental error, one-third of  $1.25 \times 10^{13}e$ , the energy of one of the strong lines of the  $\gamma$ -ray spectrum of radium-*C*, reflected from rock-salt at an angle of  $1^\circ 0'$ , as deduced by Planck's relation. Of twelve strong lines of the  $\beta$ -ray spectrum, the energies of six are multiples of  $1.285 \times 10^{13}e$ , and thirteen (including two of the first six) are multiples of another unit,  $0.74 \times 10^{13}e$ , which corresponds with the line reflected by rock-salt at  $1^\circ 40'$  in the  $\gamma$ -ray spectrum of radium-*B* and -*C*, and is believed to be a close

doublet, one component belonging to each radio-element. The two strong lines not so included in the  $\beta$ -ray spectrum correspond with twelve and ten times a third unit,  $1.75 \times 10^{13}e$ , which again corresponds with the  $\gamma$ -ray line of shortest wave-length yet observed, namely, that reflected from rock-salt at an angle of  $0^\circ 43'$ .

With regard to the  $\beta$ -ray spectrum of radium-*B*, the evidence is similar, but less conclusive, on account of the large number of lines in the  $\gamma$ -ray spectrum. Two of the strong lines are expressed by small multiples of  $0.870 \times 10^{13}e$ , to be expected of the  $\gamma$ -ray reflected at  $1^\circ 24'$ . But the  $\gamma$ -ray lines reflected at  $10^\circ$  and  $12^\circ$  do not appear to be responsible for any of the  $\beta$ -rays.

Finally, some as yet untested deductions on the relation between the spectra of  $\beta$ -rays excited by characteristic *X*-rays and the wave-length of the latter are drawn. F. S.

**Number of Ions Produced by the  $\beta$ - and  $\gamma$ -Radiations of Radium.** H. G. J. MOSELEY and H. ROBINSON (*Phil. Mag.*, 1914, [vi], 28, 327—337).—The total number, *N*, of pairs of ions produced per second by the  $\gamma$ -rays of radium-*B* and -*C* in equilibrium with 1 gram of radium is determined to be  $1.22 \times 10^{15}$ , whereas the  $\alpha$ -rays of radium-*C* produce  $8.46 \times 10^{15}$ . The ratio between these quantities are as 5.7 : 39.4, whereas the heating effects observed are 6.4 and 39.4 cal. per hour. In the following table the values of *N*, the calculated heating effect, and the average energy emitted, per atom changing, are given for the  $\beta$ - and  $\gamma$ -rays of radium-*B* and -*C*:

	<i>N</i> /10 <sup>15</sup> .	Heating effect (cal. per hour).	Average energy per atom ( $\times 10^{-6}$ erg.).
$\beta$ -Rays of radium- <i>B</i> ... ..	0.325	1.71	0.55
$\beta$ -Rays of radium- <i>C</i> ... ..	0.64	3.35	1.09
$\gamma$ -Rays of radium- <i>B</i> ... ..	0.084	0.44	0.14
$\gamma$ -Rays of radium- <i>C</i> .. ..	1.184	5.96	1.94
Total $\beta$ - and $\gamma$ -rays of radium- <i>B</i> .	0.41	2.15	0.70
Total $\beta$ - and $\gamma$ -rays of radium- <i>C</i> .	1.774	9.3	3.02

On Rutherford's original theory, the figures in the last two lines of the last column should be the energy of the  $\beta$ -particle which has escaped without exciting  $\gamma$ -radiation. In the case of radium-*C*, however, a few  $\beta$ -particles with energy as high as  $3.9 \times 10^{-6}$  erg. have been observed. In the case of radium-*B* the fastest  $\beta$ -ray observed has the energy  $0.6 \times 10^{-6}$  erg. F. S.

**Secondary  $\gamma$ -Radiation.** D. C. H. FLORANCE (*Phil. Mag.*, 1914, [vi], 28, 363—367. Compare this vol., ii, 160).—Using equal masses per unit area of thin radiators, carbon, aluminium, copper, zinc, tin, and lead, the amount of  $\gamma$ -radiation scattered by the radiator is the same for all after it has passed through 0.084 cm. of lead. After passage through 0.202 cm. of aluminium the lead radiator produced rather more scattered radiation than the others. This extra radiation from lead is probably a characteristic radiation. The scattering appears to be simply proportional to the number of electrons in the atom or to the weight of the atom, an electron in a light

aluminium atom scattering to the same extent as one in a heavy atom of lead. The loss of energy by the  $\gamma$ -ray to the electron increases with the angle of scattering, and the penetrating power of the scattered radiation depends essentially on the angle of scattering and not on the material of the radiator. F. S.

**The Distribution of Energy in the Different Types of  $\gamma$ -Rays Emitted from Certain Radioactive Substances.** [MISS] JADWIGA SZMIDT (*Phil. Mag.*, 1914, [vi], 28, 527—539).—The determination of the total number of ions each type of rays produces in air or other gases gives the ratio of the energies in the different types if it is assumed that the same proportion of the energy of different rays is spent in ionisation and that the energy required to produce an ion is the same for  $\gamma$ -rays of different penetrating power. To test the second point, the total ionisation in various gases by  $\gamma$ -rays of different hardness was determined. For the soft  $\gamma$ -rays of radium-*D* the ionisation produced in sulphur dioxide, carbon dioxide, and air is proportional to the absorption in these gases, but in the case of hydrogen sulphide greater ionisation is produced, as is the case also with *X*-rays. In the case of the hard  $\gamma$ -rays from radium-*B* and radium-*C*, the ionisation is proportional to the absorption.

Of the total  $\gamma$ -ray energy of radium-*D*, the hard  $\gamma$ -rays possess between 17 and 35%. In the  $\gamma$ -rays of radium-*B* and -*C*, the energies of the soft rays of radium-*B*, the hard rays of radium-*B*, and the rays of radium-*C* are estimated as in the ratio of 1: 45: 639. F. S.

**Ordinals or Atomic Numbers?** A. VAN DEN BROEK (*Phil. Mag.*, 1914, [vi], 28, 630—632).—The author criticises Rydberg's suggestion (this vol., ii, 599) that the frequencies of the *X*-ray spectra are related to the "ordinals" which are two units higher than the atomic numbers. The hypothesis that the frequencies are related to the atomic numbers affords a more satisfactory account of the experimental results, and also affords a basis for the explanation of observations on the scattering of  $\alpha$ -particles and of Röntgen rays.

H. M. D.

**The Absorption Coefficients of *X*-Rays.** W. H. BRAGG and S. E. PEIRCE (*Phil. Mag.*, 1914, [vi], 28, 626—630).—The new method of determining the wave-lengths of *X*-rays by reflection from crystal surfaces has made it possible to determine the relation between wave-length and absorption coefficient. The wave-lengths examined are those emitted by anti-cathodes of silver, palladium, and rhodium, each of which yields a spectrum consisting mainly of two well-defined intense lines. Each wave-length was isolated by reflection from a rock-salt crystal, and its absorption coefficient in various metals determined. Barkla's rule that the ratio of two absorption coefficients is independent of the wave-length of the rays is confirmed over a wide range.

The results suggest that the absorption coefficient of any sub-

stance of atomic number  $N$  is equal to  $CN^4$ , where  $C$  has constant values over prescribed ranges. The constant changes its value suddenly in passing through the wave-lengths of the Rh-Pd-Ag group examined. According to Darwin, the absorption coefficient varies as the  $5/2$  power of the wave-length of the rays absorbed, and this, combined with the preceding, gives the very general rule that the atomic absorption coefficient, defined as the proportion of the energy of the  $X$ -ray pencil which is absorbed on crossing a surface on which lies one atom to every square centimetre, is  $CN^4\lambda^{5/2}$ , where  $\lambda$  is wave-length of the  $X$ -ray,  $C$  is equal to  $1.79 \times 10^{-6}$  for all values of  $N$  between 13 (Al) and 46 (Pd), and to  $0.235 \times 10^{-6}$  for all greater values. F. S.

**Effect of  $X$ -Rays on the Action of Certain Enzymes.** A. RICHARDS (*Amer. J. Physiol.*, 1914, 35, 224—238).—The author describes experiments which indicate that a short exposure of pepsin, diastase, and other enzymes to  $X$ -rays increases the activity, but if the exposure be prolonged for more than five minutes the effect is to diminish the activity of the enzyme. Between these two extremes there lies a point at which the radiation is ineffective. The accelerating and the inhibiting effects are slight, but seem to be definite. H. W. B.

**Experiments on the Active Deposit of Radium.** E. M. WELLISCH (*Phil. Mag.*, 1914, [vi], 28, 417; *Amer. J. Sci.*, 1914, [iv], 38, 283—304. Compare A., 1913, ii, 905).—In a series of experiments on the distribution of the active deposit from radium emanation in ethyl ether, it was found that neither a positive nor negative potential exerts any appreciable effect, the proportion reaching the central electrode of a cylindrical vessel being 10%. Hence the particles of active deposit at the end of their recoil paths in ether are uncharged, the amount reaching the electrodes arriving there by diffusion.

When the emanation in relatively large quantity is mixed with air, the active deposit particles in the gas form large aggregates which acquire positive and negative charges from the ions present in the gas. The formation of these aggregates appears to cease abruptly when the concentration of the emanation and the degree of ionisation it produces sink below a certain value. Under these conditions, the particles in the gas are practically all neutral, and reach the electrodes through simple diffusion, the diffusion coefficient in dry air at atmospheric pressure and about  $20^\circ$  being approximately  $0.045 \text{ cm.}^2 \text{ sec.}^{-1}$ . F. S.

**The Distribution of the Active Deposit of Radium in Electric Fields.** H. P. WALMSLEY (*Phil. Mag.*, 1914, [vi], 28, 539—551. Compare A., 1913, ii, 905).—In the case of the radium active deposit, some 5 to 10% is deposited on the anode, and this has been further investigated. This part is ascribed to the diffusion of unchanged particles of radium-A, and no negatively charged particles exist. F. S.

**Origin of the Electron Emission from Glowing Solids.** FRANK HORTON (*Phil. Trans.*, 1914, [A], 214, 277—294).—Experiments on the electron emission from Nernst filaments have been made with the object of throwing further light on the origin of this emissive effect and of testing the "chemical action" theory of the working of an oxide electrode. A comparison was made of the electron emission from a filament (1) when heated by continuous and by alternating currents; (2) when heated by the passage of a current and heated without conducting the heating current; (3) heated in the ordinary manner and compared with the emission of the same material when heated on platinum. These experiments indicate that the electron emission is not connected either directly or indirectly with the electrolysis which accompanies the passage of the current. At a given temperature, the emission is the same whether the current through the filament is large or small. From this it may be inferred that the action of a Wehnelt cathode is not due to the recombination of electrolytically separated calcium and oxygen, as has been suggested.

No definite conclusion can be drawn from the results in regard to whether the electron emission is purely a thermal effect or is due in some way to chemical action. The fact that the emission increases when a chemically active gas is allowed to enter the discharge tube may or may not be due to chemical action, and it is probable that the cause of the increased activity is different in different cases.

H. M. D.

**Radium : Uranium Ratio in Carnotites.** S. C. LIND and C. F. WHITTEMORE (*J. Amer. Chem. Soc.*, 1914, 36, 2066—2082).—The samples of carnotite used in this investigation were representative of the principal occurrences in Colorado and Utah; all grades containing from 1.5% to 33% of  $U_3O_8$  were included. Samples representing large quantities of ore (from a few hundred pounds to several tons) gave a ratio Ra : U identical with that of pitchblende,  $3.33 \times 10^{-7}$ . Samples from small quantities (a few pounds) exhibited abnormal ratios, ranging from  $2.48 \times 10^{-7}$  to  $4.6 \times 10^{-7}$ . These abnormal ratios are probably due to a transposition of radium within a bed of ore, producing local differences which are neutralised when large quantities of ore are mixed.

Carnotite has a high emanating power, varying from 16% to 50%. In order to obtain concordant results by Boltwood's emanation method, it was found desirable to make the determinations of the emanating power and the emanation liberated by solution strictly complementary to each other by determining the emanation liberated by solution on the same sample from which the emanation power had just been determined. Radium can be more easily determined by the emanation method in one operation, either by solution or by ignition from tubes in which it has been sealed for a month to attain equilibrium.

E. G.

**The Electrical Resistance and Critical Ranges of Pure Iron.** G. K. BURGESS and I. N. KELLBERG (*J. Washington Acad. Sci.*, 1914, 4, 436—440).—The variation of the resistance of pure iron

with temperature has been examined between  $0^{\circ}$  and  $950^{\circ}$ . The method employed consisted in comparing the resistances of iron and platinum wires, which were wound on the same support and enclosed in an exhausted quartz tube heated in an electric furnace. With the aid of a drum-chronograph, the times at which the resistances were measured could be accurately recorded, the resistance of the platinum wire affording a measure of the temperature of the iron wire at any moment.

The results show that the resistance of iron increases at a gradually increasing rate until the neighbourhood of the first critical region ( $A_2$ ) is reached. This region is characterised by a point of inflexion on the resistance temperature curve at  $757^{\circ}$ . As the temperature is further increased, there is an abrupt fall in the resistance at about  $894^{\circ}$ , and the reverse change occurs at approximately the same temperature when the temperature is allowed to fall. This second critical region ( $A_3$ ) extends over an interval of  $25^{\circ}$ . Whilst the change  $A_2$  is reversible and does not appear to be associated with any alteration in crystalline structure, the change  $A_3$  seems to be progressive and (thermo-electrically) non-reversible, and furthermore it is associated with a change in crystalline form.

H. M. D.

**Measurement of Oxidation Potentials at Mercury Electrodes. I. The Stannic-Stannous Potential.** GEORGE SHANNON FORBES and EDWARD PAYSON BARTLETT (*J. Amer. Chem. Soc.*, 1914, **36**, 2030—2040).—The work of earlier observers on the stannic-stannous potential has not given concordant results, and the present investigation has therefore been carried out.

It has been found that mercury is superior to platinum for use in measuring oxidation potentials of low intensity as results are obtained more rapidly and are less liable to be vitiated by irregularities in surface energy of the electrode or by the presence of traces of oxygen.

The potentials of mixtures of stannic and stannous chlorides containing  $\frac{1}{4}$  gram-atom of tin per litre in hydrochloric acid of three different concentrations have been measured at mercury electrodes at  $25^{\circ}$ . Some measurements were also made of mixtures containing only  $\frac{1}{8}$  gram-atom of tin per litre. The potential has been found to be nearly independent of the concentration, but is very slightly more electro-negative in the more dilute solutions.

In order to ascertain the values which should be observed if acid could be eliminated without the appearance of hydrolysis, the potentials for selected values of the concentration ratio have been plotted against the several concentrations of acid employed and extrapolated to zero concentration of acid; the graphs thus obtained are nearly straight lines. Up to two gram-mols. of hydrochloric acid per litre the potentials are expressed accurately by the formula  $\pi = 0.426 + 0.030 \log \text{Sn}^{\text{IV}}/\text{Sn}^{\text{II}} - 0.011 \times \text{concentration of hydrochloric acid}$ , provided that sufficient acid is added to prevent hydrolysis.

E. G.

**Diffusion and Membrane Potentials.** E. B. R. PRIDEAUX (*Trans. Faraday Soc.*, 1914, 10, 160—166).—The membrane potential has been determined when two solutions of sodium benzoate, of different concentrations, are separated by parchment. Calomel electrodes are used. The potentials observed are considerably higher than the ordinary diffusion potentials. The effect appears to be to decrease the mobility of the anion as compared with that of the cation, but the membrane is never completely impermeable to the anion.

C. H. D.

**Studies on a New Kind of E.M.F. I.** REINHARD BEUTNER (*J. Amer. Chem. Soc.*, 1914, 36, 2040—2045).—The *E.M.F.* of galvanic cells composed of insoluble inorganic liquids and aqueous solutions (A., 1913, ii, 469) is discussed, and it is shown that the change of the *E.M.F.* of such systems must be due to the change of potential difference located at the junction of the organic liquid and the aqueous solution. The observations on cells containing salicylaldehyde as a middle conductor afford an imitation of the electrode-like potential differences between certain living tissues and aqueous solutions (Loeb and Beutner, A., 1912, ii, 663). It is shown that the potential difference at the junction of the two phases does not depend on ionic mobility as does the potential difference between miscible solutions, but must have properties characteristic of potentials at metallic electrodes.

E. G.

**Studies on a New Kind of E.M.F. II. Cell Arrangements of Aqueous and Nitrobenzene Solutions Containing One Common Ion in Both Phases.** REINHARD BEUTNER (*J. Amer. Chem. Soc.*, 1914, 36, 2045—2059).—In the preceding paper, reference has been made to the existence of interphase potential differences with properties resembling electrode potentials.

The *E.M.F.* of cells consisting of aqueous and nitrobenzene solutions has now been measured. The solutions in contact with each other always contain one common ion, and the potential differences at the nitrobenzene–water interphase can therefore be easily calculated from the thermodynamic formula. It is proved that the total *E.M.F.* of cells which consist of two nitrobenzene solutions in contact with each other between two identical aqueous solutions is located at the phase junctions, and not at the junction of the two nitrobenzene solutions.

Ostwald has suggested that a selective ionic permeability of membranes is the cause of physiological currents. According to this hypothesis, the *E.M.F.* produced by a water-immiscible layer is not located at the phase-junction but inside the layer or membrane. This theory does not accord with the experimental results obtained in the present investigation.

E. G.

**Passivity of Metals.** HORACE G. BYERS and SETH C. LANGDON (*J. Amer. Chem. Soc.*, 1914, 36, 2004—2011).—It has been shown by earlier work (Byers, A., 1908, ii, 1026; Byers and Darrin, A., 1910, ii, 579; Byers and Morgan, A., 1911, ii, 1057; Byers and Langdon,

A., 1913, ii, 552) that the establishment of the passive state in iron used as an anode is affected by the character and condition of the metal, the electrolyte, the temperature, the current density, the duration of passage of the current, and the character of movement of the electrolyte. Experiments are now described which indicate that another factor must be added to these, namely, the concentration of the dissolved oxygen about the anode, and that this is apparently the determining factor. When all these factors are taken into account, constant results can be obtained with respect to the time required to render iron passive with a given current in sulphuric acid, and a critical current density in nitric acid can be determined.

Passivity, when not caused by a visible film of oxygen, is considered to be due to the fact that the rate of ionisation of certain metals is not sufficient to carry a current of more than a certain density. When such current density is exceeded, oxygen electrodes, consisting of occluded oxygen, are formed in electrolytes consisting of oxygen compounds. Non-anodic passivity is also regarded as due to occlusion of oxygen and consequent protection of the metal from attack.

E. G.

**Electro-deposition of Cadmium. I. and II. FRANK C. MATHERS and HUGH M. MARBLE** (*Trans. Amer. Electrochem. Soc.*, 1914, 25, 297—318, 319—333).—I. A review of the work done in the refining and commercial plating of cadmium. Reference is made to work done with (1) sulphate solutions, (2) nitrate solutions, (3) haloid solutions, (4) silicofluoride solutions, (5) cyanide solutions, (6) phosphate solutions, (7) ammoniacal solutions, (8) oxalate solutions, (9) acetate, formate, lactate, and succinate solutions, and (10) tartrate solutions.

II. A large number of experiments have been carried out with the object of determining which salts of cadmium are best suited for giving smooth, adherent, and non-crystalline deposits. Baths were made up of various cadmium salts containing 4% of cadmium, and electrolysed between cadmium electrodes with a cathode current density of 0.4 amp. per 100 sq. cm.; the solutions were stirred at intervals. The deposits obtained from ammoniacal and alkaline tartrate baths were hopelessly spongy. The deposits from solutions of acetate, bromide, iodide, sulphate, phosphate, and chloride were rough and crystalline. A number of experiments are described with chloride baths to which various other substances had been added, for example, a bath containing 4% of cadmium as chloride, 10% of ammonium chloride, 5% of hydrochloric acid, and 0.1% of peptone gave a fairly smooth, finely crystalline deposit. A bath of the same composition as the foregoing with the addition of 10% of ferric chloride gave a much better deposit. Manganese, aluminium or chromium chlorides did not improve the deposit in the same way that iron did. The deposits obtained with solutions of bromide and iodide were crystalline and rough. Solutions of fluoride, silicofluoride, borofluoride, and perchlorate containing 4% of cadmium with 0.5—5.0% of the free acid and 0.2 gram of peptone, glue, or



phloridzin or 4 drops of oil of cloves gave excellent deposits. Sometimes in these cases spongy places, rough projections, and spots were formed, but these are attributed to the presence of particles of anode slimes, since they were not formed when the anode was amalgamated. It is shown that the same substances, oil of cloves, glue, peptone, and phloridzin, which have been previously shown to give quite good deposits in the case of lead, also produced good deposits in the case of cadmium, although it was generally much more difficult to obtain good deposits with cadmium than with lead.

J. F. S.

**A Thermo-regulator for Thermostats at Temperatures Very Close to Room Temperature.** CHARLES W. R. POWELL (*J. Soc. Chem. Ind.*, 1914, 33, 899—900).—A regulator is described for use with thermostats at temperatures either a few degrees below or above atmospheric temperature. The regulator consists of the usual toluene filled vessel, which is fitted at the top with two side-tubes at different levels; the top one leads into the thermostat and the lower one into the sink, and both serve to conduct a stream of ice-cold water. The top of the regulator is closed by a cork, which carries a glass tube, by means of which ice-cold water enters the regulator, and a copper wire which terminates at the upper end of the capillary of the regulator. A second wire is fused into the regulator in such a position that it is always in contact with the mercury column. These two wires are connected through an accumulator with a small electro-magnet. The magnet when active operates a lever which deflects the flow of ice-cold water from the sink into the thermostat, and at the same time breaks the circuit of the electrical heater, so that the temperature is regulated very quickly. Using such an instrument, the author was able to maintain a temperature of  $27^{\circ}$  within  $\pm 0.5^{\circ}$  in a 3-litre thermostat with the atmospheric temperature at  $30^{\circ}$ .

J. F. S.

**Capacity for Heat of Metals at Low Temperatures.** E. H. GRIFFITHS and EZER GRIFFITHS (*Phil. Trans.*, 1914, [A], 214, 319—357).—The specific heats of a large number of substances have been measured at the ordinary temperature, and also at liquid air and liquid hydrogen temperatures, but there have been as yet no direct measurements of the true specific heats at intermediate temperatures. In order to bridge the gap, the authors have worked out a method for maintaining the temperature of an enclosure constant at any point between that of the room and  $-165^{\circ}$  by a direct application of the Joule-Thomson effect. The method employed in the measurement of the specific heats of metals depends on the determination of the rise in temperature of a block of the metal which is suspended in the constant temperature enclosure and supplied with a measured quantity of electrical energy.

Experiments were made at various temperatures within the above-mentioned range on aluminium, copper, zinc, silver, cadmium, lead, iron, and sodium. Atomic heat temperature curves have been constructed from these data in combination with the results obtained by Nernst at liquid air and hydrogen temperatures.

On comparing the experimental curves with the requirements of the formulæ put forward by Einstein (*Ann. Physik*, 1907, [iv], 22, 800), Nernst and Lindemann (A., 1911, ii, 466), and by Debye (A., 1912, ii, 1134), it is found that none of these formulæ is capable of representing the results over the entire temperature range. Debye's formula appears to give the nearest approximation over the lowest portion of the range, but systematic divergences occur at the higher temperatures. This may be due either to the assumptions made by Debye being valid only at very low temperatures, or it may mean that heat energy, additional to that involved in the three degrees of freedom ascribed to the atom, must be taken into account. Above liquid air temperatures the three formulæ are capable of representing the results approximately, but in some cases the discrepancies are considerable. H. M. D.

**Metastability of the Metals in Consequence of Allotropy and its Significance for Chemistry, Physics and Technics.** II. ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 200—203. Compare this vol., ii, 202).—A review of the earlier literature dealing with the specific heat of the metals affords evidence that the specific heat depends in many cases on the previous thermal history of the metals. For copper, zinc, lead, aluminium, and silver the specific heat-temperature curve is not continuous, but changes abruptly at one or more points. This behaviour is in agreement with dilatometric observations, which indicate the existence of allotropic modifications of some of these metals. H. M. D.

**Determination of the Freezing Point for Salt Solutions.** F. H. VAN DER LAAN (*Chem. Weekblad*, 1914, 11, 925—927).—In determining the freezing point of a salt solution, homogeneity of the liquid must be ensured by vigorous agitation. Failure to observe this precaution leads to inaccurate readings for such solutions, but is immaterial for such liquids as water or milk. A. J. W.

**Boiling Points in Homologous Series.** S. SUGDEN (*Chem. News*, 1914, 110, 152—153, 165—168).—It is found that the boiling points of the members of homologous series of carbon compounds can be satisfactorily represented by means of the formula  $T = a\sqrt{M} + b/\sqrt{M} + aM/b$ , in which  $M$  is the molecular weight,  $T$  the boiling point, and  $a$  and  $b$  are constants. The formula is shown to be applicable to the paraffins, alkyl haloids, aldehydes, fatty acids, anines, alkyl cyanides, normal primary and secondary alcohols, hydrosulphides, esters, nitroparaffins, ethers, olefines, and aromatic hydrocarbons. The average difference between the observed and calculated boiling points for some one hundred and seventy compounds is  $1.63^\circ$ . The values of  $a$  vary to a comparatively small extent from one series to another, the aromatic hydrocarbons having the highest value ( $45.71$ ) and the olefines the lowest ( $22.89$ ). The values of  $b$  vary to a much larger extent, the extremes being shown by the alkyl iodides ( $-2038.0$ ) and the nitroparaffins ( $+890.0$ ). H. M. D.

**Vapour Pressures of Silver, Gold, and Bismuth Amalgams.** ERMON DWIGHT EASTMAN and JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1914, 36, 2020—2030).—In continuation of a study of the laws of concentrated solutions from the point of view of metallic solutions (Hildebrand, A., 1913, ii, 755), measurements have been made of the vapour pressures of silver, gold, and bismuth amalgams at about 318° by the method used in the case of the zinc amalgams (*loc. cit.*).

As silver is but sparingly soluble in mercury at 318°, only one determination was made, namely, with an amalgam containing 1.27% of silver. In this case Raoult's law was obeyed within the limits of experimental error.

Measurements with gold amalgams, at concentrations up to 23.7% of gold, showed the separation of a solid phase at about 16.5% concentration. In the more dilute amalgams the vapour pressures were greater than those calculated from Raoult's law.

Bismuth amalgams of all concentrations are liquid at 318°, and also give higher vapour pressures than those calculated from Raoult's law.

For the gold and bismuth amalgams, equations, based on one derived by Laar (A., 1910, ii, 583; 1913, ii, 670), are given which satisfactorily express the values observed. E. G.

**Method of Finding the Partial from the Total Vapour Pressures of Binary Mixtures, and a Theory of Fractional Distillation.** M. A. ROSANOFF, C. W. BACON, and JOHN F. W. SCHULZE (*J. Amer. Chem. Soc.*, 1914, 36, 1993—2004).—Rosanoff, Bacon, and White (this vol., ii, 766) have described a simple method of measuring the partial vapour pressures of liquid binary mixtures, which consists in distilling the mixtures and analysing several consecutive fractions. In some cases the analysis cannot be accurately accomplished, and the experimental determination of the partial pressures would therefore be untrustworthy.

It is now shown that the partial pressures can be calculated from the total vapour pressure by means of the general relationship:

$$d\pi/dx = [(P_1 - P_2)/(\log P_1 - \log P_2)] \log [p_1(1-x)/p_2x],$$

where  $x$  is the molar fraction of one of the components in the liquid,  $\pi$  the total pressure,  $p_1$  and  $p_2$  the partial pressures, and  $P_1$  and  $P_2$  the vapour pressures of the isolated compounds. Calculations have been made by means of this expression for mixtures of carbon tetrachloride and benzene, ethyl iodide and ethyl acetate, chloroform and acetone, and benzene and toluene, and the results agree satisfactorily with those obtained experimentally.

A theory of fractional distillation is presented for the case in which the vapour escapes from the still without having undergone any reflux condensation. This theory is based solely on the principles involved in the equation given in the preceding paragraph.

E. G.

**Measurements of Isotherms of Hydrogen at 20° and 15.5°.** PH. KOHNSTAMM and K. W. WALSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 203—216).—The authors have investigated

the compressibility of hydrogen at  $15.5^{\circ}$  and  $20^{\circ}$  for pressures ranging from about 200 to about 2300 atmospheres. The lower temperature was chosen in order to enable a comparison to be made of the results with those obtained by Amagat.

In preliminary experiments with air, it was found that at high pressures the mercury quickly became contaminated, in consequence of the formation of mercuric oxide. This prevented the carrying out of measurements on the pressure-volume relations of air and oxygen.

H. M. D.

**The Hydrogen Isotherms of  $20^{\circ}$  and  $15.5^{\circ}$  between 1 and 2200 Atmospheres.** K. W. WALSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 217–224. Compare preceding abstract).—The observations at  $20^{\circ}$  have been compared with those of Schalkwyk, and those at  $15.5^{\circ}$  with the data given by Amagat. For this purpose, the experimental results are expressed by means of an empirical equation of the form  $PV = a + bD + cD^2 + dD^4 + eD^6$ , in which  $D$  is the density and  $a, b, c, d, e$  are coefficients. In so far as a comparison is possible, the author's observations appear to be in satisfactory agreement with Schalkwyk's. Between 700 and 2200 atmospheres, the values of  $PV$  given by the author's results are somewhat greater than those calculated from Amagat's data, and the difference is particularly marked for pressures above 2000 atmospheres.

H. M. D.

**Isothermals of Monatomic Substances and their Binary Mixtures. XVI. New Determination of the Vapour Pressures of Solid Argon down to  $-205^{\circ}$ .** C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 275–277. Compare this vol., ii, 28).—The vapour pressures of solid argon have been redetermined over the temperature interval  $-189.64^{\circ}$  to  $-205.32^{\circ}$ . The pressures corresponding with these limiting temperatures are respectively 49.78 and 3.830 cm. of mercury. The experimental observations are compared with the values calculated according to the formulæ of Rankine and Bose, Nernst and Sackur. Sackur's formula, which is based on Nernst's heat theorem, affords satisfactory agreement at the higher temperatures, but there are wide divergences at the lower.

The heat of sublimation of solid argon, calculated from the temperature variation of the vapour pressure, falls from 47.36 at  $-189.64^{\circ}$  to 44.51 at  $-205.32^{\circ}$

H. M. D.

**A New Relation between the Critical Quantities and the Unity of All Substances in their Thermic Behaviour.** J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 451–465. Compare this vol., ii, 341).—A theoretical paper in which the author arrives at the conclusion that the quantity  $a$  in the van der Waals' equation is independent of the density over a very large range. The molecular attraction in both the gaseous and liquid states is therefore satisfactorily represented by  $a/v^2$ . Whether  $a$  is also independent of the temperature cannot as yet be determined with

perfect certainty. With reference to the quantity  $b$  in this equation, the evidence is distinctly in favour of its dependence on both density and temperature. The significance to be attached to  $b$  is that of the volume ( $m$ ) occupied by the molecules, and the earlier assumption that  $b=4m$  must be discarded.

The thermal behaviour of a substance is not only dependent on the quantities  $a$  and  $b$ , which determine the critical quantities, but also on the absolute value of the temperature at which the substance is considered. Every substance passes from the ordinary type to the ideal type when the temperature falls continuously and approximates to absolute zero.

H. M. D.

**Free Energy of Oxygen, Hydrogen, and the Oxides of Hydrogen.** GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1914, **36**, 1969—1993).—In an earlier paper (Lewis, A., 1913, ii, 112) an account was given of the general methods used in free energy calculations. These methods have now been applied to the determination of the free energy of oxygen, hydrogen, and the hydrogen oxides. The calculations have been made chiefly from existing data, but in some cases data have been employed which were obtained in the course of investigations not yet published.

The following are the values (in calories) of the free energy of formation ( $F^\circ$  298) from the elements in their standard states: ozone ( $O_3$ ), 32,400; hydrogen (H), 30,550; hydrogen ion ( $H^+$ ), 0; hydroxyl ion ( $OH^+$ ), -37,385; water (liquid), -56,620; water (gas), -54,567; water (solid), -56,478; hydrogen peroxide (in aqueous solution), -30,970; hydroperoxide ion ( $HO_2^+$ ), -15,110; hydrogen peroxide (liquid), -27,770; hydrogen peroxide (gas), -24,270.

E. G.

**Combustion Calorimetry and the Heats of Combustion of Sucrose, Benzoic Acid, and Naphthalene.** HOBART C. DICKINSON (*J. Washington Acad. Sci.*, 1914, **4**, 434—435).—A critical study of the stirred water calorimeter, as used for bomb combustions, has been made, and it has been found that the chief sources of error may be avoided by the use of a suitably designed calorimeter fitted with resistance thermometers. Determinations of the heat of combustion of naphthalene gave  $9622 \pm 2$  cal. per gram, with a maximum deviation from the mean of about 5 in 10,000 for groups of observations on the same sample. The value obtained for benzoic acid was  $6329 \pm 1$  cal. per gram, with a maximum deviation of about 5 in 10,000, and for sucrose  $3949 \pm 2$  cal. per gram, with a maximum deviation of about 1 in 1000.

The results indicate that benzoic acid is the most suitable of the three substances for calibration purposes. The volatility of naphthalene necessitates special precautions when this substance is employed, and sucrose is less well adapted, not only on account of the lower precision of the results, but also because of its smaller heat of combustion and its frequent failure to ignite.

H. M. D.

**Cool Flames with Ether.** ALAN LEIGHTON (*J. Physical Chem.*, 1914, 18, 619—622).—Perkin (T., 1882, 41, 363) showed that when ether was evaporated in a shallow dish on a hot sand-bath, a pale blue flame was produced, only visible in the dark, which did not ignite the ether. This phenomenon had been previously observed by Davy, Döbereiner, and others. The author has investigated this flame, and shows that it may be produced in many ways, among which may be noted the following. A copper ball is heated to dull redness, and then allowed to cool until it just becomes invisible; it is then suspended over a dish containing layers of filter paper soaked in ether, when a tall, blue flame is produced. The flame is produced at temperatures below dull redness, but above 260°. It has a comparatively low temperature, and the fingers may be placed in it with impunity. It is shown that the flame is produced when ether vapour is mixed with a small amount of oxygen, and no hot surface is necessary. It may therefore be produced by mixing ether with a non-inflammable volatile liquid and allowing the mixture to evaporate and lighting the mixture with a match, or by mixing ether vapour with a non-inflammable gas, such as carbon dioxide. Similar flames can be obtained by replacing ether by carbon disulphide; all the flames have low temperatures. That from carbon disulphide and carbon tetrachloride has a temperature of 90°.

J. F. S.

**Theory of Molecular Volumes. IV.** GERVAISE LE BAS (*Phil. Mag.*, 1914, [vi], 28 439—466. Compare this vol., ii, 173, 340, 539).—The influence of ring structure on the molecular volume has been examined by reference to the data for a large number of compounds containing one or more rings. The data in question relate for the most part to homocyclic compounds, but heterocyclic structures are also considered.

The relationships exhibited lead to the conclusion that molecular volume is influenced by ring structure to an extent which depends on the number of rings and on the number of groups in the rings. The effect in general is a contraction, which is contributed to by all the elements of the nucleus, and often by the atoms which are associated with these. The contraction is the same whether two or more rings are separated or condensed; from this it would seem that the common atoms of the two or three rings must have extraordinarily small volumes.

The contractions characteristic of the various polymethylene rings are given as: *cyclopropane*,  $-5\cdot3$ ; *cyclobutane*,  $-8\cdot6$ ; *cyclopentane*,  $-12\cdot3$ ; *cyclohexane*,  $-16\cdot1$ ; *cycloheptane*,  $-20\cdot16$ ; *cyclo-octane*,  $-24\cdot0$ . The corresponding value for the benzene ring is  $-14\cdot7$ .

The contraction attributed to the influence of atoms or groups in close association with the elements of the ring nucleus is supposed to be characteristic of atoms or groups which possess residual affinity. If this residual affinity is neutralised, the contraction, as a rule, disappears. The following values are given for the contraction effects due to the different groups in combination with the

$C_6H_5$  nucleus: OH,  $-1.5$ ; CN,  $-1.6$ ;  $CH_2Cl$ ,  $-1.9$ ;  $PCl_2$ ,  $-2.0$ ;  $NO_2$ ,  $-2.7$ ;  $COCl$ ,  $-1.8$ ;  $NH_2$ ,  $-4.4$ ;  $CO_2H$ ,  $-2.8$  to  $-4.0$ . This particular effect is described as the volume anomaly. H. M. D.

**The Unit-Stere Theory of Molecular Volume.** ERNEST VANSTONE (*Phil. Mag.*, 1914, [vi], 28, 600—606).—A criticism of the unit-stere theory advanced by Le Bas (A., 1907, ii, 754). The ratio  $V/W$ , where  $V$  is the molecular volume and  $W$  the sum of the valencies, may be considered as the product of the specific volume  $v$  and  $M/W$ , where  $M$  is the molecular weight. For any member of a homologous series of compounds,  $M/W$  is given by the quantity  $(a+n.14)/(a'+n.6)$ , where  $a$  represents the molecular weight of the first member of the series,  $n$  the number of  $CH_2$  groups, and  $a'$  the sum of the valencies for the first member. For the higher members of such a series  $M/W$  becomes practically constant and equal to  $14/6$  or  $2.33$ . Since  $v$  also tends towards constancy, the observed constancy of  $V/W$  in the higher members of homologous series can be readily explained. In so far as the lower members of such series are concerned, the observed variations in  $V/W$  can be explained by the relative variations in the values of  $v$  and  $M/W$ . H. M. D.

**The Unit-Stere Theory.** GERVAISE LE BAS (*Phil. Mag.*, 1914, [vi], 28, 607—608).—A reply to Vanstone's criticism (compare preceding abstract). The author considers that the molecular volume is not divisible into factors represented by the specific volume and the ratio of the molecular weight to the sum of the valencies. H. M. D.

**Existence of Compounds in Binary Liquid Mixtures.** J. HOWARD MATHEWS and RAYMOND D. COOKE (*J. Physical Chem.*, 1914, 18, 559—585).—Starting from the expression deduced by Batschinski (A., 1913, ii, 928), the authors show that the viscosity-specific volume curves of non-associated liquids are straight lines, whereas those of associated liquids are concave toward the fluidity axis. The authors show that further evidence of the existence of compounds in certain liquid mixtures is obtained by plotting the fluidity-specific volume isotherms of binary mixtures, and they hold that this evidence supports the view that a maximum in the viscosity composition curve of a binary mixture is indicative of the presence of a compound. Twenty-four pairs of liquids are plotted in this manner, and of these nine exhibit maxima, whilst the other fifteen give straight lines. The values used in many cases are taken from the work of Dunstan (T., 1904, 85, 817), Thorpe and Rodger (T., 1897, 71, 360), Linebarger, Faust, and others. New determinations have been made of the pairs acetic acid-aniline (56—44%), methyl alcohol-water (36—64%), propyl alcohol-water (50—50%), water-acetic acid (22—78%), water-pyridine (33—67%), acetic acid-pyridine (77—23%), ethyl alcohol-water (45—55%), chloral-water (88—12%), and chloral-ethyl alcohol (74.3—25.7%). The measurements were made at temperatures from  $0^\circ$  to  $90^\circ$ . A

very full bibliography of the work done on viscosity, as far as it applies to the chemical and molecular constitution and on the properties of completely miscible liquids, is appended to the paper.

J. F. S.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from  $-80^{\circ}$  to  $1650^{\circ}$ . I. Methods and Apparatus.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 329—365).—An arrangement of apparatus is described by means of which it has been found possible to make accurate measurements of the surface tension of liquids at temperatures between  $-80^{\circ}$  and  $1650^{\circ}$ . A capillary tube, provided with a circular knife-edge opening, is immersed in the liquid perpendicular to its surface, and a small bubble of gas is allowed to form slowly at the end of the capillary tube. The pressure in the gas bubble at the moment when the bubble is about to burst affords a measure of the surface tension of the liquid. Provided that abnormally high viscosities are not encountered, the author considers that the results obtained with his apparatus are as accurate at  $1650^{\circ}$  as at the ordinary temperature.

The results obtained at different temperatures for a number of organic substances and for several inorganic salts are recorded in detail. A comparison was also made between the surface tensions of pure water and colloidal solutions of ferric hydroxide and silicic acid. The curves showing the relation between the surface-energy and the temperature are of the same kind, but those for the colloidal solutions are situated above the curve for water.

H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from  $-80^{\circ}$  to  $1650^{\circ}$ . II. Measurements of Some Aliphatic Derivatives.** F. M. JAEGER and M. J. SMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 365—385).—Measurements of the temperature variation of the molecular surface energy ( $\mu$ ) have been made for *n*-propyl alcohol, isobutyl alcohol, diethyl ether, ethyl formate, ethyl chloro-formate, ethyl acetate, methyl isobutyrate, ethyl isobutyrate, isobutyl isobutyrate, acetone, methyl propyl ketone, ethyl acetoacetate, methyl methylacetoacetate, ethyl propylacetoacetate, methyl, ethyl, propyl, butyl, isobutyl and amyl cyanoacetates, chloroform, carbon tetrachloride, and isobutyl bromide. In most cases  $d\mu/dt$  decreases with rise of temperature. Where an increase was observed this could be traced to decomposition of the substance.

H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from  $-80^{\circ}$  to  $1650^{\circ}$ . III. Measurements of some Aromatic Derivatives.** F. M. JAEGER and M. J. SMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 386—394).—The following substances were examined: nitrobenzene, *o*-nitrotoluene, aniline, dimethylaniline, *o*-toluidine, thymol, methyl, ethyl and benzyl benzoates, salicylaldehyde, acetophenone, and



$\alpha$ -campholenic acid. The curves obtained by plotting the molecular surface energy against the temperature are concave to the axes in the case of nitrobenzene, *o*-nitrotoluene, aniline, and *o*-toluidine, indicating that  $d\mu/dt$  increases with the temperature. In this behaviour these substances resemble water, but differ from the majority of the substances examined in the previous paper (preceding abstract). H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from  $-80^{\circ}$  to  $1650^{\circ}$ . IV. Measurements of Some Aliphatic and Aromatic Esters.** F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 395—405).—The data recorded refer to amyl acetate, ethyl oxalate, ethyl malonate, ethyl bromomalonate, ethyl benzylethylmalonate, methyl and ethyl tartrates, methyl, ethyl and phenyl salicylates, methyl cinnamate, and *o*-nitroanisole. The surface-energy temperature curves indicate a sharp rise in  $d\mu/dt$  when the temperature is sufficiently high for decomposition to take place. H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from  $-80^{\circ}$  to  $1650^{\circ}$ . V. Measurements of Homologous Aromatic Hydrocarbons and Some of their Halogen Derivatives.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 405—415).—Data are given for benzene, toluene, *p*-xylene, mesitylene,  $\psi$ -cumene, cyclohexane, triphenylmethane, chlorobenzene, bromobenzene, *m*-dichlorobenzene, *p*-bromofluorobenzene, *m*-fluorotoluene, and *p*-chlorotoluene. These hydrocarbons and their halogen derivatives afford examples of both increase and decrease in the value of  $d\mu/dt$  with rise of temperature. The deviations of the surface energy-temperature curves from straight lines are so large in many cases that they cannot possibly be accounted for by error of experiment. In the case of  $\psi$ -cumene, for instance,  $d\mu/dt$  increases from 1.60 for the interval  $-21^{\circ}$  to  $0^{\circ}$  to 3.0 for the interval  $146^{\circ}$  to  $166^{\circ}$ . H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from  $-80^{\circ}$  to  $1650^{\circ}$ . VI. General Remarks.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 416—430. Compare preceding abstracts).—From the collected results recorded in the previous papers it would seem that the temperature-coefficient of the molecular surface energy may be independent of the temperature, or with rise of temperature may increase or diminish. No connexion can be traced between the type to which a particular liquid belongs and the magnitude of the molecular surface energy, or of its temperature-coefficient. The absence in general of a linear connexion between the surface energy and the temperature is supposed to be connected with the nature of surface energy, and this departure from linearity may be expected whenever the interval of temperature examined is wide enough.

With regard to the connexion between the molecular surface

energy and the chemical nature of the liquid, it is found that the surface energy at the same temperature increases in homologous series with the molecular weight. Replacement of hydrogen by halogens, by the nitro- or amino-groups, and by aromatic hydrocarbon radicles leads to an increase in the molecular surface energy when the comparison is made at a fixed temperature. H. M. D.

**The Adsorption of Vapours.** A. M. WILLIAMS (*Trans. Faraday Soc.*, 1914, 10, 167—171. Compare this vol., ii, 111).—The adsorption near to the saturated vapour pressure of a liquid is finite and independent of the temperature, but is not necessarily a maximum. C. H. D.

**"Negative" Adsorption.** A. M. WILLIAMS (*Trans. Faraday Soc.*, 1914, 10, 155—159. Compare this vol., ii, 111).—The adsorption of potassium chloride and magnesium sulphate by charcoal increases with the concentration to a maximum, decreases, passes through zero, and becomes negative. Ammonium chloride also exhibits a maximum. C. H. D.

**Action between Clay Filters and Certain Salt Solutions.** W. B. HICKS (*J. Ind. Eng. Chem.*, 1914, 6, 829—831).—Filtration through porcelain clay filters produces little or no change in the boric acid content of *N*/10-borate solutions, a slight decrease, about 0.2%, in concentration in *N*/10-alkali chloride and sulphate solutions, a larger decrease in *N*/10-alkali carbonate solutions, and a still larger decrease, 8%, in the case of *N*/1000-alkali carbonate solutions. Ammonia and potassium are also absorbed by the filters from solutions of their salts; the retained ammonia may be removed by washing the filter with potassium chloride solution, but in the case of potassium a small quantity is persistently retained by the filter even after persistent washing with water and ammonium chloride solution. W. P. S.

**The Theory of Colloid Chemistry.** WILDER D. BANCROFT (*J. Physical Chem.*, 1914, 18, 549—558).—A lecture delivered to the Montreal meeting of the American Chemical Society, in which a working theory of colloid chemistry is discussed. The theory is based on the four postulates: (1) Colloid chemistry differs from ordinary chemistry only through the variations resulting from the increasing dispersity of one or more phases. (2) Selective adsorption occurs at surfaces. (3) Sufficiently finely divided particles, which are prevented from coalescing, will be kept suspended in a medium by the Brownian movements; and (4) under fixed conditions of peptonisation an approximately definite limiting concentration is obtained corresponding with a saturated solution in the case of a true solution. J. F. S.

**Equilibria in Ternary Systems. XVI.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 169—182. Compare this vol., ii, 634).—A further discussion of the equilibrium relation-

ships for the case in which one of the three components is practically non-volatile.

H. M. D.

**New Form of Intermittent Siphon.** W. A. BRADBURY (*Chem. News*, 1914, **110**, 163).—A simple form of intermittent siphon is described, which permits of the automatic flushing of the beads in a gas absorption tube with a small quantity of liquid. The siphon is used in conjunction with a constant feed of water, and the capacity of the flush can be varied by a simple adjustment.

H. M. D.

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## Inorganic Chemistry.

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**Displacement of Acids by Hydrogen Peroxide.** V. JOACHIM SPERBER (*Chem. Zentr.*, 1914, i, 2139; from *Schweiz. Apoth.-Zeit.*, 1914, 52, 245—248. Compare this vol., ii, 557).—The action of hydrogen peroxide on halogen acids has been further studied. The affinity of the halogen hydrides for hydrogen peroxide varies as the affinity of the halogen for oxygen, hydrogen iodide being easily decomposed. The reaction depends on the order in which the substances are brought together. When hydrogen iodide is added to hydrogen peroxide, the reaction is so violent that the solid iodine which is first liberated volatilises, leaving a colourless liquid, but when hydrogen peroxide is added to an excess of the acid, although the reaction is vigorous, the iodine does not disappear. Exactly the reverse is the case with the other acids. The reaction is more energetic when hydrogen peroxide is added to the acid. The haloid salts behave in the same way, from which it appears that hydrogen peroxide first liberates the free acid and then decomposes it. This view is supported by the fact that ammonium peroxide (D'Ans and Wedig, A., 1913, ii, 1051) precipitates the peroxides from solutions of the alkaline earth haloids. J. C. W.

**The System Ammonia-Water.** A. SMITS and S. POSTMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 182—194).—Further cooling-curve observations have enabled the authors to give a more complete description of the freezing-point diagram. The two compounds  $2\text{NH}_3\cdot\text{H}_2\text{O}$  and  $\text{NH}_3\cdot\text{H}_2\text{O}$  melt at  $-78.9^\circ$  and  $-79.0^\circ$  respectively. The eutectic point at which ammonia and  $2\text{NH}_3\cdot\text{H}_2\text{O}$  co-exist as solid phases lies at 81.4 mols. % of ammonia and  $-92.5^\circ$ . The point at which  $2\text{NH}_3\cdot\text{H}_2\text{O}$  and  $\text{NH}_3\cdot\text{H}_2\text{O}$  co-exist lies at 58.5% ammonia and  $-86.0^\circ$ , and that corresponding with the co-existence of  $\text{NH}_3\cdot\text{H}_2\text{O}$  and ice at 34.7% of ammonia and  $-100.3^\circ$ . Except in the interval for mixtures containing 30—40 mols. % of ammonia, the authors' data agree satisfactorily with those of Rupert (A., 1909, ii, 726; 1910, ii, 605).

The vapour pressures of binary mixtures of varying composition have also been determined over a considerable interval of temperature, but the curves constructed on the basis of these data afford no evidence of the formation of definite compounds. H. M. D.

**Action of the Silent Electric Discharge on Mixtures of Hydrogen and Nitrogen.** M. LE BLANC (*Chem. Zentr.*, 1914, ii, 117; from *Ber. K. Sächs. Ges. Wiss., Math.-phys. Kl.*, 1914, 66, 38—63).—Earlier experiments (Le Blanc and Davies, A., 1908, ii, 653; Davies, A., 1909, ii, 30) indicated that the formation of ammonia by the silent electric discharge does not obey the law of mass action. This might have been due to alterations in the electrical conditions, caused by changes in the composition of the gaseous mixture. It is now found, however, that, even when the gases are largely diluted with a helium-neon mixture, the quantitative results are the same. The old experiments have been repeated with better apparatus, and the phenomena are found to be very complicated. The amount of ammonia formed depends on the dimensions of the apparatus, and the density and oscillation frequency of the current. J. C. W.

**Volatilisation of Arsenious Acid from Aqueous Solutions Containing Hydrochloric Acid.** BERTRAM JAMES SMART and JAMES T. PHILPOT (*J. Soc. Chem. Ind.*, 1914, 33, 900—902).—Volumes of 200 c.c. of hydrochloric acid solution of various concentrations, both above and below that of the constant boiling mixture, and containing various quantities of arsenious acid, have been submitted to fractional distillation. The distillates have been analysed with the object of ascertaining to what extent and under what conditions the arsenic volatilises with the acid. It is shown that when the solutions are distilled, those which contain the greatest concentration of hydrochloric acid give off the arsenic most rapidly. When the hydrochloric acid is present to the extent of about 190 grams per litre or more, the concentration of arsenic in the solution remaining undistilled rapidly falls as the solution is fractionated. With solutions containing less than 180 grams of hydrochloric acid per litre, the concentration of arsenic in the solution remaining undistilled rises, although some of the arsenic passes over, the ratio between acid and arsenic remaining practically constant until the solution contains about 185 grams of hydrochloric acid per litre. This point corresponds approximately with a hydrate of the formula  $\text{HCl} \cdot 10\text{H}_2\text{O}$ . When the acid becomes more concentrated the proportion of arsenic volatilised increases rapidly. J. F. S.

**The Reduction of Arsenic Acid to Arsenious Acid by means of Thiosulphuric Acid.** ROBERT M. CHAPIN (*Chem. Zentr.*, 1914, i, 2032—2033; from *J. Agric. Res.*, 1914, 1, 515—517).—Arsenic acid is completely and quickly reduced to arsenious acid in the cold by a mixture of sodium thiosulphate and a mineral acid. The speed of the reaction depends to a great extent on the concentration of the hydrogen ions, and the course of the reduction is

influenced by the amounts of the reagents and by the order in which they are mixed. The reaction is therefore complex, and appears to correspond with the reduction of a dichromate by thio-sulphuric acid (compare Stiasny and Das, A., 1912, ii, 945).

J. C. W.

**Isotherm of the Solubility of Lithium Chloride at 25° in Mixtures of Water and Ethyl Alcohol.** S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1914, 12, 343—349).—The solubility of lithium chloride in aqueous alcohol decreases regularly in solvents containing up to 70% by weight of alcohol; the solubility curve is rectilinear, the coefficient being 0.6939 per gram of alcohol. The salt during this stage exists as  $\text{LiCl} \cdot \text{H}_2\text{O}$ . The anhydrous salt is deposited from solutions in pure alcohol.

G. D. L.

**Silicate Chemistry. II and III. Lithium Aluminium Silicates the Composition of which Corresponds with that of the Minerals Eucryptite and Spodumene.** F. M. JAEGER and ANT. SIMEK (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 239—251, 251—270. Compare this vol., ii, 363).—II. A lithium aluminium silicate of the composition  $\text{LiAlSiO}_4$  has been prepared from a mixture of lithium carbonate, alumina, and silica by heating in a closed crucible at 1500°. When the fusion is slowly cooled, small, irregularly shaped crystals are obtained, for which measurements of the mean refractive index and the density gave  $n_D = 1.531$  and  $D = 2.362$  at 25°. These data indicate that the artificial silicate is not identical with the mineral eucryptite, and the synthetic product has been named *pseudo-eucryptite*. If the fusion is rapidly cooled by quenching, a pseudo-eucryptite glass is obtained, for which  $n_D = 1.541$ . This glass is metastable with regard to the birefringent crystalline modification, and is rapidly converted into this on heating at 900°. The melting point of pseudo-eucryptite is given as 1388°.

The compound  $\text{LiAl}(\text{SiO}_3)_2$  was prepared by fusion of a mixture of the same substances containing a larger proportion of silica. The purest product obtained was found to melt at 1400°, and gave  $n_D = 1.521$  and  $D = 2.411$  at 25°. Since the physical properties differ appreciably from those of the mineral spodumenes, the synthetic product has been named *β-spodumene*.

III. For the purpose of comparing the properties of the synthetic *β-spodumene* with the mineral varieties, the authors have determined the melting points and densities of a number of kunzites and spodumenes. The data indicate that, in general, the melting points of the natural kunzites are considerably higher than the values obtained for the synthetic products. It would seem that the melting points of the minerals decrease as the densities increase.

Micrographic examination of the products which are obtained when the mineral varieties of lithium aluminium silicate are fused and allowed to cool slowly afford evidence that *β-spodumene* is thereby formed. These observations lead to the conclusion that

the natural kunzites, hiddenites, and spodumenes are metastable varieties ( $\alpha$ -spodumenes) of the compound, and that  $\beta$ -spodumene is the stable form at all temperatures below  $1400^{\circ}$ . The natural spodumenes cannot therefore be produced from dry magmas, and it is probable that their formation is due to so-called "hydrothermal" synthesis.

A lithium aluminate of the composition  $\text{LiAlO}_2$  was prepared by fusion of a mixture of lithium carbonate and alumina at  $900^{\circ}$ , and then at  $1200^{\circ}$ . It forms microscopic hexagonal or octagonal plates which show pronounced double refraction. The indices were found to be  $n_D = 1.604$  and  $n'_D = 1.615$ ;  $D^{25}_D = 2.554$ . The melting point could not be determined, but it is higher than  $1625^{\circ}$ .

H. M. D.

**Cæsium Alum and Its Properties.** EDWARD HART and HENRY B. HUSELTON (*J. Amer. Chem. Soc.*, 1914, **36**, 2082—2084).—The solubilities of cæsium alum, expressed as the number of grams of the anhydrous salt,  $\text{AlCs}(\text{SO}_4)_2$ , per 100 grams of water, have been determined as follows: at  $7^{\circ}$ , 0.26; at  $19^{\circ}$ , 0.42; at  $22^{\circ}$ , 0.43; at  $24^{\circ}$ , 0.47; at  $29.5^{\circ}$ , 0.57; at  $31.5^{\circ}$ , 0.60; at  $40^{\circ}$ , 0.86; at  $41^{\circ}$ , 0.88; at  $47^{\circ}$ , 1.17; at  $49.25^{\circ}$ , 1.39; at  $50^{\circ}$ , 1.42; at  $56^{\circ}$ , 1.86; at  $60^{\circ}$ , 2.06; at  $66^{\circ}$ , 2.85; at  $68^{\circ}$ , 3.13; at  $80^{\circ}$ , 5.78. Two determinations of the specific gravity of the hydrated alum gave a mean value 1.945. The crystals melt in their water of crystallisation at  $117^{\circ}$ . These values are compared with those recorded by other observers.

E. G.

**Influence of Certain Hydroxylic Compounds on the Solubility of Mercuric Chloride in Water.** E. MOLES and M. MARQUINA (*Anal. Fis. Quim.*, 1914, **12**, 383—393).—Glycerol and sucrose increase the solubility of mercuric chloride in water, whereas tartaric and citric acids decrease it. The solubility in glycerol is 1 in  $1.25$  at  $25^{\circ} \pm 0.02$ .

G. D. L.

**Terbium.** C. JAMES and D. W. BISSEL (*J. Amer. Chem. Soc.*, 1914, **36**, 2060—2066).—Urbain (A, 1909, ii, 671) has stated that terbium is homogeneous, whereas Welsbach (*Chem. Zeit.*, 1911, **35**, 658) has expressed the opinion that it consists of three different elements. The present paper gives an account of a further study of this question.

The material employed consisted of gadolinium oxide containing terbium oxide, together with dysprosium and holmium oxides and traces of yttrium and erbium. It was converted into the bromates, which were submitted to a long and careful fractionation. The results indicate that terbium is a single homogeneous element. The bromate process effects a comparatively rapid separation of terbium from gadolinium; neodymium, if present, comes between these metals.

E. G.

**The Acidic and Colloidal Characteristics of Aluminium Hydroxide.** R. E. SLADE and W. G. POLACK (*Trans. Faraday Soc.*, 1914, **10**, 150—154).—Mahin, Ingraham and Stewart (A., 1913, ii,

139) stated that a solution of sodium aluminate is really a colloidal solution of the hydroxide in the alkali. It is now shown that the conclusions which these authors drew from their experiments, in support of the above view, were unjustified. Conductivity measurements of such solutions are against the assumption of colloidal particles, and, when hydrolysis takes place, crystalline aluminium hydroxide is deposited. The ultramicroscope affords no conclusive evidence either way.

J. C. W.

**Advances in the Metallurgy of Iron and Steel.** SIR ROBERT HAINFIELD (*Trans. Faraday Soc.*, 1914, 10, 1-43).—A lecture delivered to the Faraday Society on June 11th, 1914. C. H. D.

**Chromyl Chloride.** II. E. MOLES and L. GÓMEZ (*Anal. Fis. Quim.*, 1914, 12, 142-154. Compare A., 1912, ii, 560).—Analyses of recently prepared chromyl chloride give values very close to the theoretical, and lead to the supposition that the earlier workers probably did not examine the pure compound. No change was observed after two months, but after nineteen months a dark-coloured solid was deposited, which is possibly a polymeride.

The heat of solution was found to be 17.86 cal. (Berthelot, 16.7).

The molecular weight, determined cryoscopically in carbon tetrachloride, tin tetrabromide, and antimony pentachloride, points to the formation of molecular complexes in conformity with the tendency to polymerisation noted above.

G. D. L.

**Inorganic Solvents.** I. **Antimony Pentachloride.** E. MOLES (*Anal. Fis. Quim.*, 1914, 12, 314-343).—Pure antimony pentachloride is lemon-yellow in colour, acquiring an orange tint by the presence of chlorine. It has m. p.  $3.0^{\circ}$ , cryoscopic constant  $18.5$ , heat of fusion  $8.17$  cal., and  $D_4^{20}$   $2.3356$ .

The action of antimony pentachloride on potassium iodide probably leads to the formation of iodine monochloride. Sulphur, selenium, and tellurium yield the crystalline double compounds of their tetrachlorides with antimony pentachloride.

G. D. L.

**Dilute Solutions of Aluminium in Gold.** C. T. HEYCOCK and F. H. NEVILLE (*Phil. Trans.*, 1914, [A], 214, 267-276).—The equilibrium relations exhibited by aluminium and gold have been investigated by experiments on mixtures containing up to 5% by weight of aluminium. The actual observations consisted in the tracing of cooling curves and in the microscopic examination of ingots which had been annealed at definite temperatures and chilled by immersion in water.

The concentration-temperature diagram indicates the existence of two series of solid solutions ( $\alpha$  and  $\beta$ ), and of a compound of the composition  $Al_3Au_8$ . This compound is found in all the alloys containing from 18 to 28 atoms % of aluminium. Recalescence phenomena associated with the cooling curves of alloys containing from 10 to 27 atoms % of aluminium point also to the formation of a compound,  $AlAu_4$ . The relations between the solid phases are discussed with reference to an extensive series of microphotographs.

H. M. D.



## Mineralogical Chemistry.

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**Mixed Carbonates from Traversella.** MARIO DELGROSSO (*Atti R. Accad. Sci. Torino*, 1914, **49**, 1106—1117. Compare A., 1913, ii, 867).—The author has analysed a number of specimens from the Traversella deposits containing calcium, magnesium, and ferrous carbonates, together with small proportions of extraneous matter. The presence of ferrous carbonate is not always recognisable from the external characters, the most nearly colourless rhombohedral crystals often containing this carbonate in large proportions. In only one instance, where the conditions of deposition were evidently abnormal, was there any marked divergence from the relation  $\text{CaCO}_3 = \text{MgCO}_3 + \text{FeCO}_3$ . The conclusion is drawn that these minerals represent isomorphous mixtures of typical dolomite with normal ankerite. T. H. P.

**Melilite and Other Minerals from Gunnison Co., Colorado.** ESPER S. LARSEN and J. FRED HUNTER (*J. Washington Acad. Sci.*, 1914, **4**, 473—479).—A complex of coarse-grained alkaline igneous rocks occurs near Cebolla and Beaver Creeks in the Uncompahgre Quadrangle, Colorado. One of these rocks, named uncompahgrite, is composed largely of melilite, together with pyroxene, perovskite, magnetite, and apatite. The melilite, occurring as large cleavage plates reaching a foot across, is colourless to grey with a greasy lustre, and closely resembles nephelite in appearance. It gelatinises readily with weak acids; analysis gave I, D 2·98 (after deducting small amounts of apatite, calcite, magnetite, and perovskite). Two types of alteration of the melilite are recognised: most frequently it is altered to a fine aggregate of garnet, diopside, idocrase, etc.; and at other times to the new mineral cebollite (see following abstract):

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
I. 44·13	—	10·80	—	2·04	0·16	34·63
II. 34·30	5·08	4·46	24·09	—	—	31·06
MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.		
I. 4·35	3·40	trace	0·49	100·00		
II. 0·52	—	—	—	99·51		

Analysis II is of a black, titaniferous andradite from a sodasyenite allied to ijolite. A description is given of the perovskite present in these rocks, and also of anatase occurring as large, dark blue, translucent crystals on the joint planes of a diorite dyke.

L. J. S.

**Cebollite, a New Mineral.** ESPER S. LARSEN and W. T. SCHALLER (*J. Washington Acad. Sci.*, 1914, **4**, 480—482).—This mineral occurs as an alteration product of melilite at Beaver Creek, Gunnison Co., Colorado (see preceding abstract). It forms a dull, compact, white



### Analytical Chemistry.

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**Apparatus for the Analysis of Complex Gas Mixtures.** GUY B. TAYLOR (*J. Ind. Eng. Chem.*, 1914, 6, 845—848).—In the apparatus described the Bone and Wheeler method of absorption (*A.*, 1908, ii, 221) is combined with the usual form of compensation burette, a copper oxide U-tube for the estimation of hydrogen and carbon monoxide, and a slow combustion burette for burning hydrocarbons. The absorption vessels dip into a mercury trough; the reagents are introduced by means of curved pipettes under the lower edge of the absorption vessels, and after use are discharged by the aid of a suction apparatus. A trustworthy method for the separation of carbon monoxide, hydrogen, methane, and ethane is given. W. P. S.

**New Method for the Precise Standardisation of Hydrochloric Acid Solutions.** LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1914, 36, 2089—2091).—The following method for standardising solutions of hydrochloric acid depends on the loss of weight caused by the conversion of silver nitrate into the chloride; its accuracy is only limited by the errors of weighing.

Two similar silica or porcelain dishes, of 75—100 c.c. capacity, are taken, each provided with a light cover and one of them with a stirring rod, short enough to lie under the cover. The dish without a rod is referred to as the "companion dish." In the other are placed about 2 grams of pure silver nitrate. Both dishes are put into an oven at 160°, and the temperature is raised to 240° until the weight is constant. Fifty c.c. of 0.2*N*-hydrochloric acid to be standardised are placed in each dish, the temperature of the solution when measured being noted. The silver nitrate is stirred up with the solution until it has dissolved and the silver chloride

coagulated. Both dishes are heated at 95—100°, finally dried at 240°, cooled in the desiccator, and weighed. The increase in the weight of the companion dish represents the weight of non-volatile impurities contained in the acid, and its amount is deducted from the observed weight of the silver chloride. The normality of the solution is given by the expression  $N = (W - W_1 + w_1 - w) / (0.02655 V)$ , where  $V$  is the corrected volume of the solution,  $W$  the weight of the silver nitrate and dish,  $W_1$  the weight of the silver chloride, silver nitrate, and dish,  $w$  the weight of the companion dish before the experiment, and  $w_1$  its weight at the close of the experiment.

E. G.

**Estimation of Iodine in Connexion with Studies in Thyroid Activity** E. C. KENDALL (*J. Biol. Chem.*, 1914, 19, 251—256. Compare A., 1912, ii, 864).—The author gives additional details and slight modifications of his process for estimating iodine in the presence of chlorides, bromides, and organic matter.

H. W. B.

**Oxidation of Sulphur Compounds of Coal, and of Nitrogen in the Bomb Calorimeter, and the Correction to be Applied in Estimating the Heat Value of Coal** SAMUEL H. REGISTER (*J. Ind. Eng. Chem.*, 1914, 6, 812—822).—When the chief sulphur compound of coal, pyrites, is burned with a non-nitrogenous fuel in the calorimeter in an atmosphere of oxygen under pressure, a fairly stable condition results. This condition is intermediate between the practically complete conversion to sulphur trioxide existing under the conditions of equilibrium at ordinary temperatures, and the almost total absence of sulphur trioxide characteristic of combustions without a catalyst to convert the sulphur dioxide into sulphur trioxide as the temperature falls. The relative amount of sulphur converted into sulphur trioxide increases with the amount of nitrogen oxides formed in the bomb. The nitrogen of coal is much more efficient in forming nitrogen oxides than is the nitrogen of the bomb gases; this, in connexion with the fact that in ordinary work the concentration of nitrogen in the bomb gases before ignition is at least 5%, accounts for the almost complete oxidation of the sulphur in coal to sulphur trioxide. Much too low results are obtained when coal containing pyrites equivalent to about 7% of sulphur is burned at 20 atmospheres pressure with 0.53% of nitrogen in the bomb gases. With greater percentages of nitrogen the results are more trustworthy. Usually, in burning coal with less than 2% of sulphur in a bomb calorimeter from which the air is not removed previously, there will be sufficient formation of nitrogen oxides to ensure almost complete oxidation of the sulphur. The heating value of sulphur was found to be 4975 cal. per gram.

W. P. S.

**Chief Cause of the Loss of Sulphur Trioxide and of Chlorine by Incinerating Substances Containing these Constituents.** JAMES O'SULLIVAN (*Analyst*, 1914, 39, 425—428).—During the incineration of substances containing chlorides the latter

are decomposed and chlorine is lost, but no reduction takes place in the quantity of calcium, potassium, and sodium sulphates which may be present. Magnesium sulphate undergoes decomposition on ignition unless a carbonate is present; in the absence of a carbonate, magnesium sulphate is converted entirely into magnesium oxide. If present in sufficient quantity in a substance containing chlorides, magnesium sulphate may cause the whole of the chlorine to be lost when the substance is incinerated. W. P. S.

**Presence of Sulphates in Flour.** R. A. CRIPPS and A. G. WRIGHT (*Analyst*, 1914, 39, 429).—The quantity of sulphuric acid found in the ash of flour, amounting to about 0.02% of the weight of the ash, does not represent the amount of sulphates in the flour, since, during ignition, the hydrogen phosphates present decompose the sulphates with loss of sulphuric acid. From 0.0069 to 0.0084% of sulphur trioxide is found if the flour is extracted with dilute acetic acid and the sulphate precipitated in the solution by the addition of barium chloride, after the proteins have been removed by means of tannin solution. W. P. S.

**Calcination of Magnesium Ammonium Phosphate and Causes of its Blackening.** JOSÉ GIRAL PEREIRA (*Anal. Fis. Quim.*, 1914, 12, 109—112).—The darkening of this phosphate on calcination is due in all cases to organic matter, which also determines the eventual formation of phosphides. In the absence of organic matter, the calcined substance remains quite colourless. G. D. L.

**Estimation of Carbon in Steel by the Direct Combustion Method.** WM. BRADY (*J. Ind. Eng. Chem.*, 1914, 6, 843—845).—The method consists in the direct combustion of the metal in oxygen; the carbon dioxide produced is absorbed in a known excess of barium hydroxide solution. When the combustion is completed, the barium carbonate and excess of barium hydroxide are rinsed into a flask, and the hydroxide is titrated with standardised hydrochloric acid, using phenolphthalein as indicator. The oxygen used is passed through potassium hydroxide solution and soda-lime, and a tube containing granulated zinc is placed between the combustion tube and the absorption apparatus to prevent any sulphuric acid resulting from the oxidation of sulphur from passing into the barium hydroxide solution. W. P. S.

**Estimation of Carbon in Steels and Irons by Direct Combustion in Oxygen at High Temperature.** J. R. CAIN and H. E. CLEAVES (*J. Washington Acad. Sci.*, 1914, 4, 393—397).—In the ordinary method of estimating carbon in steels, etc., by combustion in oxygen, small additional quantities of carbon are obtained when the oxides are powdered and again heated in oxygen. The authors, in place of the latter procedure, increase the heat of the furnace, after the metal has been oxidised as far as possible under the usual conditions, and maintain the oxides in a state of fusion for about thirty minutes. In this way it was found that some steels yield

slightly more carbon and others give decidedly more, whilst with iron the increase amounts to nearly 0.02%. The barium carbonate titration method (this vol., ii, 577) was used for the estimation of the carbon dioxide.

W. P. S.

**Perchloric Method of Estimating Potassium, as Applied to Water Analysis.** CLARENCE SCHOLL (*J. Amer. Chem. Soc.*, 1914, 36, 2085—2089).—The method of estimating potassium as the perchlorate has been studied and proved to be accurate. Sulphates and ammonium salts must be eliminated before applying the test, but phosphates do not introduce any error, and therefore need not be removed.

The method as modified for use in water analysis is as follows: A measured quantity of the water is evaporated to 150 c.c., 10 c.c. of concentrated hydrochloric acid are added, and the liquid is heated until it boils. Barium chloride solution (10%) is now introduced drop by drop until all the sulphates are precipitated, and after boiling for fifteen minutes the solution is filtered, the filtrate evaporated to dryness, and the residue heated until all the ammonium salts have been expelled. The residue is dissolved in 20 c.c. of hot water, a slight excess of 20% perchloric acid solution added, and the solution evaporated to dryness. If white fumes do not appear, the residue is redissolved in 10 c.c. of water, again treated with perchloric acid, and evaporated to dryness; this process is repeated until white fumes appear. The residue is now treated with 25 c.c. of 96—97% alcohol containing 0.2% of perchloric acid, broken up with a stirring rod, collected in a Gooch crucible, repeatedly washed with the alcoholic solution of perchloric acid, dried at 120—130°, and weighed.

This method is rapid, simple, inexpensive, and accurate. E. G.

**Estimation of Zinc in Treated Wood.** M. HUME BEDFORD and R. PFANSTIEL (*J. Ind. Eng. Chem.*, 1914, 6, 811).—The following method is recommended for the estimation of zinc in red oak which has been treated with zinc chloride. Three grams of the sawdust, dried at 110°, are mixed with 35 grams of sodium peroxide and ignited in a bomb. The mass is then dissolved in water, the solution acidified with hydrochloric acid, boiled, and 2 grams of citric acid, 10 c.c. of concentrated nitric acid, and 5 c.c. of 8% ferric chloride solution are added. The mixture is rendered alkaline, 2 c.c. excess of concentrated ammonia are added, and, after dilution to 400 c.c., the zinc is titrated at 80° with standardised potassium ferrocyanide solution.

W. P. S.

**Detection of Lead in Toxicology, Particularly in Urine in Cases of Lead Poisoning.** G. MEILLÈRE (*J. Pharm. Chim.*, 1914, [vii], 10, 225—231).—Small quantities of lead in solution may be collected by adding copper sulphate to the solution, precipitating both metals with hydrogen sulphide, dissolving the mixed sulphides in nitric acid, and then separating the lead from the copper electrolytically. In the case of urine, the quantity voided during twenty-four hours is treated with 1% of its volume of hydrochloric acid,

1 gram of copper sulphate is added, and the mixture is treated with hydrogen sulphide. The precipitate is collected on a filter, washed, then dissolved in nitric acid, the solution evaporated, and the residue heated until the copper nitrate is converted into cupric oxide. This residue is dissolved in 6 c.c. of nitric acid, the solution is diluted to 100 c.c., and submitted to electrolysis. Small platinum electrodes are employed; the whole of the lead is deposited on the anode within twenty-four hours by using a current at 2 volts, and of such amperage that there is but a slight evolution of gas from the anode. The deposit of lead peroxide may be weighed, and then identified by dissolving it in nitric acid containing oxalic acid, and applying suitable tests to the solution. W. P. S.

**Method of Estimating Small Quantities of Lead in Tin, Solder, etc.** PIERRE BRETEAU and PAUL FLEURY (*J. Pharm. Chim.*, 1914, [vii], **10**, 265—273. Compare this vol., ii, 778).—The metal is fused with a mixture of sodium carbonate and sulphur, the fused mass is treated with boiling water, and the lead, copper, and iron sulphides are collected on a filter. These sulphides are then dissolved in hydrochloric acid containing bromine, the solution is treated with sulphurous acid to reduce the iron, and, after fifteen minutes, potassium cyanide and potassium hydroxide are added; the addition of sodium sulphide to the alkaline solution causes the lead to be precipitated as its sulphide, whilst the iron and copper remain in solution. The lead sulphide is collected, dissolved in hot dilute nitric acid, the solution evaporated, and the residue heated for one hour at 150°. The residue is then dissolved in water, the solution again evaporated, and heated. The lead nitrate thus obtained is dissolved in 5 c.c. of water, a small crystal of sodium acetate is added, and the solution is poured slowly into a definite excess of standard potassium dichromate solution; the dichromate solution must not be added to the lead solution. The lead chromate is then collected on a filter, washed with water, and the excess of dichromate is estimated in the filtrate. The potassium dichromate solution may conveniently contain 0.1432 gram of the salt per litre; 5 c.c. of this solution are equivalent to 0.001 gram of lead. The copper and iron may be estimated by the usual methods in the filtrate from the lead sulphide after the hydrogen cyanide has been expelled by boiling the solution with the addition of sulphurous acid. W. P. S.

**Separation of Vanadium and Phosphorus with "Cupferron."** VICENTE GARCÍA RODEJA (*Anal. Fis. Quim.*, 1914, **12**, 379—382).—After reduction of the vanadate to the hypovanadate, the vanadium is quantitatively precipitated by freshly prepared "cupferron" solution, and the phosphate may be estimated in the filtrate. G. D. L.

**An Arrangement for the Detection of Residual Acetylene Hydrocarbons in Caoutchouc.** L. LUTZ (*Chem. Zentr.*, 1914, ii, 102; from *Bull. Sci. Pharmacol.*, 1914, **21**, 193—195).—A simple arrangement of a flask fitted with a delivery tube, bent twice at

right angles, is described, in which finely cut caoutchouc may be boiled with water so that, while the water is condensed in the first vertical tube, any volatile hydrocarbons pass over into a suitable receiver.

J. C. W.

**Hydrogen Number of Some Essential Oils and Essential Oil Products.** I. Oils of Sassafras, Anise, Fennel, Clove, and Pimento. ALAN R. ALBRIGHT (*J. Amer. Chem. Soc.*, 1914, 36, 2188—2202).—Fokin (A., 1908, ii, 637) has suggested the determination of hydrogen numbers for unsaturated compounds corresponding with the iodine numbers of Hübl and Wys. It has now been found that a hydrogen number can be assigned to certain volatile oils, colloidal palladium being used as the catalyst. Some oils, especially those with a constituent containing an allyl or propenyl group, are capable of very rapid hydrogenation. Such compounds are so rapidly reduced that, in the case of an oil containing one of them, the allyl or propenyl groups are quantitatively saturated before other configurations are attacked to more than a slight extent. The hydrogen number of the oil is defined as the number of c.c. of hydrogen at 0° and 760 mm. which are absorbed by 1 gram of the oil during the period of most rapid absorption of the gas.

In order to determine the hydrogen numbers of the oils of sassafras, anise, fennel, clove, and pimento, experiments were first made with the active constituents of the oils, namely, safrole, anethole, and eugenol. Imitation oils were then prepared containing the particular active constituent in the proportion in which it occurs in the natural oil, the remainder being represented by limonene. As limonene itself absorbs hydrogen fairly rapidly, the mixtures afforded a somewhat severe test of the hydrogenation number determination. Samples of commercial oils were subsequently submitted to the hydrogenation process. The hydrogen numbers of the various substances and oils are recorded.

E. G.

**New Reaction for Resorcinol.** PARIDE TORTI (*Boll. Chim. Farm.*, 1914, 53, 265).—When a little resorcinol is heated with a few drops of nitric acid (D 1.40), an intense red coloration is formed. This reaction is visible with as little as 0.00025 gram of resorcinol, and is forty times as sensitive as the reaction with ferric chloride. When cool, the liquid deposits minute, reddish-brown, acicular crystals, which are soft to the touch, and dissolve in water, alcohol, ether, or chloroform.

T. H. P.

**Estimation of Sugar in Blood.** PHILIP A. SHAFFER (*J. Biol. Chem.*, 1914, 19, 285—295).—A method is described for estimating the dextrose in 5 c.c. of blood. Its essential features consist in removing the proteins by combined heat coagulation and the Michaelis-Rona colloidal iron precipitation, and, after heating with Fehling's solution, estimating the cuprous oxide formed, by Bertrand's permanganate method or by simply dissolving the oxide in nitric acid, treating with ammonia, and comparing with a



standard ammoniated copper solution in a colorimeter. Most of the processes, including the reduction, are carried out in centrifuge tubes, and the precipitates collected and washed by centrifugalisation.

The method previously described, involving the use of methyl alcohol for the precipitation of the proteins in the blood, gives lower results for the blood sugar, and is therefore considered unsatisfactory.

H. W. B.

**Estimation of Aldoses. I. The Action of Neutral Sodium Hypiodite.** N. BLAND and L. L. LLOYD (*J. Soc. Chem. Ind.*, 1914, **33**, 948—949).—In the examination of the action of aldehydes on sodium hypiodite, it was found that the reaction with formaldehyde proceeds quantitatively according to the equation  $\text{NaIO} + \text{CH}_2\text{O} = \text{NaI} + \text{H}\cdot\text{CO}_2\text{H}$ , and may be used for the estimation of the aldehyde in aqueous solution. Five c.c. of commercial formalin are diluted to 1 litre, and 10 c.c. of this solution are added to 50 c.c. of *N*/10-iodine solution, previously rendered slightly alkaline with sodium hydroxide. After five minutes the mixture is acidified with sulphuric acid, and the liberated iodine is titrated with thiosulphate solution. Untrustworthy results are obtained when the method is applied to paraformaldehyde and acetaldehyde.

In the case of sugars, neutral sodium hypiodite oxidises only the aldehyde group; for instance, the aldehyde group in dextrose requires one molecule of iodine or hypiodite. Lævulose and sucrose contain no aldehyde group, and do not react with neutral hypiodite, but the latter sugar, on inversion, yields dextrose and lævulose, and requires one molecule of iodine. The following results were obtained with different sugars; in each case, 25 c.c. of a 1% solution of the sugar were added to a mixture of 50 c.c. of *N*/10-iodine solution and 50 c.c. of *N*/10-sodium hydroxide solution (this produces a neutral solution); after five minutes' contact, the solution was acidified, and the liberated iodine titrated. Dextrose, 96.4 to 99.7%; lactose, 99.1 to 99.4%; maltose, 99.9 to 101.8%; sucrose (after inversion), 100.8 to 101.3%; lactose (after inversion), 99.1 to 99.4%; maltose (after inversion), 99.1 to 99.9%.

W. P. S.

**Estimation of Pentosans.** J. VAN HAARST and S. C. J. OLIVIER (*Chem. Weekblad*, 1914, **11**, 918—925).—A comparison of results obtained in the estimation of pentosans by Tollens's method and that given in the Dutch "Codex Alimentarius." The authors recommend distilling with hydrochloric acid at the standard rate of 400 c.c. in two hours. A slower rate tends to decompose part of the furfuraldehyde, while more rapid distillation fails to effect complete decomposition of pentosans containing arabinose. The results obtained by Tollens's method are more accurate than those given by the process of the "Codex Alimentarius," but none of the published tables for calculating the amount of the pentosans gives the velocity of distillation employed in their compilation.

A. J. W.

**Estimation of Hydrogen Cyanide in Feeding Stuffs, and its Occurrence in Millet and Guinea Corn.** J. R. FURLONG (*Analyst*, 1914, 39, 430—432).—The method consists essentially in the conversion of the hydrogen cyanide into Prussian-blue, and the estimation of the latter colorimetrically. One hundred grams of the ground substance are extracted for three hours in a Soxhlet apparatus with 90% alcohol. The extract is transferred to a flask, and, after the alcohol has been distilled off, 150 c.c. of 10% sulphuric acid are added, and the distillation is continued, the distillate being collected in a receiver containing 5 c.c. of 10% potassium hydroxide solution. After one hour the receiver is changed, water is added to the flask, and a second quantity of distillate collected. These operations are repeated until the evolution of hydrocyanic acid ceases. The distillate is concentrated to 15 c.c., boiled for ten minutes with the addition of 1 c.c. of 20% ferrous sulphate solution containing 1% of ferric chloride, cooled, acidified with hydrochloric acid, and 10 c.c. of glycerol are added. After about fifteen hours, the mixture is diluted with water to 50 c.c., and the blue coloration compared with that given by known quantities of hydrogen cyanide under similar conditions. When the amount of hydrogen cyanide present is not less than 0.001 gram, the standards may be made up directly, but with smaller quantities it is necessary to dilute to 150 c.c. and then concentrate, as in the preparation of the solution from the substance under examination. Estimations of hydrogen cyanide in millet and guinea-corn plants of various ages showed that all the young plants contained a cyanogenetic glucoside, whilst the full-grown plants were free from this substance. In the case of guinea corn, the yield of hydrogen cyanide reached a maximum (0.01%) in the 12-inch plants, and decreased as growth proceeded. With millet the maximum amount (0.045%) was found in the plants which had attained a height of 24 inches. W. P. S.

**Cause of Acidity of Fresh Milk of Cows and a Method for the Determination of Acidity.** LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1914, 19, 73—76).—The acidity of fresh milk is due to the presence of acid phosphates. Addition of alkali to milk leads to the hydrolysis of the calcium salts present, so that by the direct titration of milk with alkali, using phenolphthalein as indicator, results are obtained for the acidity which may be twice as great as they should be. The calcium must, therefore, be removed before titrating with the alkali, by treating 100 c.c. of milk with 2 c.c. of a saturated solution of normal potassium oxalate, and keeping the mixture for not less than two minutes. H. W. B.

**Sulphocarbon Oil.** F. CANZONERI and G. BIANCHINI (*Ann. Chim. Applicata*, 1914, 2, 1—9).—The authors describe the composition, properties, and means of detection in mixtures of the so-called "sulphocarbon" oil, that is, olive oil extracted by means of carbon disulphide. T. H. P.

**Specific Reaction of Oils of Marine Animals and their Products of Hydrogenation.** M. TORTELLI and E. JAFFE (*Ann. Chim. Applicata*, 1914, 2, 80—98).—The reactions previously described as specific for the oils and fats of marine animals are due to impurities or to products of alteration which may be eliminated during the purification, and may also be found in fats and oils of terrestrial or vegetable origin. The authors find, however, that the following test is given by the oils and fats of marine animals and by no others; the quantities in brackets represent the proportions to be taken in examining a fat obtained by catalytic hydrogenation. Into a graduated cylinder of about 15 mm. (30 mm.) in diameter and 15 c.c. (25 c.c.) in capacity, and fitted with a ground stopper, are introduced 1 c.c. (5 c.c.) of the oil or melted fat, 6 c.c. (10 c.c.) of chloroform, and 1 c.c. (1 c.c.) of glacial acetic acid, which are shaken to give a homogeneous mixture. With this 40 drops (2.5 c.c.) of a 10% solution of bromine in chloroform are vigorously agitated for a few seconds, the cylinder being then placed on a sheet of paper. If the oil is derived from a marine animal, the liquid becomes first red and, within a minute, pale green, the colour increasing in intensity for some time, and then remaining constant for an hour. The coloration is formed more rapidly with highly refined oils, and varies from green with a yellowish reflection to green with a bluish reflection, according to the origin of the oil. In the case of a hydrogenated oil, the initial coloration is reddish-yellow, and the final intense green coloration is obtained with greater rapidity than with the non-hydrogenated oils.

The reaction serves for the detection of the presence in alimentary fats of synthetic fats prepared from the oils of marine animals.

T. H. P.

**Drying Urine for Chemical Analysis.** WINFRED W. BRAMAN (*J. Biol. Chem.*, 1914, 19, 105—113).—In drying urine from herbivora for the determination of the heat of combustion, it is found that large quantities of ammonia and carbon dioxide are evolved. The methods used to remove the water are (1) to dry in a desiccator over sulphuric acid at about 5 mm. pressure at room temperature, and (2) to pass over the sample a current of dry air free from ammonia and carbon dioxide. The loss of nitrogen under these conditions may amount to as much as 50% of the total nitrogen of the urine, and arises mainly from the decomposition of ammonium carbonate, and not of urea or hippuric acid. The carbon dioxide is lost in a quantity more than sufficient to combine with the ammonia lost to form the normal carbonate.

The author estimates the total carbon and total hydrogen (including that of the water) in the fresh undried urine by combustion in an ordinary combustion furnace; this method gives consistent results.

H. W. B.

**A Permanent Preparation of Urease, and its Use in the Estimation of Urea.** DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1914, 19, 211—228).—Urease in powder form is

prepared by extracting soja bean meal with water at room temperature, and then pouring the clear extract into at least ten times its volume of acetone. The precipitated urease can be dried in a vacuum, and maintains its activity for an apparently indefinite period. It is soluble in water, and the solution, if kept at  $0^{\circ}$ , does not lose its activity for several weeks, especially if 5% of dipotassium hydrogen phosphate is also present in the solution.

For estimating urea in urine, one-half c.c. of urine is mixed with 5 c.c. of 0.6% potassium dihydrogen phosphate and 1 c.c. of a 10% solution of urease. After twenty minutes at  $15^{\circ}$ , or three minutes at  $50^{\circ}$ , to complete the decomposition of the urea, 4 to 5 grams of potassium carbonate are added, and the ammonia then aspirated into 25 c.c. of *N*/50-hydrochloric or sulphuric acid. When the aeration is finished, the excess of acid is titrated with *N*/50-alkali.

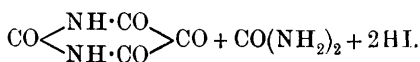
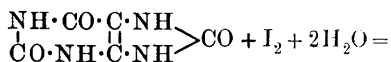
Urease is a particularly valuable reagent because it enables a direct estimation of the urea in the blood to be made, its action being so specific that no other constituent of the blood is attacked. The original paper must be consulted for the details of the methods and apparatus recommended by the authors. H. W. B.

**Estimation of Uric Acid in Urine.** DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1914, 53, 257—262).—In the author's method the following solutions are employed: (1) Salkowski-Ludwig reagent, prepared by mixing equal volumes of (a) and (b) immediately before using: (a) 26 grams of silver nitrate are dissolved in 300—400 c.c. of distilled water, and ammonia solution added until the brown precipitate at first formed dissolves completely, the liquid being then made up to 1 litre with water; (b) 100 grams of magnesium chloride and 150 grams of ammonium chloride are dissolved in about 500 c.c. of distilled water, ammonia solution in excess added, and the volume made up to 1 litre. (2) Aqueous 2% uranyl acetate prepared in the hot; this serves as a defecating and decolorising agent, mucinoid substances and uranyl phosphate being precipitated, together with pigmentary matter. (3) Decinormal iodine solution containing 25 grams of potassium iodide per litre. (4) A 0.1% aqueous solution of indigo-carmin. The procedure is as follows:

One hundred c.c. of the urine are mixed with 20 c.c. of the uranyl acetate solution, and the liquid at once poured on to a dry pleated filter. Sixty c.c. of the filtrate are introduced into a 100 c.c. beaker containing 10 c.c. of the Salkowski-Ludwig reagent, the mixture being well stirred, and, after a short time, the precipitate collected quantitatively on a small filter, and washed three or four times with water. Most of the precipitate is then returned to the precipitation vessel by means of a glass rod, and treated with about 30 c.c. of a solution of 2 grams of potassium iodide in 150 c.c. of water. The turbid liquid thus obtained is then poured through the filter containing the remainder of the precipitate, which is washed several times with the potassium iodide solution. The filtrate, consisting of about 150 c.c. of colourless, almost clear liquid, is acidified by the addition of a drop or two of acetic acid, and

rendered alkaline by means of about 5 grams of powdered borax. The solution is then made slightly but distinctly blue by 10 or more drops of the indigo-carmin solution, and is titrated and shaken with decinormal iodine solution until a single drop causes immediate change from blue to yellowish-green. The number of c.c. of decinormal iodine used, multiplied by 0.0168, gives the amount of uric acid in grams per 100 c.c. of the urine. The accuracy of the method has been tested by means of both aqueous solution of pure potassium urate and urines containing known added proportions of uric acid.

The action of iodine on uric acid in presence of borax is expressed by the following equation :



The alloxan thus formed is also acted on by the iodine, but this action is so slow as to be virtually negligible; the same is the case with the purine derivatives, other than uric acid, occurring in urine.

T. H. P.

**Separate Estimations of the Purine Substances and the Uric Acid in Urine.** DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1914, **53**, 262—265).—This method is based on the fact that the silver-magnesium precipitate yielded by the Salkowski-Ludwig reagent is, when thoroughly washed and suspended in water, neutral towards phenolphthalein. When, however, highly concentrated aqueous potassium iodide is added, the precipitate dissolves almost completely, and the liquid becomes intensely alkaline, owing to the formation of normal potassium urate and of the potassium salts of the other purine derivatives present. The alkalinity of the liquid is, therefore, directly proportional to the content of purine compounds, inclusive of the uric acid. The latter may subsequently be estimated separately in the same liquid by the method already described (preceding abstract).

The procedure is at first similar to that used in the estimation of uric acid alone (*loc. cit.*), with the exception that the precipitate given by the Salkowski-Ludwig reagent is washed with distilled water until the washing water fails to react alkaline with phenolphthalein or litmus. The solution of this precipitate in the potassium iodide solution, amounting to about 150 c.c., is titrated with *N*/20-sulphuric acid solution in presence of 5—6 drops of 1% alcoholic phenolphthalein. Four or five grams of potassium hydrogen carbonate and 10 drops of 0.1% indigo-carmin solution are then added to the liquid, which is titrated with *N*/10-iodine solution until the blue colour changes to green. Multiplication of the excess of the number of c.c. of *N*/20-sulphuric acid over that of the *N*/10-iodine by 0.0076 yields the number of grams of purine compounds, calculated as xanthine, in 50 c.c. of the urine. The number

of c.c. of *N*/10-iodine, multiplied by 0.0084, gives the grams of uric acid in 50 c.c. of the urine.

T. H. P.

**Some New Tests for Veronal.** H. LUCAS (*Pharm. J.*, 1914, 93, 424).—The odour of iodoform is observed when veronal is boiled with aqueous sodium hydroxide, and the resulting solution is cooled and then warmed with a solution of iodine.

The residue obtained by fusing veronal with sodium hydroxide gives a purplish-violet biuret reaction with a drop of aqueous copper sulphate, and liberates nitrogen (not quantitatively) by treatment with concentrated sodium hypobromite.

C. S.

**Estimation of Antipyrine.** W. O. EMERY and S. PALKIN (*J. Ind. Eng. Chem.*, 1914, 6, 751—753).—The method depends on the solubility of iodoantipyrine in chloroform. In the case of antipyrine alone, or in such admixture that after treatment with iodine no substance other than iodoantipyrine will be extracted by chloroform, a quantity of the sample containing not more than 0.25 gram of antipyrine is shaken with 20 c.c. of water, 5 c.c. of alcohol-free chloroform, 0.5 gram of sodium hydrogen carbonate, and a slight excess of iodine solution. After a short time, the excess of iodine is decomposed by the addition of a few drops of thiosulphate solution, the iodoantipyrine is shaken out with chloroform, the chloroform solution is washed with water, filtered, evaporated in a weighed flask, and the residue is weighed. The weight of the residue multiplied by 0.5992 gives the quantity of antipyrine present. When the antipyrine is mixed with phenacetin, sulphonal, or similar substance, a weighed portion of the sample is shaken with 50 c.c. of water, 20 c.c. of concentrated hydrochloric acid, and an excess of iodine solution. After some hours the liquid is decanted through a glass-wool filter, the tarry residue is washed with 5% hydrochloric acid, then dissolved in about 50 c.c. of methyl alcohol (this must be free from ethyl alcohol and acetone), the solution is treated with 50 c.c. of water and sodium hydrogen carbonate, and, after the excess of iodine has been destroyed by the addition of thiosulphate solution, the iodoantipyrine is extracted with chloroform.

W. P. S.

**Use of Manganese Carbonate in the Detection of Traces of Strychnine.** G. GUÉRIN (*J. Pharm. Chim.*, 1914, [vii], 9, 595—597).—The author finds that the sensitiveness of the test for strychnine by means of sulphuric acid and potassium dichromate is exaggerated, and that the detection of 0.01 mg. by this method is uncertain. This quantity can be readily detected by the reagents of Mandelin (0.5 gram ammonium vanadate in 100 grams of pure sulphuric acid), of Wenzell (potassium permanganate [0.5 gram] in pure sulphuric acid [100 grams]), or of Sonnenschein (solution of the alkaloid in pure sulphuric acid and addition of a particle of cerium oxide). According to the author, the last two reagents appear to be more sensitive than that first named.

A method which is as sensitive as any of those described above consists in dissolving the alkaloid in two or three drops of sulphuric

acid and adding 2—3 mg. of manganese carbonate. On stirring, a blue coloration is developed, which gradually becomes violet, and then pink.

H. W.

**Application of Tungsten Salts to the Analysis of Tanning Materials.** ALEXANDER T. HOUGH (*J. Soc. Chem. Ind.*, 1914, 33, 847—848).—Two reagents, prepared from sodium tungstate, apparently give different results (amounts of precipitate) with the same tannin, and it is suggested that it may be possible to establish the purity of a given tannin extract by the constancy of the ratio between the two results. The reagents are prepared as follows: (1) 10% sodium tungstate solution, 5 c.c.; water, 2 c.c.; 25% ammonium chloride solution, 3 c.c.; (2) 10% sodium tungstate solution, 5 c.c.; 8% hydrochloric acid, 2 c.c.; 25% ammonium chloride solution, 3 c.c. A tannin solution is made containing about 4 grams of tannin per 250 c.c., and 10 c.c. of this solution are mixed with 10 c.c. of the first reagent; the mixture is poured on a filter, and 10 c.c. of the filtrate are evaporated to dryness, and the residue is weighed (*A*). The precipitate on the filter is then dissolved in hot water, the solution is added to the remainder of the filtrate, and the whole is evaporated to dryness (*B*). The actual weight of the precipitate is  $B - A$ ; it is necessary to ascertain the weight of the precipitate by this indirect method, as it cannot be washed. A similar estimation is then made, using the second reagent. The amount of precipitate is calculated on the percentage of tanning material in the extract, and for this purpose the quantity of total solids and of tannin (*C*) in 10 c.c. of the extract is estimated. Then  $100(B - A)/C$  gives the "tungstate number" of the tannin, using the first reagent; the same formula gives the "tungstic number," using the second reagent, and, presumably, "tungstic"/"tungstate" =  $K$  for any given tanning material. The author has applied the method only to mangrove extract, in which case  $K = 1.0503$ .

W. P. S.

**Quantitative Estimation of Aspartic and Glutamic Acids in the Products of Protein Hydrolysis.** FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1914, 8, 463—480).—After hydrolysis of the protein with hydrochloric acid, the glutamic and aspartic acids are converted into their calcium salts, which are then quantitatively precipitated by the addition of alcohol. After filtration from the alcohol-soluble calcium salts of the other amino-acids present, the free acids are regenerated by dissolving in water and adding oxalic acid. Traces of accompanying impurities are next removed by successive treatment with silver sulphate and phosphotungstic acid. The resulting solution on evaporation yields a crystalline mass, which is now extracted with glacial acetic acid. The residue consists of a mixture of glutamic and aspartic acids, and the proportionate quantity of each present is calculated from the carbon content of the mixture. As the difference between the percentages of carbon in glutamic and aspartic acids is as great as 4.73, the proportion can be determined with tolerable accuracy.

A small quantity of the glutamic acid is transformed into *l*-pyrrolidonecarboxylic acid during the preliminary processes indicated above, and is found in the glacial acetic acid extract. It is estimated by measuring the amino-nitrogen before and after boiling with hydrochloric acid, which reconverts the ring compound into glutamic acid.

The actual separation of aspartic and glutamic acids is effected by fractional crystallisation of the copper salts, copper aspartate crystallising out first. When most of the aspartate has been removed, the larger portion of the glutamic acid is separated by converting it into the hydrochloride.

By means of this method, caseinogen is found to contain 21.77% of glutamic acid and 1.71% of aspartic acid, or about twice as much as has hitherto been accepted. H. W. B.

**The Ferric Alum Estimation of Casein.** H. V. ARMY and H. H. SCHAEFER (*J. Ind. Eng. Chem.*, 1914, 6, 748—751).—Two modifications have been made in a method described previously (A., 1906, ii, 407) for the estimation of casein in milk; to ensure rapid filtration, the mixture of milk and ferric alum solution is set aside for one hour before the precipitate is collected, and the final titration is made with *N*/50-thiosulphate solution. The method, as used at present, is as follows. Five grams of milk are mixed with 5 c.c. of ferric alum solution (48.2224 grams of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  per litre), and, after one hour, the precipitate is collected on a filter and washed until free from soluble iron. The filtrate is treated with 3 c.c. of 31% hydrochloric acid and 2 grams of potassium iodide, heated to 40° for thirty minutes in a closed flask, and the liberated iodine is titrated with *N*/50-thiosulphate solution. Each c.c. of the ferric alum solution required for the precipitation is equivalent to 0.05934 gram of casein. W. P. S.

**Comparison of Methods for the Determination of the Proteolytic Activity of Pancreas Preparations.** J. H. LONG and A. W. BARTON (*J. Amer. Chem. Soc.*, 1914, 36, 2151—2166).—The object of this work was to compare the different standards for the valuation of the various commercial trypsins or pancreatins. The proteolytic value of six such trypsin preparations has been compared by four distinct methods, namely, the metacasein reaction, the Fuld-Gross sodium caseinate digestion method, the formaldehyde titration of amino-acids produced by digestion, and the fibrin digestion. The results obtained by the four methods agree in placing the activities of the six preparations in the same order, but they do not agree as to relative quantitative value of the different ferments, for the strongest ferment according to the metacasein reaction appears to be about twelve times as strong as the weakest, and according to the fibrin digestion about ten times as strong, whilst by the other tests the relation obtained is as 2 or 3 : 1. Still greater irregularities appear in comparing some of the other preparations.



The products sold as trypsins or pancreatins probably contain at least two different enzymes, reacting in different ways with proteins, and the effects produced in any case depend on the proportions in which the enzymes are present. These enzymes possess different degrees of stability towards heat.

It is not at present possible to convert the proteolytic value of a tryptic ferment from the terms of one standard to those of another, since the products are made by very different processes, which probably yield mixtures of ferments in widely different proportions, together with unknown quantities of inorganic salts. A more rational definition of trypsin is desirable, and products should be made to conform to interchangeable standards. E. G.

**Electrical Method of Estimating Salt in Soil.** WILLIAM BEAM and GILBERT A. FREAK (*Cairo Sci. J.*, 1914, 8, 130—133).—In estimating the amount of soluble salts in soils by the electric conductivity method, the error due to the nature of the salts present may be corrected by constructing special tables for the particular combination of salts in the area under examination. The results are especially affected by sodium carbonate, and the resistance is also higher when much organic matter is present (Davies and Bryan, *U.S. Dept. Agric. Bur. Soils*, Bull. 61). A more important source of error is that due to the presence of calcium salts (especially sulphate), which is not only harmless, but beneficial in neutralising the effects of toxic salts. This error is avoided by extracting the salts with 40% alcohol instead of water, and comparing the results with those obtained with a solution of salt in the same solvent. The calcium sulphate may then be estimated, if desired, by extracting with water as well.

In the case of soils containing moderate amounts of salts, the method usually employed is to treat an amount of soil, containing about 20 grams of dry matter, with 100 c.c. of 40% alcohol, and shake for ten to fifteen minutes. Shaking for one minute gave nearly the same results, and variations, from 38—42%, in the strength of the alcohol are without much influence.

In testing the method with solutions of known composition a solution containing 0.030% of gypsum and 0.131% of sodium chloride was found to have a resistance of 210 ohms instead of the calculated resistance of 220 ohms. N. H. J. M.

**Estimation of the Lime Requirement of Soils by means of [Barium Hydroxide].** C. R. MOULTON and P. F. TROWBRIDGE (*J. Ind. Eng. Chem.*, 1914, 6, 835—837).—The lime requirement of a soil, as estimated by boiling the soil with an excess of  $N/10$ -barium hydroxide solution and measuring the excess by means of the ammonia set free from added ammonium chloride, is proportional to the quantity of barium hydroxide used, and not to the acidity of the soil. The result obtained is considerably lower than when the Vietch method is employed. Further, the lime requirement varies with the duration of the distillation and the volume of the distillate until the lime requirement falls to zero (compare Bizzell and Lyon, this vol., ii, 150). W. P. S.

## General and Physical Chemistry.

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**Index of Refraction and Density of Gases.** A. OCCHIALINI (*Nuovo Cim.*, 1914, [vi], 8, ii, 123—155).—Magri (1904) has shown that, at pressures up to 200 atmospheres, the refractive indices of air give values for the Lorenz and Lorentz formula which are appreciably more constant than those calculated by means of Drude's or Gladstone and Dale's expression. The author has extended Magri's observations by measuring the indices of refraction and the corresponding specific gravities of nitrogen and oxygen at various pressures up to 200 atmospheres and of carbon dioxide up to the saturation point at 21°. The maximum percentage variations of the value of the Lorenz and Lorentz formula are 0.05, 0.3, and 0.2 for nitrogen, oxygen, and carbon dioxide respectively, such variations lying within the limits of experimental error. For Drude's and Gladstone and Dale's formulæ the corresponding percentage variations are respectively 2.3 and 8.5 for nitrogen, 2.7 and 0.8 for oxygen, and 1.4 and 0.5 for carbon dioxide. The value of  $(n^2 - 1)/(n^2 + 2)D$  is  $1997 \times 10^{-7}$ ,  $1815 \times 10^{-7}$ , and  $3003 \times 10^{-7}$  for the three gases respectively.

These results show that the value calculated, by the Lorenz and Lorentz formula, for the index of refraction of a gas at any particular density is more accurate than that obtainable by direct measurement.

T. H. P.

**Fluorescence of Iodine Vapour Excited by Ultra-violet Light.** J. C. McLENNAN (*Proc. Roy. Soc.*, 1914, [A], 91, 23—29).—The fluorescence spectrum of iodine vapour, which was described in a previous paper (A., 1913, ii, 455), has been further investigated. Observations on the effect of temperature show that the spectrum is excited at all temperatures between that of the room and 1000°. In contrast with this, it is found that the resonance spectrum, excited by the yellow and green lines, is only obtained at comparatively low temperatures. No trace of this spectrum was observed at 326°.

The fluorescence spectrum is called forth when the wave-length of the exciting light falls between the limits  $\lambda$  2100 and  $\lambda$  1800. On the other hand, the resonance spectra cannot be obtained when the iodine vapour is illuminated by light from a mercury arc of wave-length less than that of the green line  $\lambda$  5460.

The investigation of a number of iodine compounds has shown that iodoform and mercuric iodide give a fluorescence spectrum which contains the seven well-marked bands of the iodine fluorescence spectrum between  $\lambda$  3315 and  $\lambda$  3175. In addition to the iodine lines, the mercuric iodide spectrum contains a number of specific bands which are absent from the iodine spectrum.

With potassium iodide, a fluorescence spectrum is obtained which does not show any of the iodine bands. It consists of two sets of

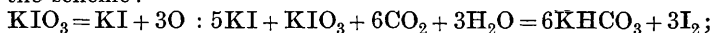
unequally spaced fine lines in the regions between  $\lambda$  4047 and  $\lambda$  3340 and between  $\lambda$  3075 and  $\lambda$  2940.

H. M. D.

**Theories of Rotational Optical Activity.** G. H. LIVENS (*Phil. Mag.*, 1914, [vi], 28, 756—757).—A reply to Bruhat (this vol., ii, 695), in which the author maintains that Drude's theory has been shown, both directly and indirectly, to be incapable of explaining the known facts in regard to optical rotatory power.

H. M. D.

**Photolysis of Potassium Iodate.** J. HOWARD MATHEWS and HARRY A. CURTIS (*J. Physical Chem.*, 1914, 18, 641—652).—The action of light of short wave-length has been investigated in the decomposition of solutions of potassium iodate. Solutions of 0.1*N*-potassium iodate were placed in a quartz flask and kept at a temperature of 30° by allowing a stream of water at this temperature to flow over them. Light from a mercury-vapour lamp was allowed to fall on the flask, when iodine was liberated. The amount of iodine liberated was estimated from time to time by titration with a 0.001*N*-solution of potassium thiosulphate. The following results were obtained: (1) When the photolysis is carried out in the presence of air, the rate of the reaction slowly decreases with time. (2) Iodine is not liberated when the solution is kept saturated with oxygen in an atmosphere of oxygen. (3) Carbon dioxide greatly increases the rate of photolysis; and (4) the rate of photolysis of potassium iodate in a solution kept saturated with carbon dioxide is linear when the amount of iodine liberated is small compared with the total amount present in the iodate. It is therefore not possible in such circumstances to determine the order of the reaction. It is suggested that the photolysis occurs according to the scheme:



the liberation of oxygen has been experimentally proved. Light accelerates the reaction between potassium iodate, potassium iodide, and carbon dioxide, but the reaction is very complex in the presence of light, and has not been quantitatively investigated. A lecture experiment to demonstrate the photochemical activity of light of short wave-lengths is described. To a solution of 0.1 gram of potassium iodate in 500 c.c. of water, 2 c.c. of a 1% solution of potassium iodide and 2 c.c. of starch solution are added. One half of the solution is placed in a quartz flask, and the residue in a glass flask. The flasks are placed at equal distances from a quartz mercury lamp, and in a few seconds the solution in the quartz flask turns blue, whilst the other remains quite colourless.

J. F. S.

**Radioactivity of Some Colorado Springs.** HERMAN SCHLUNDT (*J. Physical Chem.*, 1914, 18, 662—666).—The activity of the gases evolved by the water of a number of springs has been measured by means of a Mache-Meyer fontactometer with an ionisation chamber of 15 litres. The readings are taken from two to three minutes

after the introduction of the gas. The results are expressed in Mache units, and vary from 0.21 to 31.2 units. The equivalents in radium are calculated, and they vary from  $1.2 \times 10^{-10}$  gram to  $205 \times 10^{-10}$  gram. The gases from three of the springs were tested for thorium emanation, but the results were negative. Mention is made of the sinter deposit, round a group of radioactive springs investigated by Headden (A., 1905, ii, 2); this consists almost entirely of barium sulphate, which contains  $14.8 \times 10^{-10}$  gram of radium per gram; this corresponds with nearly 0.5% of uranium in the natural mineral.

J. F. S.

**Ionisation Potential of Mercury Vapour.** F. H. NEWMAN (*Phil. Mag.*, 1914, [vi], 28, 753—756).—Experiments were made to determine the smallest potential difference through which an electron must fall before it is able to ionise a molecule of mercury by collision. Working at  $79^\circ$ , at which the vapour pressure of mercury is about 0.1 mm., the value obtained was 5.0 volts. This agrees closely with the 4.9 volts obtained by Franck and Hertz (this vol., ii, 515).

H. M. D.

**Concentration Cells in Ionised Gases.** W. H. JENKINSON (*Phil. Mag.*, 1914, [vi], 28, 685—692).—Assuming that the passage of electricity from metal to air is a phenomenon which may be treated as thermodynamically reversible, the potential difference at the surface of contact should be given by the formula

$$\pi = RT(2x - 1)/\epsilon \cdot \log P/p,$$

in which  $p$  is the ionic pressure of either kind of electricity in the air and  $P$  is the equivalent of the "solution pressure" for the metal, the ions of which are transferred. If two wires are in contact with regions of air, in which the ionic pressures are  $p_0$  and  $p_1$ , then on the assumption that  $P$  is unaltered by the ionising agency, the two wires should form a concentration cell, the *E.M.F.* of which should be given by  $E = RT(2x - 1)/\epsilon \cdot \log p_0/p_1$ .

A cell of this kind was constructed by connecting up two carefully insulated copper wires to a Dolezalek electrometer and exposing one of the wires to the action of X-rays or of the rays emitted by radium. In all cases, a deflexion was gradually set up, which ultimately reached a steady value, and reversed its sign when the action of the ionising agent was transferred from one electrode to the other. The unprotected electrode was always found to be positive with respect to the shielded electrode. This indicates that the positive ion must be the controlling agent in the production of the difference of potential at the metal-air surface. The results suggest, in fact, that the negative ions take no part in the transfer of electricity across the surface.

It is suggested that the presence of an occluded layer of gas in the metal surface is an essential feature in the production of this difference of potential, and that  $P$  represents the ionic pressure in this occluded layer. According to this view, the transference of electricity at the surface is effected by means of positively charged air-ions.

H. M. D.

**Distribution of the Molecules of a Gas in a Field of Force, with Applications to the Theory of Electrons.** O. W. RICHARDSON (*Phil. Mag.*, 1914, [vi], 28, 633—647).—The question of the distribution of the molecules of a perfect gas in equilibrium in a field of force is discussed from the point of view of the quantum theory. The theory is also applied to thermo-electric phenomena and to the thermionic emission of electrons. H. M. D.

**Electrical Resistance of Pure Metals, etc. IX. Resistance of Mercury, Tin, Cadmium, Constantan, and Manganin down to Temperatures obtainable with Liquid Hydrogen and with Liquid Helium at its Boiling Point.** H. KAMERLINGH ONNES and G. HOLST (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 508—513. Compare this vol., ii, 163).—Further measurements of the resistance of solid mercury have been made at temperatures between  $-268.9^{\circ}$  and the melting point ( $-38.93^{\circ}$ ). The ratio of the resistances of liquid and solid mercury at the melting point is about 5. Data are also recorded showing the influence of temperature on the resistance of tin and cadmium between  $16.5^{\circ}$  and  $-268.9^{\circ}$ , of iron and copper between  $-183.7^{\circ}$  and  $-272.0^{\circ}$ , of constantin between  $-182.3^{\circ}$  and  $-258.8^{\circ}$ , of manganin between  $16.5^{\circ}$  and  $-271.5^{\circ}$ , and of gold between  $-182.3^{\circ}$  and  $-258.9^{\circ}$ .

The resistance of manganin varies with the temperature in a linear manner from the lowest oxygen temperatures down to helium temperatures. The temperature-coefficient of constantin, which is extremely small down to oxygen temperatures, increases considerably in the region of hydrogen temperatures. Between  $14^{\circ}$  and  $20^{\circ}$  (absolute) the relation between the resistance and the temperature is linear in character. It seems probable that gold may also be used for the measurement of temperatures below  $-200^{\circ}$ .

H. M. D.

**Conductivity of Certain Organic Acids in Absolute Ethyl Alcohol at  $15^{\circ}$ ,  $25^{\circ}$ , and  $35^{\circ}$ .** E. P. WIGHTMAN, J. B. WIESEL, and HARRY C. JONES (*J. Amer. Chem. Soc.*, 1914, 36, 2243—2259).—In continuation of earlier work on the conductivity of organic acids (White and Jones, A., 1910, ii, 13, 821; Wightman and Jones, A., 1911, ii, 689; 1912, ii, 1035; Smith and Jones, A., 1913, ii, 747), measurements have been made of the conductivity of malonic, *o*- and *p*-chlorobenzoic, *p*-bromobenzoic, *o*- and *p*-nitrobenzoic, 3:4-dinitrobenzoic, 3:4-dihydroxybenzoic, and tetrachlorophthalic acids in ethyl alcohol at  $15^{\circ}$ ,  $25^{\circ}$ , and  $35^{\circ}$ .

The temperature-coefficients of conductivity are very large, ranging from 15% to 50%. The conductivity often shows a rapid increase with increase in dilution, but *o*-chloro- and *p*-nitro-benzoic acids behave in the opposite manner. The conductivities of organic acids in alcohol are exceedingly small as compared with those of the same acids in aqueous solution, being in some cases several hundred times smaller; this fact cannot at present be satisfactorily explained.

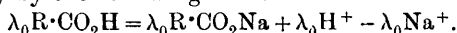
E. G.

**Sensitive Criterion of the Precision and of Constant Errors in the Conductance Data of Weak Electrolytes, the Determination of the Molar Conductance of Organic Electrolytes at Zero Concentration, and a Study of the Correction for the Specific Conductance of the Conductivity of Water.** C. G. DERICK (*J. Amer. Chem. Soc.*, 1914, **36**, 2268—2283).—The conductivity of a weak electrolyte at infinite dilution can be calculated from the expression

$$\lambda_0 = \lambda \lambda_1 (c\lambda - c_1 \lambda_1) / (c\lambda^2 - c_1 \lambda_1^2),$$

where  $\lambda$  and  $\lambda_1$  represent the molar conductivities at the concentrations  $c$  and  $c_1$ . Kendall's work on the conductivity of acetic acid in aqueous solution (T., 1912, **101**, 1283) indicates that acetic acid very nearly obeys the ideal mass law in this form, and the latter may be used in the calculation of the molar conductivity of acetic acid at zero concentration, the value of which is termed the "calculated"  $\lambda_0$ .

The molar conductivity at zero concentration can be determined independently by the following "salt method":



A comparison of the "calculated"  $\lambda_0$  for weak electrolytes, such as acetic acid, with that obtained for the same acid by the salt method affords a means of detecting constant errors in conductivity data. Kendall's data for acetic acid give the value 398 for the "calculated"  $\lambda_0$ , whilst the salt method gives 388; it is therefore evident that, assuming the mobility of the hydrogen ion is 347 for such weak electrolytes, some constant error is present in these data.

On assuming the ideal mass law to hold for transition electrolytes, and determining the values for "calculated"  $\lambda_0$  at different concentrations, a regularity was obtained in the increase of these values with decreasing concentration until a maximum constant value was reached at a concentration below which no deviations could be detected. This maximum constant value for the molar conductivity of the electrolyte should obviously be identical with the value obtained by the salt method, and this is shown to be the case with the organic acids studied by Kendall (*loc. cit.*).

The value 347 for the mobility of the hydrogen ion at 25° as given by Kendall and others is probably accurate, at least for the transition electrolytes.

It is shown that the "calculated"  $\lambda_0$  can be employed to determine whether a correction for the specific conductivity of the water used in the dilution of the organic acid should be applied to the conductivity data, the method being to calculate the values for "calculated"  $\lambda_0$  for the corrected and the uncorrected data, and compare them with the value of  $\lambda_0$  obtained by the salt method. Consideration of Kendall's results shows that no water correction should be applied to his data on transition electrolytes when the specific conductivity of the water is less than  $0.9 \times 10^{-6}$ , since his uncorrected data give "calculated"  $\lambda_0$  values which agree with those obtained by the salt method with an accuracy greater than 0.1% in the dilute solutions.

E. G.

**The Least Energy Required to Start a Gaseous Explosion.**

W. M. THORNTON (*Phil. Mag.*, 1914, [vi], 28, 734—738. Compare this vol., ii, 524).—A comparison has been made of the minimum energies of the igniting break-sparks of continuous and alternating current with those of condenser discharge between platinum poles. The observations were made with gases containing about 10% of methane or coal-gas in admixture with air, and electrodes of iron, nickel, and copper were employed in the comparison.

At voltages of 100 to 200, the least igniting energy varies from 0.02 to 0.15 joule in the case of continuous current, whilst the corresponding numbers for alternating current vary from 0.15 to 0.5 joule. The energy-voltage curves seem to indicate that the duration of any least-igniting break-spark is inversely proportional to its energy. The ignition is dependent on the nature of the gaseous mixture and of the incandescent matter which is projected into it from the poles. In continuous current ignition, the material of the poles is the important factor, whereas the nature of the gas is decisive in the case of ignition by alternating current discharge. The facts suggest that the ignition brought about by low-frequency alternating discharge is thermal in origin, and that some other factor operates in the case of ignition by continuous current discharge.

H. M. D.

**Ignition of Gases by Condenser Discharge Sparks.**

W. M. THORNTON (*Proc. Roy. Soc.*, 1914, [A], 91, 17—22. Compare this vol., ii, 524).—Experiments have been made to determine the least energy required for the ignition of explosive gas mixtures by condenser sparks between platinum poles at a potential difference of 100 volts. The observations were made with methane, ethane, propane, butane, carbon monoxide, hydrogen sulphide, and hydrogen mixed with air in varying proportions. The results are shown in the form of curves in which the capacity of the least igniting condenser discharge is plotted as a function of the composition of the gas mixture. These curves are not continuous, but so far as those mixtures are concerned which contain a smaller proportion of air than the most easily ignited mixture, they are characterised by one or more breaks or steps which indicate a sudden change in the case of ignition when the gas mixture reaches a certain composition.

In the case of methane no ignition could be obtained when the mixture contained less than 6.25% of this gas. From 6.25 to 10.5% the energy of the least igniting spark remained constant at 6.5 microfarads, but at 11.5% the necessary energy suddenly increased until 16 microfarads were required for ignition. The mixture corresponding with the formation of carbon dioxide is thus passed through without any marked change; the mixture corresponding with carbon monoxide is at 12%. At 13—13.5% of methane, 40 microfarads were necessary for ignition, and in mixtures containing a larger proportion of methane, ignition could not be brought about.

The stepped ignition curve has been found in all the gases employed in the experiments with the exception of butane, and in this case the ignition curve was not examined except in a preliminary manner.

The author suggests that the cause of the change in the resistance to ignition is probably to be found in the circumstance that when an atom of combustible gas is surrounded by molecules, with one or more of which it is eventually to combine, the difficulty of choice of any single partner is increased by the simultaneous attraction of the others, and more energy must be supplied to set up a movement sufficiently violent for any pair to be forced into "contact." In carbon monoxide the critical mixtures correspond with 3, 6, and 9 molecules of carbon monoxide for one molecule of oxygen. In methane the steps correspond with 3 and 4 molecules of oxygen to one molecule of methane, and in hydrogen the critical ratios of hydrogen molecules to oxygen atoms are 1, 2, 3, and 6.

H. M. D.

**Conductivity of Extremely Dilute Acid and Alkali Solutions.** H. H. PAINE and G. T. R. EVANS (*Proc. Camb. Phil. Soc.*, 1914, **18**, 1—13. Compare Whetham and Paine, A., 1908, ii, 802).—From measurements of the electrical conductivity of very dilute solutions of sulphuric acid, it is found that the relation between the conductivity and the concentration of the acid corresponds with a straight line provided that the concentration is not less than about  $0.8 \times 10^{-5}$  gram-equivalent per litre. For smaller quantities of acid, the observed conductivity is greater than that which would correspond with the straight line relation and the deviation between the two values increases as the concentration falls. The conductivity of the water employed in the experiments, in which the above limiting value of the acid concentration was obtained, was  $0.36 \times 10^{-6}$  mho.

It is shown that the observations can be accounted for in a satisfactory manner if it is assumed that the residual conductivity of the distilled water is mainly due to the presence of a carbonate, and experiments made with a very dilute solution of ammonium carbonate, to which gradually increasing quantities of sulphuric acid were added, support this view.

According to Kohlrausch's data, the conductivity-concentration curve for dilute solutions of potassium hydroxide deviates from the straight line at a higher concentration than that which is found for the sulphuric acid curve, but this is what would be expected on the assumption that the impurity is ammonium carbonate.

H. M. D.

**The Silver Voltameter. III. The Solvent Properties of Silver Nitrate Solutions.** T. MARTIN LOWRY (*Proc. Roy. Soc.*, 1914, [A], **91**, 53—71. Compare Smith and Mather, *Phil. Trans.*, 1908, [A], **207**, 545; Smith and Lowry, *ibid.*, 581).—Experiments have been made to determine the solubility of silver chloride, bromide,



iodide, and sulphide in concentrated aqueous solutions of silver nitrate, and also of silver chloride in concentrated solutions of sodium chloride and hydrochloric acid.

The measurements were made according to two different methods, which may be illustrated by reference to the solubility of silver chloride in silver nitrate solutions. Those at constant temperature were made by a gravimetric method, in which the weight of silver chloride precipitated on the addition of a measured quantity of sodium chloride was determined, and the quantity of dissolved salt obtained by difference. The influence of temperature on the solvent capacity of a solution of fixed concentration was ascertained by adding a measured quantity of sodium chloride under such conditions that a clear solution was obtained. The tube containing the hot solution was provided with a thermometer and stirrer, and was placed in a hot water-bath, the temperature of which was allowed to fall slowly. At a certain point the solution became opalescent in consequence of the separation of silver chloride, and this temperature was determined for a series of solutions.

*Silver Chloride* [with F. HAWKES, J. F. POTTS, and R. G. PARKER].—The data for 20° show that the quantity of silver chloride which is dissolved by 100 grams of silver nitrate increases from 0.0294 gram for the solution  $\text{AgNO}_3 : \text{H}_2\text{O} = 1 : 2$  up to 0.1372 gram for the solution 2 : 1. The quantity of silver chloride dissolved by a given solution increases with the temperature, and the temperature effect becomes more marked as the concentration of the nitrate in the solution increases. The curve obtained by plotting the dissolved silver chloride as a function of the temperature is convex to the temperature axis in the case of 1 : 2, concave for 2 : 1, and practically a straight line for the solution 1 : 1.

The data for the solubility in chloride solutions refer to 15, 20, and 28% solutions of sodium chloride, and a 20% solution of hydrochloric acid. The solubility increases in all cases with rise of temperature.

*Silver Bromide, Iodide, and Sulphide* [with R. G. PARKER].—The data for silver bromide show that the solubility of this in concentrated silver nitrate solutions is approximately three to four times as great as that of the chloride. The solubility of silver iodide in silver nitrate solutions has already been determined by Hellwig (A., 1900, ii, 723), but some observations relative to the influence of temperature on the solubility in a 25% solution are recorded. In this solution the solubility reaches a maximum at about 60°. If the solution saturated at this temperature is heated to 100°, silver iodide is precipitated; if allowed to cool, the solution becomes cloudy at about 50°, and white needles of  $\text{AgI}, \text{AgNO}_3$  are deposited. If these are left in contact with the mother liquor at the ordinary temperature, they are transformed into the double salt  $\text{AgI}, 2\text{AgNO}_3$ . Roughly speaking, the iodide is about thirty times more soluble than the bromide, and about 100 times more soluble than the chloride.

Silver sulphide is less soluble in nitrate solutions than the chloride. The black sulphide represents the stable solid phase in

contact with dilute nitrate solutions, but this is transformed into the yellow double salt  $\text{Ag}_2\text{S}, \text{AgNO}_3$  in contact with more concentrated solutions.

The quantity of silver sulphide retained per 100 grams of silver nitrate increases with the temperature, and at  $100^\circ$  amounts to 0.006 gram for a 40.8% solution, and to 0.243 gram for a solution containing 74% of silver nitrate.

H. M. D.

**Current Potentials of Electrolyte Solutions.** H. R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 615—622).—Measurements have been made of the differences of potential which result from the movement of dilute solutions of electrolytes through a capillary tube. In the apparatus used by the author, this capillary tube formed a connexion between two vessels, in which were suspended two silver electrodes covered with a layer of silver chloride. The solution was forced through the capillary at a constant speed, and the difference of potential between the electrodes measured by the Poggendorff method.

From experiments in which the solution was made to pass through the capillary at different rates, it was found that the difference of potential is directly proportional to the driving pressure.

In order to ascertain the influence of the cation, observations were made with solutions of potassium, barium, and aluminium chlorides. The curves obtained by plotting the potential difference against the concentration show that the addition of extremely small quantities of these electrolytes to conductivity water reduces the potential difference to a very marked extent. The influence increases very considerably with the valency of the cation, and the addition of  $0.8 \times 10^{-6}$  mol. of aluminium chloride per litre is sufficient to reduce the potential difference from 0.35 volt to zero. Further addition of aluminium chloride changes the sign of the potential, which, after reaching a maximum of 0.13 volt, diminishes gradually as the concentration of the aluminium chloride is further increased.

In the case of potassium and barium chlorides no change in the sign of the potential difference was observed, although the concentration was increased to  $10^{-3}$  mol. per litre for potassium chloride and to  $40 \times 10^{-3}$  mol. per litre for barium chloride.

The difference of potential observed with conductivity water is attributed to the selective adsorption of  $\text{OH}^-$  ions by the glass, and the reduction of this on the addition of the electrolytes, to selective adsorption of the respective cations.

H. M. D.

**Electric Charge and Limit Value of Colloids.** H. R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 623—629).—The data obtained in measurements of the capillary electric potential for solutions of potassium chloride and barium chloride (compare preceding abstract) show the existence of a close connexion between this phenomenon and the coagulation of colloidal particles by these electrolytes.

H. M. D.

**Electrolytic Endosmose.** HORACE G. BYERS and CARL H. WALTER (*J. Amer. Chem. Soc.*, 1914, 36, 2284—2291).—Experiments

are described which were carried out with a simple tripartite cell, consisting of two battery cups, set about  $\frac{1}{4}$  inch apart in a battery jar. In each cup a platinum electrode was placed, and an intermittent siphon, so that any rise in the level of the liquid would cause an overflow into a suitable graduated vessel. The whole apparatus was filled with the solution to be examined, and the level of the liquid in the battery jar was maintained during the experiment by adding more of the solution from a reservoir through a dropping siphon. Experiments were made with solutions of potassium permanganate, potassium perchlorate, sodium chloride, copper sulphate, copper nitrate, sodium sulphate, borax, potassium alum, and ferric chloride. Some experiments were conducted with a cell with six compartments.

The results show that endosmose is capable of producing a flow of electrolyte in the direction of the current, in the opposite direction, or in both directions simultaneously. In some cases the electrolyte flows away from both electrodes, and also may flow more rapidly from one than to the other; in each case the volume in the middle compartment of a tripartite cell is increased. In a cell with six compartments the change in volume is not confined to the anode and cathode compartments, but varies in the other compartments in an apparently erratic manner. When clay membranes are used, the endosmose is complicated by stenolysis.

E. G.

**Alternating Current Electrolysis.** JNANENDRA CHANDRA GHOSH (*J. Amer. Chem. Soc.*, 1914, **36**, 2333—2346).—Le Blanc and Schick (A., 1904, ii, 230) have expressed the view that electrolysis by means of an alternating current depends on the formation of a complex ion, whilst Brochet and Petit (A., 1904, ii, 229; 1905, ii, 672) consider that the presence of complex ions is not necessary, but that the general condition for the formation of a new compound is that the ion on reaching the electrode has had time to part with its charge before reversal produces the ion of opposite charge at the same electrode. In connexion with this question, the author has thought that as the electrode potential is due to the electrical double layer at the surface of separation between the electrode and electrolyte, a study of the amount and direction of variation of electrode potential might possibly elucidate the nature of the changes at the electrode surface.

When an alternating current is passed through cadmium in cadmium sulphate solution or through copper in copper sulphate solution, no variation in the electrode potential is produced. These results indicate that only when there is such a change as would alter definitely the chemical nature of the electrical double layer is its effect noticeable by measurements of the electrode potentials.

Experiments were also carried out to determine the changes in the electrode potentials in cells containing two platinum electrodes immersed in various electrolytes. On passing the alternating current, small variations in the *E.M.F.* were observed in all cases, but these were greatest in the case of acids, the amount of variation in this case being from 0.2 to 0.4 volt. It is evident, there-

fore, that on a polished platinum surface the chemical process is not reversible, but that the ion has time to part with its charge and form other more stable substances. Variations in *E.M.F.* were also observed when mercury electrodes were employed, but these were smaller than in the case of platinum and of a somewhat different nature. When electrodes of platinum-black were used, the variation in electrode potential almost disappeared, and in no case exceeded 0.015 volt, whence it is evident that there is not any appreciable consumption of energy at the electrode surface.

The effect of alternating currents on the single electrode potentials of combinations which have an *E.M.F.* of their own was investigated. In the case of cells containing an electrode, consisting of a metal surrounded by its insoluble salts, such as the cell  $\text{Zn}-\text{ZnCl}_2-\text{HgCl}-\text{Hg}$ , the effect of impressing an alternating current is to increase the amount of polarisation at the mercury electrode, and necessarily to increase the amount of the polarising current which the cell furnishes of itself. Several other types of cell were also studied.

E. G.

#### Thermal Expansion of Solutions of Gelatin in Water.

ARTHUR A. SCOTT (*J. Physical Chem.*, 1914, 18, 677—680).—The coefficients of cubical expansion of 2%, 6%, and 10% solutions of gelatin in water have been determined at temperatures from 0° to 10°. The solutions were sterilised with a little mercuric chloride, and filled into a glass helix made from 150 cm. of tubing of uniform bore. One end of the tube was sealed, and a meniscus produced at the other surface of the jelly by pouring in about 1 cm. of petroleum. The apparatus was then placed in a thermostat, and the position of the meniscus read by means of a microscope at every degree change in temperature. The coefficient of expansion of a 2% jelly is increasingly negative to 3°, when it becomes less negative up to 7°, where it is positive; 6% and 10% jellies have positive coefficients over the whole range 0—10°, which steadily increase as the temperature rises.

J. F. S.

Vapour Pressures in Ternary Systems. W. P. JORISSEN (*Chem. Weekblad*, 1914, 11, 964—972).—A critical summary of work previously published.

A. J. W.

#### Cryoscopic Constant of Nitrobenzene. J. BÖESEKEN and J. A.

L. M. C. VAN DER EERDEN (*Rec. trav. chim.*, 1914, 33, 301—316).—The authors have determined the cryoscopic constant of nitrobenzene used as solvent in molecular-weight determinations in the case of aromatic hydrocarbons, their haloid and nitro-derivatives, phenols and some derivatives, aromatic acids and some derivatives, aliphatic alcohols and some derivatives, aliphatic acids, aldehydes, ketones, acid anhydrides, and amines and some derivatives. The nitrobenzene is purified by drying the commercial sample over calcium chloride, and distilling it when required; the determinations are made out of contact with moist air. The m. p. of the nitrobenzene, thus prepared, is 5.60°, the value of the cryoscopic constant being

between 69 and 70. This solvent can be used for substances which do not contain either a carboxyl or a hydroxyl group. In nitrobenzene, acids are more associated than alcohols and phenols; the acids are associated at low concentrations, the association changing but little with the concentration. Alcohols show an association which increases rapidly with the concentration but diminishes as the molecular weight of the alcohol increases, and is greatest for primary alcohols and least for tertiary alcohols of the same molecular weight. The carbonyl and the hydroxyl groups have each for itself an associating action much less than that of the carboxyl group. In these respects nitrobenzene is analogous to benzene and naphthalene as a solvent, the association, however, being generally less pronounced in the former than in the last two solvents.

W. G.

**Free Energy of Iodine Compounds.** GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1914, **36**, 2259—2268).—In continuation of the study of free energy of chemical substances (Lewis, A., 1913, ii, 112; Lewis and Randall, this vol., ii, 802), the free energies of iodine and its compounds have been calculated from existing data. The following values (in calories) of the free energy of formation ( $\Delta F^\circ_{298}$ ) have been obtained: iodine, I (solid), 0; I (liquid), 460;  $I_2$  (gas), 4640; I (gas), 16965;  $I_2$  (in aqueous solution), 3926; hydrogen iodide, HI (gas), 310; iodide ion,  $I'$ , -12304; tri-iodide ion,  $I_3'$ , -12216; hypoiodous acid, HIO (in aqueous solution), -23300; iodate ion,  $IO_3'$ , -32270. .E. G.

**The Values of the Critical Quantities in Case of Association.** J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 598—606).—A criticism of the conclusions arrived at by van der Waals (this vol., ii, 342, 538). It is shown that in the case of an associated substance, there is no linear relation between the association factor and the quantities  $T'_k/p_k$  and  $s = RT_k/p_k v_k$ . Such a relation does not hold even when association is not accompanied by a change of volume, and the deviations from it may be much greater when the association is attended by volume change.

H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids between  $-80^\circ$  and  $1650^\circ$ . VII. The Specific Surface Energy of the Molten Haloids of the Alkali Metals.** F. H. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 555—571. Compare this vol., ii, 805, 806).—The method, described in a previous paper, has been applied to the measurement of the surface tension of the molten fluorides and chlorides of lithium, sodium, potassium, rubidium, and caesium, and the bromides and iodides of sodium, potassium, rubidium, and caesium. Although, in most cases, the surface energy is a linear function of the temperature, the connexion between these quantities is for certain salts more accurately given by the quadratic formula:

$$\chi_t = a + b(t - t_s) + c(t - t_s)^2,$$

in which the constant  $a$  represents the surface energy at the melting point  $t_s$ . In general, the value of the constant  $b$  is smaller for molten salts than for organic substances, but exceptions are met with in lithium, sodium, and rubidium fluorides.

The data show further that the temperature-coefficient  $b$  for the haloids of the same alkali metal decreases in all cases with increasing atomic weight of the halogen. At a given temperature the surface energy values for the series of salts formed by the same halogen with the series of alkali metals, decreases with increasing atomic weight of the alkali metal. In the same way, the surface energy of the haloids of one and the same alkali metal decreases with increasing atomic weight of the halogen if the comparison is made at a fixed temperature.

H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures between  $-80^\circ$  and  $1650^\circ$ . VIII. The Specific Surface Energy of Some Salts of the Alkali Metals.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 571—584. Compare preceding abstract).—The surface tension of molten oxygen salts of the alkali metals has been measured at different temperatures. Data are recorded for the sulphates and nitrates of lithium, sodium, potassium, rubidium, and caesium, the metaborates of lithium, sodium, and potassium, and the molybdates, tungstates, and metaphosphates of sodium and potassium. As in the case of the alkali metal haloids, the temperature-coefficient is constant for a number of the oxy-salts, but for others a quadratic formula is necessary to express the relation between the surface energy and the temperature.

At a given temperature the surface energy of a series of alkali metal salts of the same acid decreases with increasing atomic weight of the alkali metal. An exception to this rule is presented by lithium nitrate, in that its surface energy is less than that of sodium nitrate.

H. M. D.

**Adsorption and Stabilisation.** J. C. BLUCHER and E. F. FARNAU (*J. Physical Chem.*, 1914, 18, 629—640).—The various theories which have been put forward to explain the process of dyeing are discussed, and it is shown that the adsorption theory coupled with Bancroft's theory of stabilisation of the dye, to explain the process of dyeing from colourless solutions, is most nearly in accord with facts. This theory (this vol., ii, 250) states that the fibre stabilises the otherwise unstable substance which it has adsorbed. Thus blue cupric hydroxide when adsorbed by wool is not converted into oxide by heating at  $100^\circ$ . A number of other instances are quoted in the paper, including the stabilisation of blue cobalt hydroxide by cobalt sulphate and by nickel hydroxide, and of the red acid of Congo-red by aluminium hydroxide. A number of experiments are described on the stabilisation of cupric hydroxide. A number of tubes containing cupric hydroxide suspended in water are treated with small quantities of manganese sulphate, zinc sulphate, nickel sulphate, cobalt chloride, aluminium sulphate, chromium

sulphate, magnesium chloride, and mercuric chloride, and the mixtures heated at 100°. The cupric hydroxide turns black very rapidly when there has been no addition made, but with the exception of mercuric chloride all the other substances retard the formation of cupric oxide to such an extent that no blackening occurs after heating for ten minutes. The fact that silk is not dyed by a solution of picric acid in benzene is considered, and the conclusion reached that the apparent irreversibility in dyeing silk from benzene solutions of picric acid is probably a question of tautomerism as well as of slowness of attainment of equilibrium.

J. F. S.

**Measurements of the Capillarity of Liquid Hydrogen.** H. KAMERLINGH ONNES and H. A. KUYPERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 528—532).—Measurements of the surface tension of liquid hydrogen have been made by the method of capillary rise. The corrected rise is a linear function of the temperature for the interval examined. According to the linear formula, the capillary rise should vanish at 35·98° (abs.). Since the critical temperature is 31·11° (abs.), it is evident that the formula loses its validity before the critical temperature is reached.

The surface tension decreases from 3·182 dynes per cm. at 14·66° to 2·126 at 20·40° (abs.). The data yield 1·464 for the value of the temperature-coefficient of the molecular surface energy, which is much lower than the average value for so-called normal substances. It would seem that this coefficient decreases with fall in the critical temperature.

According to the theory underlying Einstein's formula (*Ann. Physik*, 1911, [iv], 34, 165), it would seem that the radius of molecular action for hydrogen is larger than for substances such as benzene.

H. M. D.

**Molecular Kinetic Elements of the Vapours of Isomeric Compounds.** A. POCHETTINO (*Nuovo Cim.*, 1914, [vi], 8, ii, 5—36).

—The author has determined, by Stefan's method, the coefficients of diffusion,  $D$ , into air of the vapours of (1) the series of esters studied by Meyer (A., 1878, 368), Meyer and Schumann (A., 1881, 504), and Winkelmann (A., 1885, 10; 1886, 11), and (2) various other groups of structural and position isomerides. The reduction of the values of  $D$  to a common temperature was effected by means of Sutherland's formula:

$$D_2/D_1 = (T_2/T_1)^{3/2} \cdot (1 + c/T_1)/(1 + c/T_2),$$

in which  $c$  represents a constant characteristic of the pair of gases under consideration; better concordance is obtained by this formula than by the relation  $D_1/D_2 = T_1^2/T_2^2$ , deduced from the old kinetic theory of diffusion. From the values thus obtained, those of  $L$ , the mean path of the molecules, of  $\sigma$ , the diameter of the sphere of molecular action, and of  $Q$ , the sum of the sectional areas of the spheres of action of the molecules in unit volume, have been calculated.

As might be foreseen, increase of the number of atoms in the

molecules of homologous compounds is accompanied by diminution in the mean path of the separate molecules and by increase in the diameter of the sphere of action. In the case of isomeric compounds with normal, and therefore equal, vapour densities, the molecules of the vapour differ in the diameters of their spheres of action, iso-compounds giving lower values than those of normal structure. This observation is related to the fact that, according to van't Hoff's hypothesis, the centres of the carbon atoms are nearer with iso-compounds than with normal ones. In the following series of isomeric compounds, the values of  $\sigma$  are in order of diminishing magnitude, whilst those of the propinquity of the carbon atoms, as judged from the steric formulæ, are in order of ascending magnitude: butyl alcohol, *isobutyl* alcohol, ethyl ether, trimethylcarbinol; propylbenzene, *isopropyl*benzene, mesitylene; butylamine, *isobutyl*amine, diethylamine; benzyl chloride, *o*-, *m*-, *p*-chlorotoluenes; ethylbenzene, *o*-, *m*-, *p*-xylenes. With isomeric compounds of the formula  $C_nH_{2n}O_2$ , leaving aside the acids,  $\sigma$  is smallest for that isomeride in which the position of the group C·O·C is such that the two atomic complexes attached to the two carbon atoms are most nearly similar; the association of the acids in the liquid state seems to influence the values of  $L$  and  $\sigma$ .

The increase in the value of  $\sigma$  produced by addition of a  $CH_2$  group varies with the molecular structure of the original compound. With the acids  $C_nH_{2n}O_2$  its mean value is  $1.12 \times 10^{-8}$ , and with the isomeric esters  $0.56 \times 10^{-8}$ .

Since the value of the coefficient  $b$  of van der Waals' equation is related to that of  $\sigma$  according to the equation  $b = 4\pi N\sigma^3/6$ ,  $b$  and  $\sigma$  should increase together in series of isomeric compounds, and this is found to hold in general, although exceptions do occur. Further, according to the Mossotti-Clausius law, the fractional volume,  $v$ , actually occupied by the molecules of a gas is connected with the dielectric constant  $K$ , and the index of refraction,  $n$ , for  $\lambda = \infty$ , by the relation  $v = (K - 1)/(K + 2) = (n^2 - 1)/3$ ; this method of comparing the molecular dimensions agrees with the values of  $\sigma$  in the case of ethyl formate and methyl acetate, but not in that of ethyl acetate and methyl propionate.

The values of  $L$  given by the diffusion method were compared, for a number of the compounds investigated, with those derived from measurements of the coefficients of internal friction of the vapours. The agreement between the two series of values is not good, but the variation observed in passing from a compound to an isomeric one is in the same direction, and approximately of the same magnitude in the two series.

Measurements of the thermal conductivity of the vapours of a number of the compounds show that, in a group of isomeric compounds, the values of the conductivity and of  $L$  increase together.

T. H. P.

**Interpretation of the Indications of Atomic Structure Presented by Crystals when Interposed in the Path of X-Rays.**  
WILLIAM BARLOW (*Proc. Roy. Soc.*, 1914, [A], 91, 1—16).—A



theoretical paper in which it is shown that the nature of the spacing of the parallel planes of atomic centres, as indicated by the behaviour of crystals towards *X*-rays, is more or less ambiguous. The arguments put forward show that an atomic system, arranged according to any one of the three space-lattices possessing cubic symmetry, may be subjected to a certain kind of deformation, sufficient in amount to alter profoundly the nature of the arrangement, without any appreciable evidence of this deformation being presented by the *X*-ray data. So far as geometrical possibilities are concerned, a similar method of modification can be applied to all kinds of space-lattice arrangements of atoms of whatever symmetry, so as to produce from them point-systems which would have an effect on *X*-rays practically indistinguishable from that produced by the unmodified space-lattice arrangements. Such modifications of the space-lattice or space-lattices leave the system of crystal symmetry unaltered, but lower the class. The fact that hemihedry is in so many cases exhibited by the crystals of simple compounds may be regarded as an indication that the actual arrangement of the atoms is of the less symmetrical kind.

In the case of a crystal of sodium chloride, the need for some modification of the model described by W. L. Bragg (*ibid.*, 1914, [A], 88, 428) is suggested by the fact that the arrangement does not lend itself to a distribution of the centres of the molecules in harmony with the crystal symmetry. If, however, the arrangement of the atoms is one derived from the cubic space-lattice by appropriate deformations, the difficulty presented by the crystal symmetry is avoided. The suggested modification is not only in harmony with the results of *X*-ray observations, but is in better agreement with the following facts: (1) that the centres of the molecules are arranged according to cubic symmetry; (2) that the symmetry is not holohedral, but hemihedral, like that of the actual crystals; (3) that stable equilibrium is indicated by the relation of each centre to the centres surrounding it. H. M. D.

**Rhythmical Precipitation of Ferrous Ferricyanide and Ferrous Hydroxide in Jelly.** HENRY JERMAIN MAUDE CREIGHTON (*J. Amer. Chem. Soc.*, 1914, 36, 2357—2360).—Liesegang (A., 1906, ii, 273; 1907, ii, 533; this vol., ii, 631) and others have investigated the rhythmical precipitation of silver chromate and other salts in gelatin. Similar phenomena have now been observed with ferrous ferricyanide and ferrous hydroxide.

The experiments were carried out in a glass tube, 2 cm. in diameter, the ends of which were bent upwards at right angles. The tubes were filled with 10% solution of agar-agar containing, in one case, small quantities of potassium ferrocyanide and sodium chloride, and, in the other case, small quantities of phenolphthalein and sodium chloride. When the jelly had solidified, the vertical arms of the tube were filled with dilute sodium chloride solution, and an iron electrode, made from a clean wire nail, was placed in the liquid in each arm. An electric current was then passed through the jelly. In the case of the tube containing potassium

ferrocyanide, blue layers or disks of ferrous ferricyanide were formed at intervals, the intervening spaces containing colourless jelly. The rate of production of these disks and the distance between them were noted. In the case of the tube containing phenolphthalein, green disks of ferrous hydroxide appeared, separated from one another by pink jelly.

E. G.

**Distribution of Colloidal Arsenious Sulphide Between the Two Liquid Phases in the System Water, Ether, Alcohol.** HARRY P. CORLISS (*J. Physical Chem.*, 1914, 18, 681—694).—The binodal curve and tie lines for the system water, ethyl ether, ethyl alcohol previously determined by Bonner (*A.*, 1911, ii, 26) were redetermined, and the specific gravity of solutions of known composition on the binodal curve were also determined. The method employed here is the same as that previously adopted (*loc. cit.*). A graph has been constructed which allows of the composition of any one pair of solutions in equilibrium being found by determining its specific gravity. A method of allowing for the effect of colloiddally dissolved arsenious sulphide on the densities has been worked out and tested experimentally. It is shown that as regards the system water, ether, alcohol, the compositions at equilibrium are not affected by the presence of colloidal arsenic sulphide. Colloidal solutions of arsenic sulphide containing alcohol and ether are more transparent, and are less readily coagulated by salts than aqueous solutions, and the amounts of different salts required to coagulate them do not vary as much as in the case of water sols. Solutions containing alcohol, ether, water, and arsenic sulphide undergo change on keeping; the amount of arsenic found in the filtrate after coagulation with acid increases, and the proportion of colloid going into the upper layer on distribution decreases. Quantitative measurements of the distribution of the arsenic sulphide between the two phases show that when one and the same colloid preparation is used, and the measurements are carried out under the same conditions, the ratio of distribution varies continuously with the composition of the phases, and that, other things being equal, the fraction of the arsenic sulphide going into the upper layer decreases with increase in the concentration of the sulphide.

J. F. S.

**Equilibria in Quaternary Systems. X. Quaternary Mixtures with two Liquid Strata, and Quaternary Alloys of Nickel-Copper-Gold-Silver.** N. PARRAVANO (*Gazzetta*, 1914, 44, ii, 279—349. Compare *A.*, 1913, ii, 763).—Six different types of quaternary systems are subjected to theoretical treatment, which does not admit of satisfactory abstraction. From the percentage variation exhibited by any one component, it is found possible to calculate the quantities of liquid and solid constituting a given quaternary mixture, and hence those of the separate liquids and solids composing the liquid and solid mixtures, for any moment during the solidification. In conjunction with P. DE CESARIS, C. MAZZETTI, and U. PERRET, the author has investigated the

ternary and quaternary systems of Ni-Cu-Au-Ag, the results obtained with the quaternary alloys being borne out by those given by micrographical examination.

T. H. P.

**Equilibrium in the System Mercuric Iodide and Aniline.** J. N. PEARCE and E. J. FRY (*J. Physical Chem.*, 1914, 18, 667—676).

—The system mercuric iodide and aniline has been studied between the temperatures of  $-11.48^{\circ}$  and  $199.1^{\circ}$ . The portion of the curve below the melting point of aniline,  $-8^{\circ}$ , is the freezing-point curve of the solution in equilibrium with solid aniline; at  $-11.48^{\circ}$ , solid aniline and the compound  $\text{HgI}_2 \cdot 2\text{NH}_2\text{Ph}$  separate out together as a eutectic mixture. The solubility of mercuric iodide in aniline has been determined at a series of temperatures between  $-6.5^{\circ}$  and  $191.1^{\circ}$ , when the following values, expressed in grams of mercuric iodide in 100 grams of aniline, were obtained:  $-6.5^{\circ}$ , 23.35 grams;  $+0.4^{\circ}$ , 28.69 grams;  $17.8^{\circ}$ , 42.85 grams;  $21.1^{\circ}$ , 47.55 grams;  $26.9^{\circ}$ , 55.47 grams;  $30.1^{\circ}$ , 62.05 grams;  $36.2^{\circ}$ , 75.80 grams;  $42.9^{\circ}$ , 96.49 grams;  $48.8^{\circ}$ , 128.1 grams;  $63.6^{\circ}$ , 163.8 grams;  $70.82^{\circ}$ , 184.1 grams;  $76.2^{\circ}$ , 201.6 grams;  $95.9^{\circ}$ , 246.7 grams;  $115.7^{\circ}$ , 281.8 grams;  $137.2^{\circ}$ , 285.2 grams;  $181.1^{\circ}$ , 297.9 grams; and  $199.1^{\circ}$ , 863.2 grams. The solubility of the iodide increases rapidly up to  $46.8^{\circ}$ , and is in equilibrium with a white, crystalline solid,  $\text{HgI}_2 \cdot 2\text{NH}_2\text{Ph}$ , which melts at  $58.6^{\circ}$ . The temperature  $46.8^{\circ}$  is a quadruple point, where  $\text{HgI}_2$ ,  $\text{HgI}_2 \cdot 2\text{NH}_2\text{Ph}$ , solution and vapour are in equilibrium; at  $108^{\circ}$ , the solid phase is the red variety of mercuric iodide, but here the yellow iodide is formed, and a second quadruple point exists; at about this temperature a greenish-yellow solid begins to be formed, which has the composition  $\text{HgI}_2 \cdot \text{NH}_2\text{Ph}$ . The various saturated solutions were analysed by dissolving weighed quantities in an acetic acid solution of potassium iodide, and then precipitating the mercury with hydrogen sulphide, filtering on a Gooch crucible, washing with water and absolute alcohol, drying and removing free sulphur, and finally heating at  $70^{\circ}$  until of constant weight. It is shown that mercury sulphide is decidedly volatile at temperatures above  $70^{\circ}$ ; for example, 0.6879 gram lost 0.0194 gram when kept at  $80^{\circ}$  for three hours, whilst at  $110^{\circ}$  2.3076 grams lost 0.2946 gram in two hours.

J. F. S.

**Influence of Some Substituents in the Benzene Nucleus on the Velocity of Reaction in the Synthesis of Sulphones.**

S. C. J. OLIVIER (*Rec. trav. chim.*, 1914, 33, 244—251).—Using the method, slightly modified, already described for determining the velocity of reaction of *p*-bromobenzenesulphonyl chloride on benzene and its mono-substituted derivatives in the presence of aluminium chloride (this vol., i, 818), the author has determined the effect of replacing the bromine in *p*-bromobenzenesulphonyl chloride by other substituents on the velocity of its reaction with benzene in the presence of aluminium chloride. Using 1 mol. of aluminium chloride for each mol. of acid chloride, the reactions are all unimolecular, the constant of the reaction being proportional to the concentration of the aluminium chloride introduced.

The substituent groups,  $\text{CH}_3$ , H, I, Br, Cl,  $\text{NO}_2$  (in the meta-position), arranged here in the order of diminishing velocity constant, have the same proportionate influence whether introduced into the nucleus of the acid chloride or of the benzene, except that the influence is in general greater in the latter case. W. G.

**Catalytic Action.** J. BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 546–554).—In the main, this is a re-statement of the author's views on catalysis, recorded in a previous paper (this vol., ii, 554). An ideal catalyst is defined as a substance which reacts reciprocally with one of the substances which are to be rendered active in such a manner that the thermodynamic potential and chemical resistance simultaneously approximate to zero. H. M. D.

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## Inorganic Chemistry.

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**Production of Neon and Helium by the Electrical Discharge.** J. NORMAN COLLIE, HUBERT S. PATTERSON, and IRVINE MASSON (*Proc. Roy. Soc.*, 1914, [A], **91**, 30—45).—A detailed account is given of the experiments already published (T., 1913, **103**, 419; P., 1913, **29**, 233, 271), and also of the results obtained in new experiments. For as yet unexplained reasons, many of these experiments have yielded negative results.

The apparatus used was partly of the transference type, in which the gas to be examined was transferred from one vessel to another by means of a tube standing over mercury, and partly of the non-transference type, in which the testing apparatus could be placed in connexion with the experimental tube by opening a tap.

The hydrogen was removed by means of heated copper oxide or by explosion with oxygen; in the latter case, the oxygen was removed by sodium potassium alloy or by charcoal. The residue was examined in capillary tubes so fine that the mercury, once admitted, could only be withdrawn by strongly heating the tubes.

The least quantity of neon detectable corresponds with that in a few cubic millimetres of air. If this were due to leakage, then since the ratio of argon to neon in air is 700 : 1, the argon should have been readily detected and also probably some nitrogen.

The main results obtained in positive experiments are the following: *A.* Using discharge tubes of various kinds and electrodes of palladium, copper, lead, thallium, lithium, sodium, and potassium, helium or neon was obtained, and in many experiments both gases were detected. *B.* Experiments in which platinum, thallium, uranium, potassium fluoride, chloride and iodide, rubidium chloride and caesium carbonate were subjected to bombardment by cathode rays, gave helium and in some cases neon. *C.* According to earlier

observations on the mercury arc, considerable quantities of helium and neon were obtained in this form of discharge; but according to more recent experiments it would seem that this may be due to diffusion of air through the silica walls of the discharge tube. Further work on the electrodeless discharge has also shown that the conditions under which helium is produced are as yet not known with certainty.

It is to be noticed that, especially in experiments falling under A and C, considerable quantities of hydrogen disappear during the passage of the discharge.

In all experiments, great precautions were taken to ensure the purity of the gases used. Although control experiments seem to eliminate the possibility of air leakage, special experiments were made in which traces of air were admitted into the apparatus. After running the discharge tube for some time under these conditions, it was found that nitrogen was absorbed by the mercury, but that argon was left behind which could be readily detected in the examination tube, and formed a very sensitive test for a leak. A further quantity of argon could be obtained by heating the electrodes. This test for argon is therefore extremely delicate as a means of detecting air leakage.

The negative results obtained by Strutt (this vol., ii, 201) are attributed (1) to the use of too large a charcoal bulb which may have resulted in the absorption of the neon produced, (2) to the use of relatively wide capillary examining tubes, (3) to possible absorption by "splashed" metal, (4) to the type of discharge which has a considerable influence on the yield.

In a former paper it has been shown that the positive results are not due to permeation of the glass. That they are not due to occlusion has been shown by dissolving or melting the glass and the electrodes, when no helium or neon was obtained.

The authors draw no definite conclusion from the observations, but they consider that the trend of the results is towards conclusions which, if true, would be of obvious importance. H. M. D.

**The Ternary Systems Potassium [Potassium Hydroxide]-Phosphoric Acid-Water and Ammonia-Phosphoric Acid-Water.** E. G. PARKER (*J. Physical Chem.*, 1914, 18, 653—661).—The object of the work was to ascertain whether a stable compound of potassium, ammonia, and phosphoric acid could be produced with the purpose of thus obtaining a concentrated chemical fertiliser. The two above-mentioned ternary systems were therefore examined. Solutions of orthophosphoric acid from 1.4 to 9.77 mols. per 1000 grams of solution were shaken at 25° with potassium hydroxide of 8.56—0.12 mols. per 1000 grams of solution until equilibrium with the existing solid phase was set up. The liquid and solid phases were then analysed, and equilibrium isotherms plotted. It is shown that the solid phases stable in contact with the solutions are:  $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ ;  $\text{KH}_2\text{PO}_4$ ;  $\text{K}_3\text{PO}_4$ ;  $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ ; and  $\text{KOH} \cdot 2\text{H}_2\text{O}$ . Similar experiments were carried out with ammonia 2.77—14.08 mols. per 1000 grams of solution,

and phosphoric acid 6.09—0.41 mols. per 1000 grams of solution. The solutions were treated similarly, and it is shown that the stable solid phases are  $\text{NH}_4\text{H}_2\text{PO}_4$ ;  $(\text{NH}_4)_2\text{HPO}_4$ ; and  $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ . The four-component system, potassium hydroxide, ammonia, phosphoric acid, and water was then investigated in the same way. A solution containing all four substances was then placed over sulphuric acid and allowed to remain there until it ceased to lose weight, that is, until the point of lowest vapour pressure was reached. The solid which had separated and the solution were then analysed, the latter containing 1.81 mols.  $\text{NH}_4$ , 4.95 mols. K, and 3.96 mols. of  $\text{PO}_4$  per 1000 grams of solution. The solid was shown by optical examination to contain  $\text{KH}_2\text{PO}_4$  and  $\text{K}_3\text{PO}_4$ , whilst ammonia was rapidly evolved. It is shown that to produce a stable compound of the type desired, it will be necessary to employ more acid solutions than those used here. J. F. S.

**Structural Changes in Industrial Brasses.** DOMENICO MENEGHINI (*Ann. Chim. Applicata*, 1914, 2, 154—158).—The brass parts of incandescent gas burners were found to become very brittle, and, in some cases, to fracture spontaneously. Analysis revealed no change in the composition of the brass, which contained 64.5% of copper, 35.0% of zinc, 0.3—0.4% of lead, and traces of iron. Micrographical examination showed that the majority of the specimens consisted solely of the homogeneous  $\alpha$ -solution, although in a few instances traces of  $\beta$ - and  $\gamma$ -solutions were observed; no sign of the polyhedral structure noticed in analogous cases was detected. After the fragments of brass were reheated at  $700^\circ$ , they were found to have undergone a marked diminution in the superficial hardness, such diminution varying from point to point of one and the same fragment. These effects are probably the result of, first, the mechanical treatment to which the metal is subjected during the shaping of the parts, and, secondly, electrolytic action due to the sulphur dioxide formed during the combustion of the gas and to moisture. In order to avoid the so-called "Forcier-Krankheit," that is, the formation of internal tensions caused by the heating of brass which has been worked below its final temperature of solidification, the metal should contain at least 70% of copper. Even with such alloys, consisting entirely of the  $\alpha$ -solution, trouble may occur unless, after they have attained their final shape, they are rendered stable by suitable reheating. T. H. P.

**The System : Copper Sulphate, Copper Chloride, Potassium Sulphate, Potassium Chloride, and Water at  $30^\circ$ .** F. A. H. SCHREINEMAKERS and (Miss) W. C. DE BAAT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 533—545).—The corresponding systems containing ammonium and sodium in place of potassium have been described in previous papers (A., 1909, ii, 403; 1911, ii, 592). In the present case the solubility data indicate that the solid phases occurring at  $30^\circ$  are the simple salts  $\text{K}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , the double salts  $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $2\text{KCl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,

and a salt corresponding with the formula  $\text{K}_2\text{SO}_4, \text{CuCl}_2$  or  $2\text{KCl}, \text{CuSO}_4$ , which sometimes separates in combination with one molecule of water and at other times in the anhydrous condition. The spatial model which serves to represent the equilibrium relationships is accordingly characterised by seven surfaces of saturation, each one of which corresponds with one or other of the above-mentioned solids. In addition, it has been found that a substance of the composition  $6\text{KCl}, 2\text{CuSO}_4, \text{H}_2\text{O}$  sometimes separates out as a metastable phase.

Data showing the composition of solutions saturated with respect to one, two, and three solid phases are recorded in a series of tables.  
H. M. D.

**The Stokes Method for the Determination of Pyrite and Marcasite.** E. T. ALLEN and J. L. CRENSHAW (*Amer. J. Sci.*, 1914, [iv], **38**, 371—392).—Stokes' method (A., 1902, ii, 87) has been used in connexion with the authors' work on the artificial production of crystallised forms of iron sulphide (A., 1911, ii, 1093; 1912, ii, 354). The details of the method and its limitations are here stated more fully.  
L. J. S.

**Effect of Temperature and Acidity in the Formation of Marcasite and Wurtzite.** E. T. ALLEN and J. L. CRENSHAW; with *Microscopic Study* by H. E. MERWIN (*Amer. J. Sci.*, 1914, [iv], **38**, 393—431).—The authors' earlier results on the formation of the unstable forms (marcasite and wurtzite respectively) of iron sulphide and zinc sulphide (A., 1912, ii, 354, 1055) have been re-investigated and confirmed, and new data determined.  
L. J. S.

**Constitution of Aluminates.** II. EDWARD G. MAHIN (*J. Amer. Chem. Soc.*, 1914, **36**, 2381—2383).—The author criticises Blum's paper (A., 1913, ii, 963), and maintains the accuracy of the view expressed by Mahin, Ingraham, and Stewart (A., 1913, ii, 139) that the solubility of aluminium hydroxide in alkali hydroxide solutions is due rather to its colloidal properties than to the formation of salts.  
E. G.

**Constitution of Aluminates.** WILLIAM BLUM (*J. Amer. Chem. Soc.*, 1914, **36**, 2383—2384).—In reply to Mahin (preceding abstract) the author advances certain considerations in justification of his contention that definite aluminates of the composition  $\text{MAlO}_2$  probably exist in aqueous solution.  
E. G.

**Behaviour of Ammonium Phosphomolybdate with Ammonium Hydroxide.** PULIN BIHARI SIRCAR (*J. Amer. Chem. Soc.*, 1914, **36**, 2372—2374).—Gibbs (A., 1884, 560, 713) has shown that a solution of ammonium phosphomolybdate in ammonia deposits crystals of the compound  $2(\text{NH}_4)_3\text{PO}_4, 5\text{MoO}_3, 7\text{H}_2\text{O}$ .

It has now been found that when excess of solution of ammonia (D 0.91) is added to dry ammonium phosphomolybdate, heat is



developed, and a white, crystalline *salt*,  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7, 3\text{NH}_3$ , is produced, which gradually loses ammonia. If more dilute ammonia (D 0.92) is employed, a precipitate is not formed, but a solution is obtained which on evaporation yields crystals of the *compound*  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7, 3\text{NH}_3$ ; the salt described by Gibbs is but seldom obtained. When ammonium phosphomolybdate is treated with a large excess of strong solution of ammonia (D 0.90), the crystalline precipitate is first produced, and, on further addition of ammonia, dissolves to form a solution from which a gelatinous substance separates; the latter *compound*,  $(\text{NH}_4)_2\text{HPO}_4$ , is very hygroscopic. Ordinary ammonium molybdate was found to have the composition  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}, 4\text{H}_2\text{O}$ .  
E. G.

## Mineralogical Chemistry.

**Rubidium Microcline.** V. I. VERNADSKI (*Bull. Soc. franç. Min.*, 1913, **36**, 258—265. Compare A., 1911, ii, 122).—Analysis of the bluish-green microcline (Amazon-stone) from the Ilmen Mountains, Urals, showed the presence of 3·12%  $\text{Rb}_2\text{O}$ , corresponding with 10·89% of the silicate  $\text{Rb}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ . Spectroscopic examination of orthoclases from the neighbourhood of Mursinka, Urals, suggested the presence of even larger amounts of rubidium. The very frequent presence of rubidium and caesium in potash-feldspars and in micas accounts for the wide distribution of these elements in the earth's crust and in sea-water.

L. J. S.

**Searlesite, a New Mineral.** ESPER S. LARSEN and W. B. HICKS (*Amer. J. Sci.*, 1914, [iv], **38**, 437—440).—This new mineral was washed from a sample of clay from a boring at Searles Lake, San Bernardino Co., California. It has the form of small, white spherulites, which are composed of radial fibres, the optical characters of which suggest monoclinic symmetry. The mineral is rather soft, and fuses below red-heat to a nearly clear glass. It is readily decomposed by hydrochloric acid, and is appreciably soluble in water. The optical constants show a gradual change when the material is treated with acids. Analysis of the impure material gave I, and deducting  $\text{CaCO}_3$  (present as calcite) 21·63%,  $\text{MgCO}_3$  6·41%, insoluble (quartz, feldspar, chlorite, etc.), and hygroscopic water, these results are re-calculated under II:

	$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{FeO}$	$\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}$ , >105°	$\text{H}_2\text{O}$ , <105°	$\text{CO}_2$	Insol.	Total.
I.	31·00	9·80	7·70	0·60	12·10	4·20	1·14	0·22	5·72	0·78	12·84	11·88	100·98
II.	56·41	16·26	12·78	1·00	—	1·82	1·89	0·37	9·47	—	—	—	100·00

The formula  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  when written in the form  $\text{NaB}(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$  shows an analogy to that of analcite,  
 $\text{NaAl}(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$ .

L. J. S.

**The Decomposition Products of Aluminium-containing, Siliceous Rocks, and in Particular of the Laterites of Madagascar.** A. LACROIX (*Compt. rend.*, 1914, **159**, 617—622. Compare *Nouv. Arch. Muséum*, 1913, **5**, 255).—A comparison of the rock formations in Madagascar and French Guinea, and the changes which these rocks undergo on weathering. In Madagascar the surface of the land is covered by red earth, and not by a rocky crust, although the latter is visible in places. There is an absence of the specialisation in the manner of weathering according to the nature of the original rock, which was found in Guinea. The diabases, basalts, and syenites decompose, giving gibbsitic laterites. Total transformation also occurs, in some cases, into colloidal aluminium silicate and colloidal aluminium hydroxide, this mode of decomposition being seldom, if ever, found in Guinea. The gneisses, mica-schists, and granites, forming the greater part of the central rock system, most frequently decompose, giving a mixture of aluminium silicate and hydroxide. This is the change which occurs in most of the red earths. In one place bauxitic laterite was found comparable to that of the African zone of concretion. A further change, taking place at the expense of the granite and the pegmatite, yields a kaolin identical with that of temperate climates, but sometimes containing a little free aluminium hydroxide and some colloidal aluminium silicate. A final method of decomposition, not observed in Guinea, consists in the production of a gibbsitic laterite, comparable to that from the diabases, except that the unattacked quartz remains, and owing to the extreme poverty in iron, or even its absence, these laterites are very light in colour, and sometimes even quite white. A point worthy of note is that the same rock, for example, pegmatite, undergoes different methods of decomposition at the same altitude and in localities only a few kilometres apart and under similar conditions. No satisfactory explanation is at present given of this difference. The author states that the red earths of Madagascar are improperly called laterites, and should rather be named lateritic clays. W. G.

**Hydrographical Chemistry. Relation Between the Different Salts in Sea-Water.** A. MANUELLI (*Ann. Chim. Applicata*, 1914, **2**, 132—153).—The author gives a summary of the literature dealing with the saline composition of sea-water and with the methods suggested for calculating the total salinity from the proportion of one constituent ion, for example, chlorine. A description is given of the work carried out by Sørensen (*Mem. Acad. Roy. Sci. Lett. Danemark*, 1902, [vi], **12**, No. 1). The statement made by various investigators that no constant relations exist between the proportions of the different constituents of sea-water has been controverted by Ruppin (A., 1911, ii, 123), who demonstrated, in particular, the constancy of the ratio, sulphate to chloride. Ruppin examined only two samples of water from the Mediterranean, and the author has now extended the investigation to a number of other samples from the Mediterranean and Adriatic Seas. The mean value of the ratio  $100\text{SO}_3 : \text{Cl}$  is found to be 11.614, the maximum diverg-

ence being  $+0.041$  to  $-0.029$ ; Ruppin's value is  $11.597$ . Waters collected near the mouths of rivers naturally show varying values for this ratio.

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T. H. P.

## Analytical Chemistry.

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**Weighing Burette.** H. S. BAILEY (*J. Ind. Eng. Chem.*, 1914, 6, 941).—A burette for weighing out quantities of such liquids as oils, etc., consists of a graduated glass tube holding about 30 c.c.; the top of the tube is closed with a stopper, and the lower end is narrowed and then drawn out to a jet. This jet is closed by a glass rod which passes through a hole in the stopper and extends down the centre of the tube, the bottom of the rod being ground into the jet. The lower narrow part of the tube is also ground on its exterior, and fits into a small glass foot, so that the apparatus may stand on the balance pan. To discharge a portion of the contents of the tube the latter is removed from the foot and the centre rod raised slightly.

W. P. S.

**Methods for Extractions by means of Immiscible Solvents from the Point of View of the Distribution Coefficients.** II. J. W. MARDEN and VANNA ELLIOTT (*J. Ind. Eng. Chem.*, 1914, 6, 928—934. Compare this vol., ii, 483).—The distribution coefficients of a number of substances have been investigated with a view to ascertaining the best conditions under which to make extractions. It is shown that chloroform is a better substance than ether for the extraction of aconitine and codeine from their aqueous solutions. Chloroform is also a better solvent for strychnine than mixtures of chloroform and ether, whilst ether answers well for the extraction of cocaine. The distribution of citral between lemon oil and 45% and 50% alcohol is discussed; the latter strength of alcohol yields the better results, since 90% of the citral is extracted when 1 volume of the oil is shaken with 18 volumes of 50% alcohol. No rapid method has been devised for the extraction of morphine, but a use of the distribution ratio is suggested in order to avoid continued extractions.

W. P. S.

**Method for Preparing a Neutral Ammonium Citrate Solution.** J. M. McCANDLESS (*J. Ind. Eng. Chem.*, 1914, 6, 921—922).—The citric acid to be employed is well mixed and ground, and a weighed portion of 0.35 gram is titrated with *N*/10-alkali hydroxide solution, using phenolphthalein as the indicator; if the acid is pure and uneffloresced, exactly 50 c.c. of the alkali solution will be required. One thousand eight hundred and fifty grams of the pure acid, or its equivalent in effloresced or impure acid, are then placed in a large stoppered bottle, dissolved in about 7 litres of water, and

a quantity of ammonia is added in the ratio of 1 part by weight of actual ammonia to 3.765 parts of anhydrous citric acid. The ammonia solution added must be titrated previously, using methyl-orange as indicator, and may be used in the form of the concentrated solution or after dilution; in the latter case less water is employed to dissolve the citric acid. The mixture is shaken until any remaining citric acid is dissolved, cooled, and diluted to D 1.09. The volume of the resulting solution is about 10 litres. The accuracy of the solution may be confirmed by the distillation method, by the method described by Patten and Marti (A., 1913, ii, 790), or by that of Eastman and Hildebrand (this vol., ii, 675).

W. P. S.

**Accuracy of Neumann's Method for the Estimation of Phosphorus.** H. S. HALCRO WARDLAW (*J. Roy. Soc. New South Wales*, 1914, 48, 73—93).—The results obtained in the estimation of phosphoric acid by Neumann's method (A., 1903, ii, 243; 1905, ii, 68) are always too high, the error increasing with the amount of phosphate present. The application of the method to pure phosphates and to milks shows that when dealing with 22 mg. of phosphoric acid ( $P_2O_5$ ) the average error is +4%. The error is due to an excess of molybdenum carried down with the ammonium phosphomolybdate precipitate; it does not depend on the rate of addition of the precipitant or on the time of contact of the precipitate with the mother liquor. To ensure complete precipitation of the phosphoric acid, it is necessary to make the precipitation at 70—80°; the error cannot be eliminated by lowering the temperature, as this leads to incomplete precipitation.

W. P. S.

**Rapid and Accurate Method for the Estimation of Carbon in Iron and Its Alloys.** ERNST SZÁSZ (*J. Soc. Chem. Ind.*, 1914, 33, 994—997. Compare A., 1913, ii, 621).—The apparatus described previously is modified. An electrical crucible furnace is employed, and the boat containing the iron is placed in one end of a porcelain tube which is open at both ends. This tube is surrounded by a similar, slightly larger tube closed at the end which is placed in the furnace; the space between the two tubes may contain a mixture of cobalt oxide and fire-clay. The outer ends of the tubes are connected by a stuffing-box, and surrounded by a cooling jacket. The oxygen is supplied to the outer end of the inner tube, and the combustion gases leave the apparatus by a side-tube on the outer porcelain tube, and are conducted to the gas-measuring apparatus or to an absorption vessel. Dilute sulphuric acid (1 : 10) is used in place of mercury in the gas-measuring burette. Both the method and apparatus are patented.

W. P. S.

**Properties of Some Calcium and Magnesium Salts, and their Bearing on the Quantitative Separation of these Metals.** C. BLOMBERG (*Chem. Weekblad*, 1914, 11, 1002—1008).—A criticism of methods recommended for the separation of calcium and magnesium. The author condemns the method of crystallising magnesium oxalate recommended by Jannasch, but advocates the dilution

method of Hefelman and of Richards, the cold precipitation and the double precipitation methods of Fresenius, and the method involving the solution of magnesium oxalate by addition of excess of oxalate.

A. J. W.

**Rapid Methods for Glass Analysis.** E. C. SULLIVAN and W. C. TAYLOR (*J. Ind. Eng. Chem.*, 1914, 6, 897—899).—A method for the analysis of glass containing silica, lead, sodium, potassium, and small quantities of iron, aluminium, calcium, and magnesium, consists in decomposing the glass with hydrofluoric acid, the fluorides in turn being decomposed by oxalic acid. One gram of the powdered glass is treated with hydrofluoric acid and 2 grams of oxalic acid, the mixture is evaporated to dryness, and heated sufficiently to expel the excess of oxalic acid; this evaporation with oxalic acid (and water) is twice repeated. The residue of oxalates is treated with hot water, cooled, and filtered; the insoluble portion consists of lead oxalate, with a trace of calcium oxalate, and the lead may be estimated as sulphate. The filtrate from the lead oxalate is evaporated to dryness, the residue is ignited to decompose the oxalates, dissolved in hydrochloric acid, and the solution employed for the estimation of the bases. If arsenic and antimony are present, they must be removed from the soluble oxalates by treatment with hydrogen sulphide before the oxalates are decomposed.

In the case of borosilicate glasses the boric acid may be estimated by the method described by Wherry (A., 1909, ii, 92), but untrustworthy results are obtained when the glass also contains lead and zinc unless the method is modified as follows: 0.5 gram of the glass is fused with 3 grams of sodium carbonate, the mass is treated with water, and the solution filtered. About 7 c.c. of concentrated hydrochloric acid are added to the filtrate, the solution is heated to boiling, and excess of calcium carbonate is introduced, the process being then continued as described by Wherry. W. P. S.

**Sulphate Method for Standardising a Magnesium Salt Solution.** C. W. FOULK and O. R. SWEENEY (*J. Amer. Chem. Soc.*, 1914, 36, 2360—2372).—In the course of an investigation into the causes of the discrepancies in the results obtained in the precipitation of magnesium as magnesium ammonium phosphate by different methods and by different workers, a study was made of the preparation and standardisation of a solution of a magnesium salt.

A sample of magnesium chloride, which contained sodium, was purified by precipitating the magnesium as magnesium ammonium carbonate (Bray, A., 1909, ii, 431), converting this into magnesium ammonium chloride, and heating the latter in a current of dry hydrogen chloride. Weighed quantities of the anhydrous magnesium chloride thus obtained were converted into the sulphate. In order to accomplish this operation, a special form of apparatus was devised, which enables a substance to be heated in a combustion tube and transferred to a weighing bottle without exposure to the air. Six experiments were made on the conversion of the anhydrous chloride into the sulphate, and the results obtained

agreed very closely with those calculated, and thus furnished evidence of the accuracy of the sulphate method for standardising magnesium salt solutions. E. G.

**Use of Hydrofluoric Acid in the Separation of Copper and Lead from Tin and Antimony by means of the Electric Current.** LEROY W. MCCAY (*J. Amer. Chem. Soc.*, 1914, **36**, 2375—2381).—In an earlier paper (A., 1909, ii, 351) the author described a method for the separation of antimony from tin by precipitation with hydrogen sulphide from a solution containing hydrofluoric acid; the tin, under these conditions, remains in solution.

It has now been found that when a hydrofluoric acid solution containing both antimony and tin in their higher states of oxidation is submitted to the action of the electric current, neither metal is precipitated. If copper, or lead, or both are also present in a nitric acid solution containing hydrofluoric acid, the copper is deposited at the cathode and the lead, as peroxide, at the anode. Experiments are described which show that this method can be employed for the quantitative separation of copper or lead from tin or from antimony, and for the analysis of alloys containing all four metals. It has also been found that from a nitric acid solution containing hydrofluoric acid, copper can be separated from tungsten, and mercury and silver from tin and antimony. E. G.

**Estimation of Calomel in Calomel Tablets.** J. W. MARDEN and O. E. CUSHMAN (*Amer. J. Pharm.*, 1914, **86**, 511—516).—A method described by Kohn and Ostersetzer (A., 1913, ii, 436), in which mercury haloids are boiled with water and sodium peroxide, the precipitated mercury separated by filtration, and the halogen estimated in the filtrate, was found to be trustworthy for the estimation of calomel in calomel tablets. Methods depending on the estimation of the mercury as sulphide, volatilisation of the mercurous chloride, reduction of the calomel to metallic mercury, or the iodometric titration of the calomel, yielded untrustworthy results. W. P. S.

**Alcoholometry. II.** A. F. JOSEPH and W. N. RAE (*J. Soc. Chem. Ind.*, 1914, **33**, 991—992. Compare A., 1913, ii, 884).—Results of determinations of the densities of solutions containing from 0 to 1.7% of alcohol are recorded; a 1% (by weight) alcohol solution was found to have  $D^{32.5} 0.99299$ . It is pointed out that the ordinary density tables in the books supplied for use with Syke's hydrometers contain an inaccurate statement to the effect that 1 gall. of distilled water at 60° F. weighs 10 lb.; this is true at 62° F. (as given in Bedford's tables), and the densities given in "Table I" therefore refer to water at 62° F. There are also slight inconsistencies between the main hydrometer table and the density table (Table I). Bedford's tables are more trustworthy, both at high and low temperatures, and any error in these tables rarely exceeds that which would be caused by an error of one division in the reading of the hydrometer. W. P. S.



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# ERRATA.

## VOL. C (ABSTR., 1911).

Page	Line	
i, 230	19*	for "KOLLISCH" read "KÖLLISCH."
i, 231	3	,, "1-Acetyl-2-methylindole" read "2-Acetyl-1-methylindole."

## VOL. CIV (ABSTR., 1913).

i, 235	17	for "ROCAS" read "ROXAS."
i, 482	24	,, " $C_{15}H_{18}O_6N_2$ " read " $C_{14}H_{18}O_6N_2$ ."
ii, 532	13*	} ,, "tungstate" read "molybdate."
,,	12*	
,,	11*	
,,	10*	
,,	9*	} ,, "molybdate" read "tungstate."
ii, 967	12	
		,, "SCHWARTZ" read "SCHWARZ."

## VOL. CVI (ABSTR., 1914).

i, 69	5*	for "Oil of Citrons" read "Citronella Oil."
i, 97	12	,, "Contant" read "Constants."
i, 444	2*	,, "eleven" read "above."
i, 596	1	,, "Chloro- <i>p</i> -aminobenzeneazobenzene" read "Chloral- <i>p</i> -aminobenzeneazobenzene."
i, 670	2	,, " $R \cdot N : C(OEt) \cdot S \cdot C_6H_7O_5(OAc)_4$ " read " $R \cdot N : C(OEt) \cdot S \cdot C_6H_7O_5Ac_4$ ."
,,	10	,, " $C_3H_5 \cdot N : C(SET) \cdot S \cdot C_6H_7O_5(OAc)_4$ " read " $C_3H_5 \cdot N : C(SET) \cdot S \cdot C_6H_7O_5Ac_4$ ."
,,	25	,, " $SO_2Me \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot N : C(SET) \cdot S \cdot C_6H_7O_5(OAc)_4$ " read " $SO_2Me \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot N : C(SET) \cdot S \cdot C_6H_7O_5Ac_4$ ."
,,	14*	,, " $C_7H_7 \cdot N : C(OEt) \cdot S \cdot C_6H_7O_5(OAc)_4$ " read " $C_7H_7 \cdot N : C(OEt) \cdot S \cdot C_6H_7O_5Ac_4$ ."
i, 673	2 and 30	,, "benzyl" read "benzoyl."
i, 778	24	,, "FAGINOLI" read "FAGIUOLI."
i, 933	24 before	" <i>d</i> - or <i>l</i> -bromocamphorsulphonate" insert "silver."
i, 980	12* after	"H. SIMONIS" insert "P. REMMERT."
ii, 70	14	for "Nitrating" read "Titrating."
ii, 75	15	,, "ROSEBLATT" read "ROSENBLATT."
ii, 135	10*	,, "Thorium" read "Thallium."
ii, 285	10	,, "Zaldwar" read "Zaldivar."
ii, 613	28	,, "boxwood" read "beechwood."
ii, 1033	30 col. i,	insert "Biringuccio, Vannoccio, work of (MIELI), A., ii, 45."

## COLLECTIVE INDEX, 1903-12 (AUTHORS).

275	7 col. i	} for "Kollisch" read "Köllisch."
629	27 col. ii	
280	31 col. i	
		,, "2253" read "2353."

\* From bottom.

## ERRATA (*continued*).

Page	Line	COLLECTIVE INDEX, 1903-12 (SUBJECTS).
39	14*	col. i <i>for</i> "1-Acetyl-2-methylindole" <i>read</i> "2-Acetyl-1-methyl-indole."
39	13*	col. i , , "KOLLISCH" <i>read</i> "KÖLLISCH."

### ANNUAL REPORTS, 1913, VOL. X.

140	2*	<i>for</i> "It appears to have, etc." <i>read</i> "It gives with nitric acid a product which appears to have, etc."
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### INDEXES, 1913.

Title page for Vol. CIV. Part I. *for* "Organic Chemistry" *read* "Organic, Physiological, and Agricultural Chemistry."

Title page for Vol. CIV. Part II. *for* "Physical, Inorganic, Mineralogical, Physiological, Agricultural, and Analytical Chemistry" *read* "Physical, Inorganic, Mineralogical, and Analytical Chemistry."

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\* From bottom.